IN-SITU ULTRASONIC COMPATIBILIZATION OF BINARY BLENDS OF FLEXIBLE CHAIN POLYESTERS AND AROMATIC LIQUID CRYSTALLINE POLYMERS

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ABSTRACT

The objective of this research was to improve the properties of immiscible polymer blends by developing a new ultrasonic extrusion process. The ability of ultrasonic treatment to induce recombination reactions in polymer blends was anticipated to result in fast in-situ compatibilization of immiscible blends. In order to test this hypothesis, a new ultrasonic extruder operating at a frequency of 20 kHz at amplitudes of 5, 7.5, and 10 µm was developed. Polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and wholly aromatic liquid crystalline copolymesters (LCPs) were selected to illustrate the effect of ultrasonic treatment on copolymerization of components through transesterification reactions in blends. The LCPs studied were a copolymer of hydroxybenzoic and hydroxynaphthoic acid (LCP1) and a copolymer of dioxydiphenyl, terephthalic and isophthalic acid (LCP2). PET/PEN, PET/LCP1, PEN/LCP1, and LCP1/LCP2 blends and their components were subsequently injection molded and spun into fibers.

PET underwent homopolymerization and degradation, respectively, at ultrasonic amplitudes of 7.5 µm and 10 µm, while PEN underwent degradation at all amplitudes. MALDI-TOF mass spectroscopy revealed greater amounts of hydroxyl and carboxyl terminated oligomers in ultrasonically treated PET and PEN. Transesterification (copolymer formation) was observed in PET/PEN blends, which was enhanced with ultrasonic treatment, as indicated by $^1$H NMR and MALDI-TOF. Oxygen permeability of
compression molded films of untreated and ultrasonically treated PET/PEN blends followed theoretical predictions for miscible blends.

Ultrasonic treatment of LCP1 at amplitudes of 7.5 and 10 µm led to improved mechanical properties of its injection moldings. On the other hand, LCP2 underwent degradation with treatment, leading to a reduction of mechanical properties of LCP2 and LCP1/LCP2 blends. However, due to enhanced fibrillation, these blends retained synergism such that moldings exhibited mechanical properties above the rule of mixtures. At the same time, mechanical properties of spun fibers followed the rule of mixtures.

Ultrasonically induced copolymer formation, further enhanced with higher residence time in the ultrasonic zone, was also detected by MALDI-TOF in PET/LCP1 and PEN/LCP1 blends. LCP fibrillation in moldings and spun fibers of these blends was controlled by the viscosity ratio of matrix polymer to LCP1. Homopolymerization of PET in PET/LCP1 blends, along with copolymer formation at 7.5 µm, improved fibrillation of LCP1 phase and interfacial adhesion. On the other hand, PET degradation and copolymer formation at 10 µm led to a competition between the reduction of LCP1 fibrillation and the improvement of interfacial adhesion. This competition dictated the mechanical properties of blends. Similar effects were observed in PEN/LCP1 blends.

The addition of transesterification catalysts (antimony trioxide and tetrabutyl orthotitanate) to PEN/LCP1 blends induced degradation of PEN without and with ultrasonic treatment, leading to reduced LCP1 fibrillation, and therefore poor mechanical properties. However, treatment of PEN/LCP1 blends at an amplitude of 10 µm in the presence of catalysts induced greater copolymerization and higher mechanical properties.

Observations were supported by rheological, thermal, and morphological analysis.
DEDICATION

To Yeliz… She gave me her endless love and devotion, and we are living it.
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CHAPTER I
INTRODUCTION

Thermotropic liquid crystalline polymers (LCP) combine superior service performance with ease of processing. Many commercially available LCPs have highly rigid chemical structures, which gives them extraordinary stiffness and strength, dimensional and thermal stability, high barrier properties and good solvent resistance. The primary benefit of thermotropic LCPs is the alignment of rigid rod segments during processing, which also lowers viscosity. In spite of all the advantages of LCPs, their extensive application is still hindered by high cost, arising from expensive raw materials.

Blending of polymers is an economical approach to improving the properties of commonly used materials. The effective blending of LCPs with flexible chain thermoplastics leads to very high mechanical properties, while also allowing ease of processing [1]. The main problem facing the commercialization of LCP/thermoplastic polymer blends is the immiscibility of these blends, and their brittleness. Compatibilization of LCP blends can lead to creation of stronger in-situ or self-reinforced composites.

Compatibilization of immiscible polymer blends is carried out by methods including the addition of chemical additives, reactive extrusion of grafted polymers, and incorporation of specially synthesized block copolymers to blends [2], including those containing LCPs [3]. These methods have shortcoming for large-scale production.
A continuous in-situ compatibilization process offers commercial value and allows faster single step processing of polymer blends. The ultrasonic extrusion process induces in-situ compatibilization in polymer blends [4, 5, 6] and could improve the properties of LCP blends.

Ultrasonic treatment of polymer with functional groups in the melt state promotes the formation of reactive end groups at short residence times [7]. These reactive species can then recombine to create copolymers. Copolymers formed by ultrasonically induced chain scission and recombination reactions reside in the interface in case of immiscible blends, leading to in-situ compatibilization. In the case of treatment of polyesters, recombination reactions are expected to proceed by transesterification. Ultrasonic treatment can lead to changes in molecular weight distribution and formation of copolymers by treatment in the melt state [4, 5, 6]. Ultrasonically induced copolymerization reactions have been induced in batch solution processing [8], and continuous melt processing [5, 6, 9, 10].

The objective of the current study was to develop a new ultrasonic extruder and extrusion process for blending and in-situ compatibilization of immiscible polymer blends at short residence times and to determine their effects on the properties of components and their blends. In particular, ultrasonic extrusion of flexible chain and liquid crystalline polyesters and their blends were investigated. The effects of ultrasonic treatment on their structure and the mechanical properties were evaluated to test the hypothesis whether ultrasound could induce fast in-situ compatibilization leading to improved properties. The effects of ultrasonic amplitude, residence time, mixing conditions, and presence of catalysts during ultrasonic extrusion of these blends were
evaluated with the intent of identifying favorable processing conditions to improve compatibility of blends. The ultimate goal was to create novel in-situ reinforced high performance composites by the ultrasonic extrusion process.

As the chemical structure of materials influences the effects of ultrasound on their properties, several commercial polyesters were chosen for this study. The effects of ultrasonic treatment in the melt state on the pure materials and their blends were studied. The viscosity ratio of the flexible chain polymer to the LCP, among other parameters, has a significant impact on the resulting morphology and mechanical properties [11]. This effect was investigated by using the less rigid poly(ethylene terephthalate) (PET) and the more rigid, higher melting point poly(ethylene naphthalate) (PEN), and their blending with LCP. Furthermore, the transesterification reaction between these two flexible chain polyesters in the presence of ultrasonication was investigated. The effect of ultrasound was also studied on a blend of two LCPs (LCP1 based on hydroxybenzoic and hydroxynaphthoic acid, and LCP2 based on terephthalic and isophthalic acid, and dioxydiphenyl) that exhibits superior mechanical properties by enhanced fibrillation [12]. Results obtained were compared to miscibility criteria and theories of LCP droplet deformation in order to provide a good understanding of the effect of blending and ultrasonic treatment.

This dissertation consists of 10 chapters. The literature survey is given in Chapter II. It presents background information on LCPs, miscibility of polymer blends, transesterification of PET/PEN, compatibilization of blends containing LCPs and effect of ultrasound on polymers. Experimental methods including the processing and characterization of studied systems are described in Chapter III. Chapter IV presents and
discusses results on the effects of ultrasonic treatment, residence time, and extruder setup on PET/LCP1 blends. Results on the ultrasonic extrusion of PEN/LCP1 blends are presented and discussed in Chapter V. Chapter VI illustrate effects of ultrasonic extrusion on PEN/PET blends. Results on the ultrasonic extrusion of LCP1/LCP2 blends are given in Chapter VII. Effect of transesterification catalysts on ultrasonic extrusion of PEN, and PEN/LCP1 blends is presented and discussed in Chapter VIII. Chapter IX presents mechanical properties of fibers spun from PET, PEN, LCP1, LCP2, PET/LCP1, PEN/LCP1, PET/PEN, LCP1/LCP2, and morphological studies of fibers spun from PEN/LCP1 blends. Finally, conclusions and recommendations are given in Chapter X.
CHAPTER II

LITERATURE SURVEY

The primary focus of the literature survey was on LCPs, miscibility in blends, transesterification reactions of polyesters, compatibilization of blends containing LCPs, and use of ultrasound to promote copolymerization.

Section 2.1 on LCPs includes an overview of liquid crystallinity, historical development of LCPs, structure properties relation of LCPs, their rheology, affects of annealing on their structure, and their morphology in injection moldings and spun-fibers. Section 2.2 is on the miscibility of polymer blends and interchange reactions involving polyesters. Section 2.3 describes literature on transesterification of PET/PEN polyester blends. Section 2.4 discusses the compatibilization of LCPs by addition of copolymers, in-situ transesterification reactions, the morphology of these blends with respect to LCP phase fibrillation, rheology of these blends, and a detailed literature survey on LCP containing blends of particular interest. Section 2.5 is on ultrasound and presents its mechanism, models on sonication of polymer melts, compatibilization of immiscible blends by ultrasonic treatment in the melt, and effect of ultrasound on particle filled polymers. Finally, conclusions of the literature survey and how it relates to objectives of the current study are presented.
2.1. Liquid crystalline polymers (LCP)

Liquid crystalline polymers are typically in the nematic state during processing, leading to the formation of strongly anisotropic wood-like fibrous structures under flow. Extraordinary mechanical properties and dimensional stability often results in injection moldings and fibers of LCPs due to this fibrillation behavior [1].

In this section, the nature of liquid crystallinity and historical development of LCPs are studied.

2.1.1. Liquid crystalline behavior

The term liquid crystallinity is used to describe molecules that exhibit well defined, solid like order in the liquid phase. Reinitzer was the first to recognize liquid crystallinity [13]. He discovered it during his studies of the phase transition behavior of cholesteryl benzoate in 1888, upon observing a cloudy liquid phase between 145.5°C and 178.5°C. Lehmann also studied this thermotropic cholesteric molecule in 1889 [14]. Following this, many liquid crystalline molecules were studied [15]. Friedel defined the mesomorphic phases observed in liquid crystalline systems in 1922 [16]. The mesomorphic phases are shown in Figure 2.1. The presence of a particular liquid crystalline mesophase is solely dependent on molecular structure and the governing thermodynamics. Many liquid crystalline materials change from a solid crystalline phase into a nematic phase upon heating. Upon further heating, the material reaches an amorphous, isotropic state. The transition temperature from thermotropic to liquid isotropic state is known as the clearing temperature [17].
The degree of orientation in the liquid crystalline state is described by the order parameter S.

\[ S = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \]  \hspace{1cm} (2.1)

\[ \langle \cos^2 \theta \rangle = \frac{\int_0^{\pi/2} I(\theta) \sin \theta \cos^2 \theta d\theta}{\int_0^{\pi/2} I(\theta) \sin \theta d\theta} \]  \hspace{1cm} (2.2)

where \( \theta \) is the angle between the chain axis and the director, shown in Figure 2.1. S=1 for perfect orientation, while S=0 for an isotropic system. In small molecule liquid crystals, the order parameter S usually lies between 0.5 and 0.7 [17].

In all liquid crystalline phase arrangements, the resulting fluid is turbid. In the nematic phase, the molecules are ordered in one dimension and the viscosity is low. In the smectic phase, two-dimensional order exists, resulting in higher viscosity. In the cholesteric phase, many nematic layers are arranged in a helical order, again resulting in high viscosity [17].

Depending on the conditions under which the liquid crystalline phase forms, liquid crystals are classified as either lyotrophic or thermotropic. Lyotropic means that the
anisotropic structure is formed when molecules are dissolved in solution. Thermotropic liquid crystals, on the other hand, exhibit ordered structure in melt [17]. There are also some mesogens that exhibit liquid crystallinity in both solution and melt. An example is P(Az6Bu) described by Ujiie et al. [18]. P(Az6Bu) is a liquid crystalline polymethacrylate with amphiphilic-mesogenic side-chains, which also contained 2-hydroxyethyl side-groups for water solubility. P(Az6Bu) exhibited smectic A and C mesophases upon heating and cooling, and smectic C lyomesophase in water.

Liquid crystal (LC) molecules are easily oriented under external forces, including magnetic and electrical fields, temperature gradients, mechanical stresses and surface forces. The induced orientation results in anisotropic rheological, optical, electrical and magnetic properties. Preferential orientation created under mechanical stresses will result in reduced viscosity during flow. Birefringence results due to orientation in liquid crystals, and this property is often used in their characterization. Anisotropy in susceptibility to magnetic and electric fields allows low molecular weight LCs to align in such fields [15]. The external forces acting on LC systems can induce the formation of local orientations separated by boundaries. The resulting polycrystallinity can lead to uneven properties and difficulty in experimental measurements. The polycrystallinity and uneven texture of LC systems should always be considered during experimental studies such as rheological measurements [15,19].

Phase equilibria of LC systems have been extensively studied. Warner and Flory developed a theory to study the phase transformations in thermotropic LC systems; the phase diagrams are predicted for single rods in solution and for two component rod systems by deriving free energy of mixtures using chemical potentials [20].
Molecules showing nematic and smectic LC phases often exhibit flat and elongated structure made of aromatic rings, connected by polarizable groups with symmetric substituents. These include biphenyl and phenyl molecules linked with amide, ester or azomethine linkages with para disubstitution [21].

2.1.2. Development of LCPs

The historical development of LCPs has been reviewed in literature [22], and will be briefly summarized in this section. The widespread study of polymeric liquid crystals started in the 1940s on natural and synthetic lyotropic biopolymers. The tobacco mosaic virus studied by Bawden and Pirie in 1937 [23], other viruses such as the potato and cucumber viruses studied in 1940s and the double helix structure of DNA are all examples of lyotropic liquid crystalline biopolymers [22].

In 1923, Vorländer, who is now recognized as the father of LCPs, synthesized rod-like polymers based on benzene rings para linked with ester bonds [24]. He identified the increase in phase transition temperature by using one, two and three bonded benzene rings in the structure. He also synthesized poly(p-benzamide):

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{H}
\end{array}
\]

Vorländer identified it as a birefringent powder that does not melt, having a very high LC transition temperature [15].

In 1956, P. Flory suggested that rigid rod-like polymer forms a lyotropic structure in a solvent at appropriate concentrations [25]. The lyotropic aromatic amide fiber
Kevlar® (poly(p-phenylene-terephthalamide)), which is spun in concentrated sulphuric acid solution, was developed in 1965 by Dupont [15]:

\[
\begin{array}{c}
\text{[}\begin{array}{c}
\text{O} \\
\text{N} \\
\text{N}
\end{array}\text{]}_n
\end{array}
\]

The development of Kevlar® increased the commercial interest in LCPs and promoted the development of thermotropic LCPs. Ekkcel I-2000 was developed by J. Economy, Carborundum in 1970 [15]:

\[
\begin{array}{c}
\text{[}\begin{array}{c}
\text{O} \\
\text{N} \\
\text{N}
\end{array}\text{]}_n
\end{array}
\]

It was an aromatic copolyester based on bisphenol monomer, exhibiting melt anisotropy. At that time, the liquid crystalline nature of the polymer was not realized [15].

In 1974, X7G®, the first widely studied thermotropic LCP, was developed by Eastman Kodak Company:

\[
\begin{array}{c}
\text{[}\begin{array}{c}
\text{O} \\
\text{N} \\
\text{N}
\end{array}\text{]}_n
\end{array}
\]

X7G was a copolyester of PET and HBA. This development was followed by release of wholly aromatic thermotropic copolyesters by Celanese and Dupont [26].

Numerous commercial main chain thermotropic LCPs are established. These are shown in Table 2.1.
Table 2.1. Commercial thermotropic LCPs.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Chemical structure</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ekonol</td>
<td>Homopolymer of hydroxybenzoic acid (HBA)</td>
<td>Transition to smectic phase at 340°C, formed by high pressure molding or sintering and further machined [15]. Developed by Carborundum, now manufactured by Saint-Gobain.</td>
</tr>
<tr>
<td>Rodrun</td>
<td>Copolymer of HBA and ET Rodrun LC5000: 80/20 HBA/ET Rodrun LC3000: 60/40 HBA/ET [15]</td>
<td>Developed as X7G (60/40 HBA/ET) by Eastman Kodak, now manufactured by Unitika.</td>
</tr>
<tr>
<td>Sivera</td>
<td>Copolymer of HBA and ET</td>
<td>Low ET content, heat deflection of 250°C, good weld line strength [15]. Developed by Toray.</td>
</tr>
<tr>
<td>Sumika Super</td>
<td>Similar composition to Xydar®, with the addition of a small amount of isophthalic acid (IA) monomer [15]</td>
<td>The isophthalic acid monomer allows spinning of polymer into fibers; mainly for injection molding [15]. Developed by Carborundum, and previously marketed as Ekonol® by Sumitomo.</td>
</tr>
<tr>
<td>Ultrax</td>
<td>Copolyesters of terephthalic acid (TA) (x), IA (y) and dioxydiphenyl (z) [27]</td>
<td>Developed by BASF.</td>
</tr>
<tr>
<td>Vectra</td>
<td>Vectra® A: copolyester containing 73% HBA and 27% hydroxy naphthoic acid (HNA) Vectra® B: copolyester-amide with 60% HNA, 20% HBA and 20% phenylamide Vectra® C: Same as Vectra® A, but with more HBA. T_m=330°C [22] Vectra® E: Based on same components as Xydar® Vectra RD500: 52% HBA, 28% HNA, 10% TA, 10% hydroquinone (HQ) [27]</td>
<td>Developed by Hoechst Celanese in 1985, now marketed by Ticona. Most widely studied class of commercial LCPs in literature. Vectra A is soluble in pentafluorophenol [26].</td>
</tr>
<tr>
<td>Xydar</td>
<td>Copolymer of HBA, terephthalic acid, and biphenol [15]</td>
<td>Developed by Carborundum, now manufactured by Solvay. Very good high temperature properties [15].</td>
</tr>
<tr>
<td>Zenite</td>
<td>Undisclosed proportions of HBA, TA, biphenol, HQ and 2,6-naphtalene dicarboxylic acid, with other disubstituted aromatic diols and dicarboxylic acids [15]</td>
<td>Range of copolymers marketed by DuPont, good high temperature properties [15].</td>
</tr>
<tr>
<td>K161 or KU-9211</td>
<td>Aromatic copolymer of HBA, HQ, TA, HBP (4.4'-hydroxybiphenyl), and IA [15]</td>
<td>Marketed by Bayer AG.</td>
</tr>
</tbody>
</table>
The high cost of LCPs limits their production. Global production capacity was about 10,000 tons per year in 2005 [15], but has been growing since at 12% per year [28]. Accordingly, global capacity today could be projected at about 16,000 tones/year.

Current market prices for unfilled LCP resins range from $9.45 to $11.80 [29]. Manufacturing of specialized LCP injection moldings, utilizing favorable rheological, thermal and mechanical properties, is promoting growth in capacity [15, 28]. LCPs are mainly used for components in computer hardware, multiway electrical connectors, transformer bobbins for silicon chips, under the hood automobile applications, high performance sports goods and many domestic appliances [1, 15].

2.1.3. Tailoring Mesogens in LCPs

Among the mesophases described previously (section 2.1.1), the nematic phase is the most desirable during processing of LCPs, as it leads to high orientation and low viscosity. The nematic phase exists in LCPs, which have backbones with semi rigid linear structure, mesogens in side chains attached to a flexible backbone with flexible spacers, and rigid linear backbone segments connected by flexible spacers [15, 21]. It is critical to obtain a good balance between chain rigidity for high mechanical properties and processability with a reasonable solid to nematic transition temperature. The phase transition temperature is mainly dependent on the excess enthalpy of melting, as evident from the thermodynamic relation:

$$\Delta G_m = 0 = \Delta H_m - T_m \Delta S_m$$

(2.3)

For first order transitions, free energy is zero. The entropy of melting in polymer phase transition is dependent on the increase in chain movement going from solid to
liquid state. This change is small for the solid to nematic phase transition in LCPs. The enthalpy change ($\Delta H_m$) must also be small in order to limit the phase transition temperature to a processible range. In order to improve the processability of wholly aromatic liquid crystalline polymers, various flexible linkages are incorporated into the structure [19], some of these are shown in Figure 2.2.

![Figure 2.2. Structures incorporated into aromatic LCP to improve their processability.](image)

The flexible spacers are usually $-(\text{CH}_2)-$ or $-(\text{OCH}_2\text{CH}_2\text{O})-$ units. To achieve a reduction in $T_m$ and yet to preserve liquid crystallinity, the rigid rod units must exceed a specific length while the flexible segments must be below a specific critical length [19]. The transition temperature from solid to anisotropic state increases with increasing rigid rod length. Increasing the length of flexible spacers results in a broader temperature range for the smectic mesophase. The number of flexible spacers also affects the mesophase stability, as the most stable trans-gauche conformations will depend on the spacer length.
Increasing the length of flexible spacers lowers the $T_m$ and $T_g$ of the LCP while increasing its miscibility in blends with other polymers. However, this approach also leads to a decrease in the mechanical properties of the polymers as the degree of aromaticity is related to chain rigidity. In studies of the effect of relative composition in a liquid crystalline copolymer of HBA/PET, it was found that $T_m$ decreased from 300 to 230°C with the increase of spacer length $n$ from one to four [30,31]. A mesophase with no evident clearing temperature was formed at only 10% HBA content in the copolymer.

Modification of structure with the introduction of large side groups, kinks and sidesteps in the LCP backbone also has the effect of reducing $T_m$, which is desirable for easier processing [19]. Meta linkages and tetrahedral bonds allow kinks in the backbone. Addition of naphthoic units will also slightly reduce the melting temperature, due to the sidestep structure. Bulky side groups can be substituted on the alternating phenyl rings in the LCP. This has the effect of distorting chain packing, leading to lower crystallizability and melting temperature. The random attachment of side groups on the phenyl ring can increase this effect. Crystallizability of LCPs has a great impact on their processability. Random copolymerization of mesogenic units with different length, such as HBA and HNA, is commercially used to reduce the long-range periodicity of these polymers.

2.1.4. Rheology

In this section, the rheology of liquid crystals (LC), lyotropic and thermotropic LCPs is reviewed.
2.1.4.1. Rheology of liquid crystals

The rheology of liquid crystals is highly dependent on their orientation created by external forces and on their mesomorphic state, which depends on temperature [32]. Studies on low molecular weight LCs should be considered while studying rheology of LCPs.

Porter and Johnson reviewed the rheological behavior of p-azoxyanisole, a material showing nematic order in its LC state [33]. They studied the temperature dependence of viscosity for p-azoxyanisole under magnetically induced orientations in the LC state. Magnetic orientation was observed to reduce viscosity in flow direction by four times. The viscosity in the lower temperature ordered nematic phase was lower than that in the isotropic phase occurring at higher temperature. The increase in viscosity is the increasing temperature is due to loss of orientational order above the clearing temperature in liquid crystalline systems.

2.1.4.2. Rheology of lyotropic LCPs

Although the main focus of this research is on thermotropic LCPs, the rheology of lyotropic and thermotropic LCPs have similarities [34]. Onogi and Asada suggested the three region flow behavior of lyotropic LCPs [35]. This behavior is schematically shown in Figure 2.3.
Figure 2.3. Three region flow behavior of lyotropic LCPs.

In the first region, LCPs exhibit shear-thinning behavior due to yield stress and flow history dependence of rheology. In the second region is a quasi-Newtonian plateau, followed by the shear thinning region III at higher shear rates.

The range of shear rates in region II depends on the molecular weight, and on the concentration of lyotropic LCPs. Doi extended the rigid rod solution Doi-Edwards theory [36] to greater concentration range; the predicted relationship is shown below [37]:

\[ \eta \sim C^3 M^6 \] 

This theory predicts the dependence of viscosity on solution concentration (C) and molecular weight (M) of lyotropic LCP. The extension of region II for lyotropic LCPs to thermotropic LCPs requires understanding the effects of intermolecular interactions and flow fields on the formation of liquid crystalline phase for these polymers [17].

The onset of shear thinning in region III depends on the anisotropy in the liquid crystalline state [17]. Shear thinning in anisotropic solutions begins at a shear rate several decades lower than in isotropic solutions of the same viscosity. The detailed comparison
of region III behavior of thermotropic LCPs requires studies above the clearing temperature, which is beyond the degradation temperature of commercial thermotropic LCPs. Nevertheless, this brief summary of the three region flow of lyotropic LCPs shades light on the rheology of thermotropic LCPs.

2.1.4.3. Rheology of thermotropic LCPs

Thermotropic liquid crystalline polymers are highly shear thinning and exhibit low viscosity during processing [38, 39]. This property is of great commercial importance since it reduces the energy required for processing in pure LCPs and in their blends with traditional thermoplastic polymers. In LCPs, it is the elongation flow that results in orientation of bundled rigid rods, rather than shear flow [17, 38].

Samples of LCPs should always be handled with care due to the effect of thermo-mechanical history on their rheology [17]. Yield stresses are present in shear flow and orientation decays slowly upon the cessation of flow [40]. The testing of commercial LCPs need to be performed in the anisotropic liquid state, as the clearing temperature typically lies above the degradation temperature. While the rigid structure of commercial LCPs leaves little chance for oxidative degradation during testing for short times, testing in inert gas atmosphere has been suggested to improve reproducibility. Rheological testing of LCPs can be carried out in both rotational and capillary rheometers [41]. The potential complications associated with both methods will be discussed in this section.

Small amplitude oscillatory shear in rotational rheometers allows the efficient study of a wide range of shear rates. Cox-Merz rule is used to equate $\eta^*(\omega)$ to $\eta$ obtained in steady shear. It is typically valid for flexible chain polymer melts. The shape of the
flow curve is the same for oscillatory and steady flow measurements for LCPs based on aromatic polyester. The liquid crystalline poly-texture clearly prevents the use of the Cox-Merz rule [41]. It is found that as the strain amplitude increases, the value of complex viscosity decreases due to alignment in the nematic state. Moreover, while the value of first normal stress difference $N_1$ is double the elastic storage modulus $G'$ in isotropic melts, $N_1$ can be up to ten times $G'$ in thermotropic polymers. Regardless of the unsuitability of the extension of dynamic measurements to steady shear, small oscillatory shear measurements can be used for comparative studies for different samples of a polymer.

Wissbrun et al. suggested that thermotropic liquid crystalline polymers can follow the shear rate dependence of viscosity proposed by Asada and Onogi for LCs [42]. Namely, there is a highly shear thinning region I followed by a plateau region II. Gotsis and Baird also observed a transition to plateau in viscosity for thermotropic PET/HBA copolymer X7G at high shear rates [43].

Yang and Krigbaum studied the yield stress observed in TLCPs, in particular HBA/HNA copolyesters with different compositions [44]. They found that the entrance pressure drop increases with shear rate, which can be interpreted as due to high melt elasticity but is in fact associated with the energy required to orient the director of LCP domains at the entrance to the capillary. Unless the temperature is high enough to melt all crystals, high yield stress will be observed at the onset of flow. However, due to the absence of a clearing temperature in these polymers, increasing temperature leads to the formation of more blocky domains and does not eliminate the yield stress. On the other hand, in thermotropic hydroxypropylcellulose, which has a clearing temperature, the
yield stress in the liquid crystalline phase disappears with transition to the isotropic phase [40]. This isotropic transition results in an increase of viscosity.

The end correction in capillary rheometry and the viscosity highly depends on shear and temperature history. In rotational rheometry, variations in gap dimensions and shear history lead to irreproducible results. In dynamic rotational rheometry of Vectra A, the standard deviation of $\eta^*$ and $G'$ measurements were found to be 10% upon 5 measurements [42]. The linear region of $G'$ and $G''$ extends to a maximum strain amplitude of 2% at low, and 0.5% at high frequencies [45]. Change of gap distance from 0.2 to 2 mm results in a 1.5 fold change in viscosity. During testing of Vectra A in rotational rheometers at 290-300°C, the viscosity was constant for 8 minutes and then increased by more than 50% in 15-20 minutes [42]. Viscosity increase by an order of magnitude was recorded upon annealing at 300°C for 18 hours. Through intrinsic viscosity measurements, it was confirmed that MW does not change, but rather it is the perfection of crystalline order during annealing that leads to increase of melt viscosity. The melt viscosity of these polymers is highly dependent on temperature below 300°C, where the activation energy for flow is 50 kcal/mole, as opposed to 10 kcal/mole above 300°C. Between 280-300°C, there exists a large amount of unmolten polymer leading to partial order which acts as crosslinks. Local variations in temperature can cause significant viscosity variations due to slippage and irregular flow, leading to poor reproducibility below 300°C.

The rheological measurements of LCPs are directly related with the texture of the polymer. Presence of oriented domains can yield different results. Therefore, it is important to note the initial poly-domain structure in LCPs [17]. Kim and Han performed
transient rheological studies in steady shear flow on a thermotropic polyester, poly-
[(phenylsulfonyl)-p-phenylene-1,10-decamethylenebis(4-oxybenzoate)], exhibiting a
clearing temperature [46]. They found that the morphology of TLCP is defined by its
thermo-mechanical history and is directly related to its rheology. No decrease in shear
stress occurs after the establishment of the final melt morphology. It should be noted that
the melting of all crystal structures is not a necessary prerequisite for the flow of LCPs
[47]. Care should be taken to maintain good temperature control during measurements.

The loading of samples into rotational rheometer and subsequent squeezing can
influence the determination of the first normal stress [17]. The normal stress is expected
to relax by radial flow of the sample; however, this relaxation is very slow for some
TLCPs. The presence of even small residual normal stresses at the start of experiments is
enough to lead to irreproducible results. Different approaches to removing the normal
stress are suggested, including preheating of samples at high temperatures to melt out
residual crystallites before cooling to start the test [8, 45], preshearing the sample after
thermal equilibration followed by relaxation [48, 49] and equilibration under vacuum in
the rheometer for long times.

The rheology of a thermotropic LCPs composed of 60/40 PHB/PET and 80/20
PHB/PET was studied in both capillary [50] and rotational rheometers [43, 50]. In
rotational rheometry gap adjustment by squeezing the melt introduces flow history to the
samples. Good reproducibility is obtained by employing the same rate of squeezing flow
and waiting for the same time for each sample [43]. In cone-and-plate and parallel plate
measurements, the LCP remained shear thinning even at very low shear rates and did not
exhibit significant yield stress upon cessation of shear [43]. Both capillary and rotational
rheometry gave the same viscosity values [43]. Jerman and Baird also studied rheology of PET/LCP blends in capillary rheometry [50]. They observed much higher entrance pressure drop and shear stress as compared to pure LCP, with negligible elastic recovery at the capillary exit.

Giles and Denn studied Vectra A and showed that bubbles varying in diameter, up to almost the thickness of the sample, formed in vacuum molded samples during testing in a rotational rheometer [34]. The off gas species from samples of this polymer were identified to be low molecular weight oligomeric components of Vectra A. Transition of the low molecular weight species into gaseous phases at melt temperatures and the consequent coalescence of bubbles results in the testing of partially hollow samples and detachment from the rotational rheometer platens. Small bubbles acted as rigid spheres in a suspension and increased viscosity while the displacement of melt by large bubbles lead to a decrease in viscosity.

Giles and Denn also studied the viscosity of Vectra A in a pressurized capillary rheometer, which inhibited bubble formation [34]. They observed that the viscosities from the pressurized capillary rheometer and rotational rheometers at atmospheric pressure exhibited similar shear rate dependence, but viscosity values obtained in the rotational rheometer were greater. They observed a decrease in the viscosity during measurements in the high-pressure capillary rheometer at long times, due to the effect of thermal history on liquid crystalline texture. Shear thinning behavior at low shear rates in both rotational and high-pressure capillary rheometers resembled the three region flow behavior observed in lyotropic LCPs.
2.1.5. Annealing of thermotropic LCPs

Heat treatment of LCP fibers, generally applied 10-30°C below the melting point (T_m), leads to increases in tenacity, modulus, elongation at break, melting point as well as greater chemical and thermal stability. The improvements are due to solid state polymerization, removal of critical flaws in morphology and increase in size and perfection of crystals [38, 51, 52, 53, 54]. For efficient molecular weight increase with heat treatment, end groups and side chains of end group must be balanced [52].

Mechanical load transfer in oriented LCPs is governed by intermolecular interactions and failure occurs at the more randomly oriented chain ends [38]. The number of chain ends is inversely proportional to the molecular weight, leading to greater strength at higher molecular weights. Increase in modulus is directly related to increased orientation. Findings summarized in this chapter show that reactions can take place in LCPs even though they are made of rigid molecules.

Luise observed increase in tenacity of fibers spun from main chain aromatic LCPs upon heat treatment below T_m under vacuum for 30 minutes to 4 hours. The studied LCPs included HBA/HNA and PET/HBA copolyesters, among others. He disclosed that the increase in tenacity was due to increased orientation and molecular weight upon heat treatment. Polymerization reactions in liquid crystalline polyesters require carboxyl or hydroxyl end groups, or the spontaneous removal of end capping groups during heat treatment [55]. Yoon et al. also showed that heat treatment of HBA/HNA fibers at 270°C for 30 minutes increased intrinsic viscosity (I.V.) from 7 to 30 dl/g and tenacity from 1.5 to 3.0 GPa [38].
Muramatsu and Krigbaum studied liquid crystalline copolyester of 58/42 HBA/HNA [56]. Heat treatment of as spun fibers resulted in increased in MW, inherent viscosity, and degree of perfection of crystalline structure. However, improvements in fiber tenacity and modulus with annealing were only observed at high draw down ratios (DDR) in fiber spinning. Fibers must be highly oriented for mechanical properties to be improved with annealing. While some increase in I.V. was recorded for fibers at different DDR, this did not directly translate into improved mechanical properties. In the heat treatment process, the effect of solid-state polymerization is coupled with improvements in crystalline perfection. The reaction is governed by diffusion rates of reactive end groups and byproducts [54].

Karis et al. studied the rheology Vectra E and observed that its annealing at 300°C under nitrogen atmosphere increased its melting temperature to 380°C, possibly through end group reactions [57]. Values of the loss tangent (\(\tan \delta\)) decreased from 1 to 0.1 with annealing for 43 hours. The annealed LCP became insoluble in pentafluorophenol and the nematic texture was not observed even at very high temperatures. On the other hand, solid state polymerization upon annealing can also lead to the conversion of isotropic phase into the nematic state, similar to observations on HBA/PET copolymers [58].

2.1.6. Morphology of thermotropic LCPs

The molecules in LCPs organize themselves into domain structures in melt state under quiescent conditions. The domain texture size in LCPs ranges from 0.1 to 100 \(\mu\)m. Upon the start of flow, oriented finer domains are created [59]. The morphology observed in injections moldings and in fibers is discussed in this section.
2.1.6.1. Injection molding morphology

Unlike lyotropic LCPs, which can only be processed in solution, thermotropic LCPs can be injection molded like thermoplastics. Strong anisotropy is observed in injection moldings, with greater variation in cross-section as the thickness of moldings increases. The low thermal expansion coefficient and anisotropic melt of LCPs allows very precise moldings. Skin-core morphology is typically seen in moldings of TLCPs. Generally, there is a highly oriented outer skin layer, axially oriented inner skin layers and a randomly oriented core. The morphology of injection molded LCPs is schematically shown in Figure 2.4. With increasing orientation, the relative ratio of skin to the core regions in moldings also increases [60].

![Figure 2.4. Typical morphology of injection molded LCP.](image)

In injection moldings of 60/40 and 80/20 PHB/PET thermotropic copolyesters, PHB rich skin and PET rich core region are formed. This is due to partial phase separation in the melt and fountain flow forming the PHB rich phase at the flow front. The microstructure is dependent on the thickness of moldings, with the number of oriented layers increasing with thickness. Joseph et al identified four-layer structure in injection molded LCP [61]. Hsiung et al. also identified four-phase morphology in their study of the effect of injection speed on moldings of Ultrax 4002 [62]. In studies by
Dreher et al., the greatest orientation was found to lie 1 mm below the surface in injection molded dumbbell shaped of LCP (Vectra A) [63].

Thapar and Bevis studied the injection molding of a thermotropic copolyester of 70/30 p-acetoxybenzoic acid/p-acetoxynaphtoic acid. They observed improved tensile strength and modulus at higher barrel temperatures. Low injection speeds was found to result in greater thickness of the skin layer by allowing more uniform and highly oriented flow. A decrease in sample thickness from 4 to 1 mm led to an increase in Young’s modulus from 11 to 30 GPa. The tensile modulus is directly related to orientation and using thinner samples reduced the proportional size of the core region [64].

Ophir and Ide studied an all-aromatic thermotropic copolyester polymerized from 60% p-acetoxybenzoic acid, 20% terephthalic acid and 20% naphthalene diacetate. They compared the morphology of injection moldings of LCP and short glass fiber filled composites. In converging flow, glass fibers are oriented parallel to the flow while in diverging flow, they are oriented in the transverse direction. The flex modulus in injection molded discs of LCPs was more anisotropically distributed than that of 30% glass filled PBT, with the maximum lying in the injection direction [65].

2.1.6.2. Fiber spinning morphology

LCPs are oriented easier in elongational flow fields. Spun fibers of LCPs and their blends with thermoplastics exhibit higher stiffness and strength compared to their injection moldings [66].

Sawyer and Jaffe observed three distinct microfibrillar structures of 5 µm, 0.5 µm and 50 nm diameter in uniaxially oriented extrudates of thermotropic polyesters with
naphthalene moiety. At a fibril diameter of 50 nm, the aspect ratio of molecules is much greater, leading to greater orientation along the microfibril axis. Defect structures, i.e. regular deviations from the rod like structural order and packing, are also present [60].

A very high degree of crystalline order is developed in extrudates of LCPs as they form into fibrils. The incremental increase in orientation with additional drawing is not very significant and is usually undetectable [47].

Kenig suggested that the molecular orientation of LCPs is determined by the elongational strain during elongational flow. The average orientation angle ($\phi$) is related to the draw ratio (DDR) and the orientability parameter $\lambda$ as follows:

$$\tan \phi = C * \text{DDR}^{-\lambda}$$  \hspace{1cm} (2.5)

where C is a constant, which represents the orientation at DDR=1, and can be determined by WAXS. The orientability parameter $\lambda$ shows how fast the LCP will orient when subjected to elongational flow strain. As $\lambda$ directly ties in with mechanical properties in the orientation direction, it is useful for comparison of different LCPs [67].

Radhakrishnan et al. studied the fiber spinning of sheath-core type PET/LCP (Rodrun LC3000, as the core) where the components were co-extruded in two separate extruders and then combined in the spinning head to form the fibers, which were drawn at speeds of up to 8 km/min. The orientation of PET was suppressed in the blends, while the LCP core was highly oriented due to the high level of stress produced during the fiber spinning process, leading to high tensile modulus values, matching predictions of the rule of mixtures. However, a plateau in LCP orientation was reached at 3 km/min take-up speed. While spinning of LCP as a single component led to breakage at the point of concentrated deformation near the spinneret, the deformation occurred downstream of the
spinneret and spinnability was improved in the bicomponent fibers. It is in these bicomponent LCP/PET blends that continuous increase in tensile modulus with take up speed was recorded, which was mostly due to increase in modulus of the LCP phase and not the PET. The thermal and stress histories experienced by fibers is different in bicomponent spinning. Due to the higher solidification temperature of LCP, the orientation of the bicomponent blends no longer occurs above the $T_g$ of PET, which then relaxes and loses a certain degree of orientation [68]. Brody reported that the addition of small amounts of LCP (Vectra A950) to PET leads to suppression of PET orientation during fiber spinning, allowing operation at higher drawing speeds without fiber breakup [69].

Preparation of self-reinforced laminate structures comprising blends of LCP with a flexible chain thermoplastic and blends of two LCPs was described by Isayev et al. [70, 71]. Unidirectional and quasi-isotropic laminate structures of polyphenylene oxide (PPO)/PS alloy with LCP (Vectra A950) were prepared by compression molding of extruded preregs of the blends below the melting temperature of the LCP by Isayev and Viswanathan [72]. The drawn LCP fibrillar structures imparted high stiffness and strength, forming self-reinforces laminate structures. Laminates of PPO with two different LCPs (Vectra A950 and Ultrax KR4002) and of PPO/PS alloy with Ultrax KR4002 [73], PEI with Vectra A950 [74], and PP with Vectra A950 [75] were also studied. These structures also indicated highly orientated LCP fibrils in the laminates.

In another study involving the bicomponent fibers of PP/Vectra A950, continuous fibers of the LCP were uniaxially arranged in the core and were compression molded in a sheath of PP, above the $T_m$ of PP but below that of LCP. Spinning of the bicomponent
fibers resulted in the orientation suppression of the PP sheath, due to relaxation of the softer PP phase orientation following the freezing of the LCP. The tensile modulus and strength of LCP was also higher in the bicomponent fibers than it was in single component fibers [76].

2.2. Miscibility

Majority of polymer blends are immiscible and phase separate. The physical properties of immiscible blends are limited by inhomogeneity and transient morphologies, large domain sizes, and poor interfacial adhesion. Polymer blends are compatible when they resist gross phase separation and give desirable properties [77]. Difference between immiscible and compatible blends is illustrated in Figure 2.5.

<table>
<thead>
<tr>
<th></th>
<th>MISCIBLE</th>
<th>IMMISCIBLE</th>
<th>COMPATIBILIZED</th>
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<tbody>
<tr>
<td>Domain size</td>
<td>approaches $R_g$</td>
<td>$&gt;&gt; R_g$</td>
<td></td>
</tr>
<tr>
<td>Chain conformation</td>
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Figure 2.5. Miscibility and compatibility in polymer blends.

The domain size of dispersed phase commonly approaches the radius of gyration ($R_g$) in miscible blends [78]. In immiscible blends, large ununiform domains are present after mixing. The domain size of compatibilized blends commonly lies between miscible and immiscible blends and is generally stabilized. While immiscible blends exhibit a
distinct interface, an “interphase” with greater interaction between the phases is commonly observed in compatibilized blends.

Compatible blends may contain two or more phases. On the other hand, the term miscible is used to describe polymer blends that are homogenous on a molecular level [79]. Miscibility of polymers generally requires the existence of specific interchain interactions such that the free energy decreases upon mixing. Although the chemical structure of a polymer pair may be similar, polymers are generally immiscible unless specific interchain interactions exist [80].

Heterogeneous polymer blends can have useful applications. In the case of LCP blends, immiscibility of the components allows ease of processing and leads to stiff materials. However, interfacial adhesion dictates the failure mechanism in blends, and lack thereof leads to adhesive failure between the LCP fibrils and the thermoplastic polymer matrix. Insufficient interfacial attraction in blends usually results in brittleness [81]. Increases in Young’s modulus of up to 70% have been realized in blends with good interfacial adhesion [82]. Elongation at break is drastically reduced in blends with poor interfacial attraction [30].

Compatibilizers are commonly added to immiscible polymer blends in order to reduce interfacial tension. Compatibilization leads to a finer phase morphology and formation of stable interphases. Commonly accepted methods for improvement of interfacial adhesion include the additions of grafted polymers and tailored block copolymers to blends [80, 83], and in-situ reaction between functional groups in the polymers [77]. The latter is particularly useful for polycondensation polymers, as they
contain reactive functional groups on the backbone and can undergo exchange reactions under suitable conditions.

Miscibility is often determined by investigating optical, morphological properties, glass transition temperature and crystalline melting behavior of the mixture. A common $T_g$ is often interpreted as the indicator of compatibility. However, when broad $T_g$ is displayed, a conclusion about miscibility should not be drawn using only this indication. Optical and morphology analyses can be performed to characterize the miscibility of polymer phases by determining when the glass transition temperatures of the blended polymers are similar [79].

Binodal and spinodal curves are used to represent polymer miscibility. The cloud point curve is associated with phase separation on heating and is referred to as the lower critical solution temperature (LCST) phase diagram. LCST, which is common for high MW polymer-polymer systems, is concave upward. The upper critical solution temperature (UCST) phase diagram is exhibited by low MW oligomers and in the mixing of polymer- solvent or two liquids and is concave downward. The Flory-Huggins theory is used in modeling phase diagrams [79].

In completely miscible systems, a single $T_g$, lying between those of the pure components, is observed. Fox suggested the following empirical relation for determining the miscibility of polymer blends [84]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$  \hspace{1cm} (2.6)

where $T_g$ is the glass transition temperature of the miscible blend, $T_{g1}$ and $T_{g2}$ are the glass transition temperatures of the components, and $w_i$ are their weight fractions. Strictly
speaking, the Fox equation cannot be applied to systems containing semicrystalline polymers, as the density of the amorphous and crystalline fractions are different. In the present study, this equation was used for comparative purposes.

For random copolymers, the Gibbs-DiMarzio theory can be used to calculate glass transition temperature with composition [85, 86]. According to Shi and Jabarin, using universal value of 2.26 for $\varepsilon/\kT$ can be used to describe the Gibbs’s-DiMarzio equation as [87]:

$$T_g = X_1 T_{g1} + X_2 T_{g2} \tag{2.7}$$

where $T_g$ of the random copolymer system is shown to depend on the $T_g$’s of the components ($T_{g1}$ and $T_{g2}$) and their mole fractions ($X_1$ and $X_2$). In random copolymers, the $T_g$ predicted by eq. 2.7 is expected to lie closer to experimental observations than predictions by the Fox equation (eq. 2.6), which represents miscible systems. Shi and Jabarin showed the presence of random copolymer due to transesterification of PET/PEN blends by showing closer dependence of $T_g$ to Gibbs-DiMarzio equation [87].

In crystallizable polymer blends, melting point depression is also observed and can be utilized to determine miscibility. The Flory-Huggins theory for determining the Gibb’s free energy of mixing applies to very high molecular weight polymers [88]:

$$\frac{1}{T_1} - \frac{1}{T_{10}} = \left( \frac{R}{\Delta H} \right) \left( \frac{V_2}{V_1} \right) \left( \phi_1 - X_{12} \phi_1^2 \right) \tag{2.8}$$

where $T_1$ is the melting point of a component, $T_{10}$ is the melting point of the perfect crystal of that component, $R$ is the gas constant, $\Delta H$ is the excess enthalpy of interaction, $V_i$ and $\phi_i$ are the molar volumes and volume fractions of the components, respectively,
and $\chi_{12}$ is the Flory interaction parameter. Porter et al. studied the application of this theory to blends of LCPs in order to calculate the interaction parameter $\chi_{12}$, which describes the interfacial interaction in the blend [89].

Isayev and Shah measured the interfacial adhesion of LCP fiber to the thermoplastic matrix for a variety of materials. Following fiber spinning of pure LCP in a capillary rheometer, the fiber is embedded into the matrix by compression molding at a temperature just below the melting of the LCP. In pullout tests of the single fiber, stress maxima corresponding to the debonding strength of the fiber from the matrix are observed. It is envisioned that a debonding crack forms initially with the load and grows, with total debonding occurring at the maximum force. Following debonding, complete extraction of fiber from the matrix takes place, with the embedded and extracted fiber length being the same due to poor interfacial adhesion. The maximum debonding strength is reproducible and is a good measure of interfacial adhesion. It was found that polyesters, especially PBT, have greater affinity to LCP as opposed to polyolefins. This is due to similarity in chemical structure with the thermotropic copolymers studied [90].

Partially miscible polyetherimide (PEI)/LCP (DuPont HX1000 and HX4000) blends showed shifts in storage modulus peaks with LCP concentration in dynamic mechanical thermal analysis (DMTA) [91]. A decrease in $T_g$ of PEI/HX4000 blends was recorded upon annealing, which was attributed to the free LCP chains dissolving in the PEI rich phase [92]. Improvements above that of the pure components were recorded for tensile strength in most blends and for flexural modulus in blends with more than 40% LCP weight concentration. On the other hand, drastic reductions in elongation at break were observed with LCP content due to the already low elongation of pure LCP (1.8%).
While the fibrillation in partially miscible blends occurred at greater LCP content than immiscible blends, finer fibril formation was observed by increased mixing with multi-pass extrusion in partially miscible blends [92].

Seppala et al. studied the mechanical properties of injection molded blends of LCP (Vectra A950) with PP and PPS. While improved thermal and dimensional stability were observed for all blends, the increase of heat deflection from 52°C for pure PP to 110°C in the 50/50 PP/LCP blend was the most significant. HDT of pure LCP was measured at 154°C. The crystallinity of PP and PPS did not increase with LCP addition [93].

Kwon and Chung studied the effect of flexible spacer length in LCPs on the miscibility of LCP/PC blends by synthesizing various LCPs and comparing them to Vectra A950. They found that the interfacial adhesion was improved with increased spacer length but the mechanical properties decreased. While FT-IR studies did not indicate any reaction, a change in the structure of PC was found through $^1$H-NMR studies, indicating little transesterification. The improvement in interfacial adhesion was attributed to better mixing at interface through the increased mobility of LCP with flexible spacers, which leads to entanglements and prevents interfacial slip [94].

Schleeh et al. studied the effect of laterally substituting flexible alkoxy groups on a synthesized aromatic liquid crystalline polymer on the miscibility between the LCP and PET. It was observed that the laterally substituted terephthaloyl moieties in the LCP increased the homogeneity of blends. Tailoring of laterally substituted units to LCPs can control phase segregation of blends through inducing entanglement of chains and increased partial miscibility [95].
Zhuang et al. studied blends of several thermoplastics with LCP based on 60/40 PHB/PET copolymer. It is suggested that the LCP forms a two-phase structure, one rich in PET, and the other in PHB. PS was found to be completely immiscible with this LCP. PC is partially miscible with the PET phase of the LCP, whereas PET is completely miscible with the PET phase of the LCP. In all these blends, large reductions in viscosity were observed with the addition of the LCP phase [96].

Carfagna et al. identified interfacial adhesion as the most important parameter for the utilization of the reinforcing properties of LCPs in their blends. While single fibers of the LCP (40/60 PET/PHB copolymer) fragment at 2% elongation, the PC matrix reinforced by a single LCP fiber did not fragment at up to 8% deformation. It was found that there is slip between the matrix and fiber until considerable necking in the matrix, which allows frictional forces to carry on the shear stress across the matrix/fiber [97].

It should be noted that while improved interfacial adhesion through compatibility can enhance mechanical properties of blends containing LCPs, compatibility is not always a prerequisite to obtain good mechanical properties. Subramanian and Isayev observed an improvement in the tensile and impact properties of LCP (HBA/HNA copolymer)/poly(phenylene sulfide (PPS) blends with increasing LCP concentration [98].

2.2.1. Methods for improving miscibility

In-situ compatibilization can promoted through the reaction of functional groups with the polymers to form block or graft copolymers. The in-situ formed copolymer must then move to the interface between the immiscible polymers and improve interfacial
attraction. Using a polymer with functional end groups as the third component is a commonly practiced method for improving compatibility of polymer blends [80, 83].

A common method used to improve miscibility of blends is to add a third component with a similar chemical composition to one of the polymer phases in the immiscible blend. Interfacial reactions can occur through the reaction of functional groups of the added components with the end groups of the polymers in the blend. Through effective mixing and the addition of a catalyst, the rate of reaction can be increased. The challenge in this case is achieving migration of in-situ formed copolymer to the interface between immiscible phases [80, 83].

Another method used to compatibilize immiscible blends is to add a reactive block copolymer that is incompatible with either blend component. The block copolymer should have functional end groups with equal likelihood of reacting with the functional groups of the polymers in the blend. The added block copolymer will already reside at the interface due to its immiscibility with the other polymers. Provided that the reaction rates between the copolymer and the two incompatible polymers are comparable, in-situ copolymer will be formed directly at the interface. In order to make the polymers in the blend equally likely to react with the added block copolymer, prior functionalization of the polymers is necessary [83].

Through studying blends of PC with LCPs differing in the flexibility of their backbone structure, La Mantia et al. showed that flexible spacers in semi-rigid LCPs improve interfacial adhesion in blends. The wholly aromatic LCP was Vectra A950 while the flexible LCP was a copolyester of 1:1:2 sebacic acid: 4-4’-hydroxybiphenyl: p-hydroxybenzoic acid. The modulus and strength in blends containing the semi-flexible
copolyster LCP were lower than for blends with Vectra, while the elongation at break was much greater [99].

Polyesters are made by polycondensation reactions and have carboxyl groups which can go through esterification and transesterification reactions [100]. Depolymerization of polyesters in the presence of water requires stringent drying prior to processing and testing under nitrogen atmosphere to prevent oxidative degradation.

The rate of in-situ compatibilization through reaction of end groups can be controlled through reactive group concentration, catalyst addition and processing conditions like temperature, extent of mixing and residence time [83].

2.2.2. Interchange reactions in polyesters

Copolymer formation during reactive extrusion is useful for compatibilizing immiscible blends. Polyesters react with compounds containing hydroxyl and carboxylic acid groups at elevated temperatures. The possible exchange reactions for the formation of copolymers include alcoholysis, acidolysis, and direct transesterification [77,101]. These are commonly referred to together as transesterification. The interchange reactions of polyesters, redrawn after Kotliar [101], are shown in Figure 2.6.

Interchange reactions can occur by chain scission and recombination during reactive extrusion. However, the reactions processing through chain scission tend to form block copolymers with broad molecular weight distributions. Copolymers formed in this way commonly have lower chain lengths then the sum of the homopolymers. The degree of randomness (DR) is also initially low in this reaction route through chain scission [77].
Interchange reaction by the interchange of end groups leads to formation of block and graft copolymers. However, the low reactivity of polymer end groups and end-capping of most commercial polymers limits interchange reactions. In some systems, presence of residual polycondensation catalyst has been reported to increase reaction rates in exchange reactions [102].

<table>
<thead>
<tr>
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<th>![Reaction Equations]</th>
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<tbody>
<tr>
<td><strong>Intermolecular</strong></td>
<td></td>
</tr>
<tr>
<td><strong>alcoholysis</strong></td>
<td>![R1-O-C-R2 + R3-OH → R1-O-C-R2 + R3-O-C-R2]</td>
</tr>
<tr>
<td><strong>acidolysis</strong></td>
<td>![R1-O-C-R2 + R3-C-OH → R1-O-C-R3 + R2-C-OH]</td>
</tr>
<tr>
<td><strong>Ester-ester exchange</strong></td>
<td>![R1-O-C-R2 + R3-C-O-R4 → R1-O-C-R3 + R2-C-O-R4]</td>
</tr>
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</table>

Figure 2.6. Types of interchange reactions in polyesters.

The exchange mechanism of reactive polymers in melt state reactive is shown in Figure 2.7. Direct exchange reactions can take place between inner functional groups. For
inner-inner exchange reactions, the reaction rate is independent of MW. In end-capped polymers, catalysts are generally required for inner-inner interchange reactions below 300°C. Reaction of reactive end groups does not require catalysts. Interchange reactions are dependent on polymer molecular weight, as chain ends must diffuse to find one another. Mixing enhances reaction rates in molecular interchange reactions in the melt. Reactive inner groups include –CO-O, O-CO-O, -CO-NH-; reactive outer groups include –OH, -COOH, -NH₂ [103].

Figure 2.7. Exchange mechanism of reactive polymers in the melt.

Residual titanium and antimony compounds are known to accelerate transesterification reactions in many blends containing polyesters [104, 105, 106, 107,
Stewart et al. reported that the addition of these catalysts did not affect the rate of transesterification in PET/PEN blends [111].

2.3. Transesterification of PET/PEN polyester blends

PEN is superior to PET in its mechanical, thermal, barrier, properties, and chemical resistance. Due to its high $T_g$, steam sterilization and multi-cycle use of articles made from PEN are possible. High melt viscosity of PEN allows it to be used in processes requiring high melt strength, such as extrusion blow molding, tubular film blowing, etc. Dimethyl-2-6 naphthalene dicarboxylate used in PEN manufacture is a high cost monomer. Combining the economy of PET and the high performance of PEN can yield materials with enhanced thermal and barrier properties [112]. PET is lacking in hot fill packaging, and blending with PEN can allow higher temperature processing and improve barrier properties for packing of oxygen sensitive materials [113]. PET/PEN blends are useful for their improved mechanical, thermal and barrier properties over PET. They have been widely studied in industry and academia.

While these blends are immiscible at any temperature/composition [114], they react by annealing or melt processing to form copolymers through interchange reactions. The in-situ copolymer thus compatibilizes the blends. Physical mixture of PET/PEN can easily be transesterified, this was shown by annealing for 1 minute at 305°C, which led to a single narrow $T_g$ [111]. Transesterification reaction kinetics are controlled by temperature, time, catalyst (including residual from polymerization) and mixing in internal mixers, extruders, etc. In the initial stages of transesterification, larger blocks are formed leading to block copolymers. Later on, the sequence lengths of PET and PEN
 decrease as the degree of randomness (DR) increases, leading to random copolymers. At a DR of 1, statistical random copolymer is formed. Number average molecular weights ($M_n$) of PET and PEN are around 18-20,000. Molecular weight distribution is expected to broaden with transesterification through chain scission and inter-reaction during melt processing of these blends [77]. Transesterification level increase with temperature, following a 1$^{st}$ order Arrhenius dependence [111]. Matching melt viscosities promotes transesterification in blends [115]. This is because the droplet size is smallest in blends when viscosity ratio equals one [116]. Medina et al. modeled thermally induced ester-ester exchange in PET/PEN blends as a reversible second order reaction [117]. The rate of forward reaction was found to be 4 times greater than that of the reverse reaction.

Miscibility of PEN/PET blends influences their clarity. Optical clarity was possible with good mixing at a degree of randomness (DR) above 10% [111]. Blending PET/PEN blends reduces crystallinity with increased extent of transesterification. Commonly, the cold crystallization temperature also increases, while enthalpy of melting is decreased [114,118]. Strain-induced crystallization decreases above a certain level of transesterification. Maruhashi suggested that a DR of 17-40% is required to achieve phase solubility while retaining crystallinity and stretch molding properties [119].

Up to three passes through a single screw extruder may be necessary to achieve optical clarity [120]. However, extended processing of these blends can induce thermal degradation. Production of optically clear PEN/PET blends in a single pass commonly requires the design of a special screw, or processing in a twin screw extruder [121]. It is imperative to achieve more uniform thermal distribution and good mixing in extrusion. Tharmapuram and Jabarin found that the required processing melt temperature for
obtaining the critical transesterification in a single pass in a twin screw extruder was 50°C higher than the equilibrium melting temperature of blends [122].

Above a critical transesterification level, thermal properties are stabilized and will not change with further copolymerization. Rhee et al. found no cold crystallization or melting peaks for unstretched 50/50 PET/PEN blends, while stretching was found to induce significant crystallinity [113]. Patcheak and Jabarin suggested that there is a critical copolymer block length below which the minor component does not crystallize [123]. The critical length depends on ratio of homopolymers in the blend. It was found to be 11 for PEN block, which was achieved after the 4th extrusion pass in 80/20 PET/PEN blend.

Tant et al. studied permeability of PEN/PET blends [124]. PEN had 2.5 times the O₂ barrier of PET in unoriented amorphous state. Biaxial stretching reduced concentration of free volume sites, and allowed PEN chains pack more efficiently than PET, hence reducing the permeability. While heat setting was found to decrease permeability of PET, it had little effect on that of PEN. Decreasing the free volume and its connectivity through the film led to improved barrier properties. Density of PET and PEN films were found to increase with stretching up to a draw ratio of 4, subsequently decreasing their permeability to O₂. Permeabilities of PET and PEN were 0.45 and 0.15 cm³/cm/(m²*atm*day) before, 0.18 and 0.02 cm³/cm/(m²*atm*day) after drawing, respectively [125].

Wu et al. studied permeability of PET/PEN in biaxial stretching [126]. Orientation introduced micro-continuous PEN layers, which were shown to provide a torturous path for diffusion of gasses. Results for permeability were correlated with
observed morphology with the “generalized Maxwell model for gas transport in heterogeneous media”, as shown by Petropoulos [127]:

\[
P_{blend} = P_c \left[ \frac{P_d + A(P_c \phi_c + P_d \phi_d)}{AP_c + P_d \phi_c + P_c \phi_d} \right]
\]  

(2.9)

where \(P_{blend}\) is the permeability of the blend, \(P_c\) and \(P_d\) are the permeabilities of the continuous and disperse phases, respectively, \(\phi_c\) and \(\phi_d\), are the volume fractions of the continuous and disperse phases, respectively, and \(A\) is the geometry factor for the dispersed phase. The following cases were defined [127]:

1. \(A = 0\), oriented domains of dispersed phase perpendicular to gas flow direction

\[
P_{blend} = -\frac{P_d}{\phi_c + P_d \phi_d}
\]  

(2.10)

2. \(A = 2\), dispersed phase forms spherical domains

3. \(A = \infty\), oriented domains of dispersed phase parallel to gas flow direction

\[
P_{blend} = P_c \phi_c + P_d \phi_d
\]  

(2.11)

In case 1 oriented domains of dispersed phase are perpendicular to the flow direction, yielding the lower limit of permeability in blends. In biaxially stretched PET/PEN blends, 30% and 50% volume fractions of PEN phase were shown to follow the lower limit [126].

Fermeglia et al. performed molecular modeling simulation of PET/PEN homopolymer mixtures without and with PET/PEN copolymer [112]. In unit cells of 92/8 and 80/20 PET/PEN blends, more uniform distribution was achieved with complete transesterification. Copolymer overcomes repulsion between PET/PEN and prevents phase separation. It was suggested that greater phase separation of crystalline PEN
domains, as in physical mixtures, would provide better barrier properties to oxygen than copolymers. However, crystallinity above a certain level may not always be desirable as it reduces optical clarity.

Stewart et al. described the detailed procedure for determining transesterification of PET/PEN blends from $^1$H NMR [111]. Maruhashi also studied transesterification of PET/PEN blends [119]. A 7:3 mixture of deuterated chloroform and deuterated acetic acid trifluoride was prepared. Dried pellets weighing 10 mg were dissolved in 1 ml of the specified solution. The transesterification content in the blend is given by the intensity of PET-PEN transesterification peak over the sum of intensities of the former and the pure PET and PEN glycol proton peaks as obtained through $^1$H NMR. It was also shown that the transesterification content in PET/PEN blends increased with increasing injection molding cycle time. With transesterification of more than 5 mol%, the blends were transparent.

Wagner et al. studied phase separation in biaxially oriented films of PET/PEN through dynamic rheology [128]. Due to higher interfacial area and corresponding stresses in biaxially oriented PEN layer, phase separation was found to occur even in blends with transesterification. A thick interface was formed and PET/PEN melting peaks overlapped due to transesterification. Dynamic rheological experiments were performed and applicability of time-temperature superposition (TTS) was studied. TTS was shown to break down at low frequencies and high temperatures for 90/10, 80/20 and 70/30 PET/PEN blends._slope of the storage modulus ($G'$) approached 1, and become similar to that of the loss modulus ($G''$). TTS showed the least deviation for 70/30 PET/PEN blends, probably due to greater extent of transesterification at this concentration. At high
frequencies, which obeyed TTS, the surface tension was masked by entropic elasticity of polymer. At low frequencies, the difference between surface energies of PET and PEN required more energy, and was characterized by $G'$ as it is an elastic effect. The deviation from TTS was more pronounced at higher temperatures, as the relaxation of polymer chains increased with temperature.

In a study by Tharmapuram and Jabarin, transesterification reaction between PET and PEN was found to be coupled with degradation [129]. Changes in viscosity could not be quantified as being due to transesterification alone. Nevertheless, the polydispersity index ($M_w/M_n$) is expected to approach a value of 2 through interchange reactions and increasing degree of randomness. As the polydispersity of polycondensation polymers are usually above 2, transesterification could be expected to reduce the weight average molecular weight. This could lead to a reduction in viscosity with increased degree of randomness (DR). In the study by Tharmapuram and Jabarin, melt viscosity decreased up to 10% concentration of PEN due to disruption of PET monomer sequence by naphthalene linkage following transesterification [129].

2.4. Compatibilization of blends with LCPs

In this section, addition of block copolymers, transesterification of thermotropic LCPs and flexible chain thermoplastics, and the effects of catalysts for transesterification in these blends will be discussed.
2.4.1. Addition of block copolymers

O’Donnell et al. studied the effect of adding maleic anhydride (MA) grafted PP to PP/LCP (Vectra B950) blends [130]. MA grafted PP acted as a compatibilizer, improving the tensile strength and modulus of the blends. The viscosity of the PP/compatibilizer system was lower than that of pure PP. Compatibilized blends with more than 30% LCP concentration showed a higher viscosity. The addition of compatibilizer made the blends stiffer and more brittle through the creation of finer domains with increased surface area. Datta et al. also studied the same blend system and found improvements in the tensile modulus and strength, but not elongation at break and toughness, with compatibilization [131]. The compatibilized blends were less phase-separated, and the LCP fibrils were finer and more uniformly dispersed. While ductile failure was observed for the uncompatibilized 80/20 PP/LCP blends, brittle failure was seen in the compatibilized blends due to improved interfacial adhesion between the reinforcing fibers and the PP matrix, with the failure occurring due to fiber pullout.

Chiou et al. have demonstrated that ethylene-glycidyl methacrylate copolymer (EGMA) acts as a compatibilizer in PP/LCP (Vectra A900) blends [132]. A grafting reaction takes place between EGMA and LCP, as identified by FT-IR spectroscopy by a decrease in the size of the epoxy peaks after blending, leading to increased viscosity in the blends. It is suggested that EGMA reacts with the –COOH group of the LCP rather than –OH end groups due to difference in acidity. Through compatibilization, smaller LCP domains are created and the phase interfaces are blurred; fibrillar morphology is less pronounced and smaller fibrils are found. The ultimate strength and stiffness are reduced upon compatibilization as the high amount of compatibilization hinders the fibril
formation through the creation of finer domains. On the other hand, the elongation at break and unnotched impact strength are considerably improved with the addition of EGMA as well as a small amount of ethyl triphenylphosphonium bromide catalyst.

Zheng et al. studied the effect of adding different copolymers, including styrene-maleic anhydride (SMA), glycidyl methacrylate grafted PP (PP-g-GMA) and maleic anhydride grafted PP (PP-g-MA) on the mechanical properties of PA6/LCP (Vectra A950) blends [133]. They also studied the effect of adding Zn-sulfonated polystyrene ionomer, which release ions having specific interactions with polar groups on polymer chains. The distinct LCP droplet morphology of the blends disappeared and was replaced by finer domain morphology with the addition of compatibilizers. The interfacial adhesion was also improved. Although all compatibilizers lead to some improvement in the tensile strength, Young’s modulus and elongation at break, the highest mechanical properties were recorded with SMA. However, it was unclear if these increases were due to a compatibilization reaction between PA6 and LCP. Molecular weight of PA6 increased, which could improve fibrillation of the LCP phase. Homopolymerization of PA6 is possibly caused by higher reactivity of the amide group in PA6 as compared to the functional groups of the rigid LCP.

Kobayashi et al. studied incompatible blends of a liquid crystalline polymer based on polycarbonate (LCPC) with polystyrene [134]. A block-graft copolymer with LCPC in the backbone and polystyrene segments in the side chains was synthesized. An addition of this block-graft copolymer was observed to compatibilize the immiscible blend of PS and LCPC. Improvement in mechanical properties was observed with addition of 5 wt% PS grafted LCPC copolymer to the blend. At higher concentrations of the graft-
copolymers, in the elongation at break was improved, but the stiffness and strength of the blends were decreased. Slight reductions in $T_m$ and change in $T_g$ were observed for the compatibilized blends.

Wei et al. studied the compatibilization of PC/LCP (Vectra A900) blends by the addition of a small fraction of copolyester formed by the transesterification reaction of PC with liquid crystalline poly(oxybenzoate-co-ethylene terephthalate) (60/40 POB/PET copolyester) [135]. The interfacial adhesion of the blends was improved, leading to greater tensile strength and up to 7 times the elongation at break of the uncompatibilized blends. The compatibilizer was prepared with internal mixing at 290°C for 4-20 minutes and showed a single $T_g$. Occurrence of transesterification reactions, which also led to reduced molecular weight through chain scission. Ester and ethylene peaks of the PC component were observed in the insoluble fraction after the extraction of PC from the blend. In order to control degradation and prevent further transesterification while obtaining a uniform compatibilizer, 0.05 wt% of the inhibitor triphenylphosphate was added after 4 minutes of melt blending.

Yazaki et al. studied the effect of adding polyethersulfone (PES) oligomers with reactive –ONa end groups to PES/LCP (Vectra A950) blends [136]. The flexural modulus of the blends was found to increase linearly with LCP content, while the tensile strength decreased with the addition of up to 40 wt% LCP. Addition of the oligomer did not affect the modulus, but the tensile strength was improved by up to 50% with the addition of 20 wt% oligomer. While the $T_g$ of LCP was unaffected, the PES $T_g$ decreased with LCP content. Incorporation of oligomer significantly decreased the temperature corresponding to the tan $\delta$ peak of PES, suggesting compatibility of PES with the
oligomer. With the addition of oligomer, droplet morphology in the core region of the injection molded blends was replaced by fine fibrillar morphology. It was suggested that the –ONa end groups of the oligomer could be attacking the ester bonds of the LCP, and forming a copolymer which then acts as a compatibilizer.

Bruggeman and Tinnesmans blended PET-anhydride with Vectra A900 in the presence of liquid crystalline polyhydroxyether [137, 138]. They observed increases in the tensile strength and modulus of 60 MPa and 4 GPa, respectively, over PET/Vectra and PET-anhydride/Vectra blends. They measured the change in viscosity of PET-anhydride/polyhydroxyether over time and recorded MW buildup resulting in more than doubling in viscosity. They observed better fibril formation in the case of 80/20 PET-anhydride/Vectra blends with 0.75 wt% polyhydroxyether. They attributed the increased mechanical properties to MW buildup of PET and improved LCP fibrillation.

Chin et al. compatibilized PET/LCP (Vectra A900) blends with the addition of a bisphenol-A solid epoxy resin with a MW of 5,000 and triphenylphosphonium bromide catalyst [83]. The addition of epoxy increased the viscosity of the blends, and even greater increases were observed with the addition of catalyst. The addition of epoxy and catalyst increased the uniformity and number of LCP fibrils as well as the crystallinity of the PET phase. The addition of 2% epoxy and 0.02% catalyst to the blends resulted in improvements in the tensile strength, modulus, elongation at break and unnotched impact strength. Similar results were obtained with compatibilization of the same blend with the addition of up to 1% of a tetra-functional epoxy resin [139].

Kobayashi et al. used a thermotropic block-graft copolymer to compatibilize blends of liquid crystalline PC and poly(p-phenylene oxide) [140]. The range of liquid
crystallinity increased with the inclusion of the compatibilizer to the blends. It was shown through morphological, thermal and thermomechanical analysis that the compatibility of blends improved and the $T_g$ of PC shifted as the block-graft copolymer was able to penetrate both phases of the blend.

Addition of chlorinated PP to PP/LCP blends improves dispersion and interfacial adhesion since the chlorine groups in the added PP have strong affinity to the ester groups of the LCP [141]. Addition of dimethylglyoxime to these ternary blends further improves interfacial attraction between the LCP and matrix. It probably acted as a crosslinking agent, as indicated by changes in ester peaks in FT-IR spectra.

Heino et al. studied the compatibilization of PP/LCP (Vectra A950) blends through the addition polymers including ethylene-polypropylene copolymer, PP-g-MA, an ethylene based reactive terpolymer, and EPDM rubber [142]. Maleic acid/anhydride grafted PP with high acid content and the ethylene-based reactive terpolymer promoted transesterification reactions in the blend. The reactive terpolymer was shown to be the most effective compatibilizer; 4-5 fold improvements in Charpy impact strength were recorded, with slight reductions in the tensile strength and modulus. $T_g$ of PP was unchanged in the compatibilized blends. Reduction in heat distortion temperature from 81°C for the uncompatibilized 70/30 PP/LCP blend to 52°C for the blend containing 10% ethylene based reactive terpolymer was observed. It is suggested that existence of copolymer compatibilizer only at the interfaces would be ideal for improved mechanical properties.
2.4.2. Transesterification reactions in blends with LCPs

Transesterification of polyesters is a common method of improving interfacial adhesion and mechanical properties of immiscible blends. In some cases, the crystalline and liquid crystalline morphology is also affected by transesterification due to the alteration of regular chain structure, and can result in reduction of mechanical properties [143]. It is important to control the extent of transesterification to achieve good results in polyester/LCP blends.

Amendola et al. studied the transesterification reactions in PC/LCP (copolymer of 40/60 PET/PHB) [144]. FT-IR spectroscopy showed that four different functional groups, shown in Figure 2.8, were formed through ester exchange reactions upon mixing of 50/50 PC/LCP blend in an internal mixer in the presence of 0.5 wt% tetra(butyl-o-titanate) (TBOT) catalyst at 275°C for 3.5 hours.

McCullagh et al. studied FT-IR spectroscopy of PC/LCP blends with transesterification [144]. FT-IR absorption peaks of relevant ester groups are indicated in

![Figure 2.8. FT-IR absorption peaks of ester groups in PC/LCP blends.](image)

McCullagh et al. studied FT-IR spectroscopy of PC/LCP blends with transesterification [144]. FT-IR absorption peaks of relevant ester groups are indicated in
Figure 2.8. Group b was formed through the condensation reaction of the p-HBA units, and was difficult to differentiate from group a. Reaction times up to 210 minutes were studied. With increasing the reaction time, the relative intensities of the aliphatic and aromatic ester units (a and b, respectively) were reversed and the concentration of aromatic ester groups increased, while the absorption of the carbonate group decreases. The copolymer formed through these transesterification reactions was then added to 90/10 PC/LCP blends at 5% concentration. The copolymer acted as a compatibilizer, increasing the interfacial adhesion in the blend and leading to greatly improved fibrillation through improved interfacial load transfer in compatibilized blends.

McCullagh et al. used x-ray to study the transesterification kinetics in HBA/HNA copolymers [145]. Using a random ester interchange model for a miscible blend, they determined the activation energy for transesterification and the rate constant to be 142 kJ/mol and $2.3 \times 10^{-4}$ s$^{-1}$, respectively, at 315°C. While the activation energy for transesterification was similar to that for isotropic polymers, the rate constant was an order of magnitude lower, due to the lower mobility in the LC state.

MacDonald et al. studied transesterification of a main-chain aromatic polyester by small angle neutron scattering [146]. The LCP was partially deuterated and prepared from deuteriohydroquinone and deuteriohydroxybenzoic acid. They calculated the activation energy of transesterification in this wholly aromatic LCP as 157 kJ/mol. This value was very similar to that for transesterification of PET. Transesterification of the LCP was suggested to take place through active chain ends.

Radmard and Dadmun studied transesterification in PC/LCP (6040 PET/PHB copolymer) blends prepared by solution processing, and consecutively annealed under
nitrogen atmosphere [143]. They demonstrated increase in peak area and formation of new peaks in $^{13}$C-NMR spectra related to transesterification upon annealing at high temperature. They found that the reaction of PHB segments of LCP with bisphenol-A oxybenzoate is favored. A decrease in the Young’s modulus and in birefringence with annealing for 30 minutes leading to disruption of the LC structure was observed. Upon further annealing, an increase in the modulus resulted as the interphase stabilized through copolymer formation.

Wei et al. studied blends of PC with LCP poly(p-oxybenzoate-co-p-phenyleneisophthalate), which exhibit a single $T_g$ [147]. Transesterification reactions take place in the blend upon annealing above the $T_m$ of the LCP, leading to miscibility. During the reaction, the liquid crystalline nature in the blends is retained only for a few minutes, after which an amorphous polymer is created through the reaction between the isophthalate and oxybenzoate moieties in the LCP with the bisphenol-A in the PC, as confirmed by IR and NMR studies.

Zhou et al. used $^1$H NMR to study the transesterification kinetics of LCP (PET/copoly(oxybenzoate-p-terephthalate) and PET in the presence of chain extender BOZ (bis(5-amidino-benzimidazolyl)methanone zinc) [148]. The blend was dissolved in deuterated trifluoroacetic acid and the analysis was carried out at 55°C with tetramethylsilane as the internal standard. They concluded that the activation energy required for PET/LCP blends is 84.4 kJ/mol, which is less than that for LCP polycondensation (89.7 kJ/mol). This activation energy is also lower than in the case of LCP/PA6 transesterification (100 kJ/mol).
Gopakumar et al. performed reactive blending of PPS/LCP (Vectra A950) blends in the presence of dicarboxyl-terminated polyphenylene sulfide (PPS) [149]. An in-situ block copolymer was formed by transesterification of the carboxyl groups of dicarboxyl-terminated PPS and ester bonds of the LCP. They recorded a decrease in heat of melting and crystallization temperature, and improved tensile and impact properties in compatibilized blends. Increase in modulus from 6.6 GPa to 9.3 GPa was achieved for compatibilized blends while toughness followed the rule of mixtures, as a result of improved fibrillation and interfacial adhesion with compatibilization.

Wu et al. studied the transesterification reactions in blends of a synthesized LCP with low clearing temperature and PC [150]. They found out that there is an optimum degree of transesterification, which leads to improvement in tensile and impact properties of the blends, and above which the mechanical properties decay. Transesterification became more significant above the clearing temperature of the LCP.

Lee and DiBenedetto studied melt blending of two liquid LCPs, a 40/60 PET/PHB copolymer (X7G) and a wholly aromatic copolymer of HBA, terephthalic acid (TA), hydroquinone (HQ), isophthalic acid (IA) and 4,4”-hydroxybiphenyl [151]. Upon blending in an internal mixer at 345°C for 30 minutes, strong interfacial interactions were found in melt-spun fibers, which showed shifts in $T_g$. $^1$H and $^{13}$C NMR studies were performed by extracting the 60/40 PHB/PET copolyester phase in suitable solvents and comparing the intensities of peaks from the blend components. The ratio of EG (ethylene glycol) to HBA and TA (terephthalic acid) groups was found to decrease. This was attributed to the EG dissolving less in the solvent or a transesterification reaction taking place between the two liquid crystalline copolymers, occurring by means of the
degradation of PET/PHB component, as verified through decreases in $T_g$ and viscosity following blending. An interphase of 50 nm thickness was formed between the phases, possibly by chain scission of 60/40 PHB/PET leading to formation of new ester bonds as evidenced by $^1$H and $^{13}$C NMR studies [152]. Hence, X7G acted as a compatibilizer at the interface between the wholly aromatic polyester LCP and PET

Han et al. transesterified polyarylate (PAr) and Rodrun LC5000 by annealing at 310°C for 30 minutes [153]. These partially miscible blends had Flory-Huggins interaction parameters $\chi_{12}$ between 0.069 and 0.076, which were largely independent of polymer anisotropy due to the high degree of order of LCP in the blends. The blends exhibited two $T_g$’s, which shifted closer together upon annealing. New ester peaks were detected by FT-IR spectroscopy after annealing.

Engberg et al. studied blends of Vectra A950 with polyethersulfone (PES), PC and aromatic poly(ester carbonate) (APEC) prepared by blending in a twin screw extruder at 335°C for the PC and APEC, and at 345°C for blends of PES and LCP [154]. Randomization of the components in blends of PC and APEC with LCP was observed as a result of transesterification reactions. Increase in melt viscosity was recorded in PC/LCP blends with increasing LCP composition, even though the pure LCP viscosity was lower than that of PC. Increases in the modulus and strength of APEC/LCP blends were observed above 27% LCP concentration, due to improved orientation and interfacial adhesion. Moreover, as the LCP domain size was larger at high LCP concentrations, the extent of transesterification was consequently lower due to reduced interfacial area [155]. This led to a reduced loss in fibrillation upon transesterification reaction in blends containing higher amount of LCP. No transesterification reactions were observed in the
incompatible PES/LCP blends. Significant viscosity reductions were recorded with the addition of LCP in blends with PES.

2.4.2.1. Catalysis of transesterification in blends with LCPs

Various catalysts have been added to blends containing LCPs in order to promote transesterification reactions and improve compatibility of the blends. Among these are antimony trioxide (Sb$_2$O$_3$) [156], zinc acetate [156], tetra(butyl-o-titanate) (TBOT) [157, 158], strong acids [159], and chain extenders [148, 160].

Heino and Seppala investigated the effect of mixing time and catalysts on the transesterification reactions between PET and two different LCPs (Vectra A950 and Rodrun LC3000) [156]. They employed mixing for long times (1-8 hours) in a mixing chamber with and without the addition of catalysts. The catalysts included antimony trioxide (Sb$_2$O$_3$), stannous octoate (C$_{16}$H$_{30}$O$_4$Sn), and zinc acetate (Zn(O$_2$CCH$_3$)$_2$).

Melting temperature of PET decreased by 22°C and 8°C after mixing for 8 hours in the case of blends with Rodrun and Vectra, respectively. They stated that the reduction in T$_m$ in the case of PET/Rodrun blends was due to the overlap in the melting endotherms of these polymers. For mixing time of 2 hours in the PET/Vectra system, the melting point was reduced by 5°C upon the addition of 0.5 wt% mixture of Sb$_2$O$_3$ and zinc acetate catalyst. The crystallinity of PET matrix did not change with catalyst addition. Melting point depression of PET at long times is possibly due to thermal scission of the polymer chains, which could result in recombination to form copolymers. While shift in T$_g$ of PET in the Vectra/PET system was only 3°C, the shift in the more flexible Rodrun system was 7°C upon mixing for 8h without catalyst. The increase in T$_g$ and decrease in T$_m$ of PET
phase indicated transesterification reactions in the blends. LCP droplets were larger in Vectra/PET blends compared to Rodrun/PET blends due to the lower viscosity ratio of Rodrun/PET. Following longer mixing times, the phase boundary between spherical LCP droplets and PET became indiscernible. LCP particles coalesced at long mixing times and also with the addition of Sb$_2$O$_3$ and zinc acetate catalysts. Changes in FT-IR spectra at around 1260 cm$^{-1}$ in both LCP systems were attributed to stretching of C-O-C bonds in esters and thus the formation of new esters possibly via transesterification reactions. No clear shift was found in the strong peak of the ester group at 1730 cm$^{-1}$. This indicated that even if transesterification occurred, the new peaks in this area would be masked by other carbonyl peaks. While new peaks in ester area indicated formation of new ester groups and transesterification, shifts could also be explained by enhanced physical interaction between the polymers induced by mixing.

Stachowski and DiBenedetto studied blends of PC with 60/40 PET/HBA (random copolymer Rodrun LC3000, and block copolymer X7G) without and with 0.15 and 0.3 wt% TBOT catalyst [157]. 50/50 PC/LCP blends were prepared by melt mixing for 30 minutes at 300°C. Transesterification was also observed without TBOT in blends of PC with both Rodrun and X7G. Addition of TBOT was observed to improve phase dispersion and interfacial adhesion. The amount of ethylene terephthalate groups on extracted PC was observed to increase with TBOT concentration, indicating a greater extent of transesterification in the presence of TBOT. While the two $T_g$'s of the block X7G corresponding to the PET and PHB segments shift upon blending with PC, the single broad $T_g$ of Rodrun LC3000 narrows and shifts with addition of catalyst in blending with PC.
Stachowski and DiBenedetto also studied binary blends of LCPs. The LCPs used were Vectra A905, K161 (p(HBA/HBP/TA/IA/HQ)), and 60/40 PET/PHB with and without TBOT catalyst. Blends of various compositions were prepared by melt mixing for 30 minutes at 300°C [157,158]. Presence of TBOT was also found to improve interfacial adhesion in blends of K161 with 60/40 PET/PHB. Reactions between the phases were confirmed by NMR analysis of extracted PHB/PET fractions. Blends of Rodrun LC3000 with Vectra A950 were only compatible with the addition of TBOT catalyst. By the analysis of NMR peaks, increases in the aromaticity of Rodrun and aliphaticity of Vectra were recorded with the addition of 0.3 and 0.6 wt% TBOT. It was suggested that the copolymers formed through transesterification of wholly aromatic thermotropic polyesters with semi-flexible LCPs containing alkyl chains can be further used as a compatibilizer in blends with thermoplastics.

Chen, Sr. et al. patented a process for using a catalytic mixture containing boric acid and polyphosphoric acid or sulfuric acid to catalyze transesterification reactions of a LCP having ester groups with another polymer having hydroxyl and ester end groups [159]. The addition of strong acids catalyzed the esterification reaction of LCPs and improved the compatibility of their blends.

In a study by Zhou et al., chain extender bis(5-amidino-benzimidazolyl) methanone zinc (BOZ) promoted transesterification between LCP (PHB/PET containing 60 mol% PHB) and PET [160]. Through characterization by $^1$H NMR and thermal analysis, increasing mixing time and BOZ concentration were shown to increase the amount of transesterification, resulting in shorter sequence lengths in the blend. This led
to a reduction in crystallinity. A higher cold crystallization temperature and lower melting temperature were observed.

2.4.3. Morphology development in blends containing LCPs

Blending is often used to combine two polymers with different desirable properties, in order to achieve a superior material. In LCP/thermoplastic blends, there is a competition between the choice of a rigid LCP with high mechanical properties and a flexible one with greater potential for compatibility in blends. The mechanical properties of LCPs are directly related to their aromaticity. However, high rigidity also reduces chemical interaction of LCPs in blends, leading to incompatibility. The incorporation of long flexible spacers leads to partial miscibility, but the stiffness and strength of blends are commonly reduced at the same time [94, 161, 162]. The exploration of these blends and compatibilization methods could allow for better utilization of rigid LCPs in blends with extraordinary mechanical properties.

LCP blends are highly anisotropic, often leading to improvement of mechanical properties in the orientation direction and their reduction in the transverse direction with orientation in molded articles, films and fibers. Mehta and Isayev showed the anisotropy of LCP (HBA/HNA) with polyetheretherketone (PEEK) through dynamic mechanical measurements in torsional and flexural modes on injection molded specimens of these immiscible blends [163].

The properties of LCP blends are directly related to the polymer matrix and its interaction with the reinforcing LCP. Viscosity ratio of the matrix to the LCP phase, and interfacial adhesion between the blend components play critical roles in determining
blend morphology and the resulting properties [164, 165]. While lack of adhesion between phases in a polymer melt usually leads to lower viscosity in melt due to interfacial slip, lower strength and brittleness is observed in solid composites. Hence, it is desirable to achieve a compromise between good processability and high mechanical properties. This is often done by introducing an intermediate layer at the interface of the polymers, which has specific interactions with both phases [166].

Since the morphology of the blend dictates its performance, it is essential to understand the effect of mixing and interfacial adhesion on blend morphology. Distributive and dispersive mixing are both important to achieve uniform phase distribution and reduce the dimensions of the phases in blends [167]. In dispersive mixing, solid agglomerates or liquid droplets held together by interfacial tension must be subjected to mechanical stress in order to reduce their length scale. Therefore, the most important flow characteristics determining dispersive mixing efficiency are the magnitude of shear stresses generated and the quality/strength of the flow field (elongational flow components). In distributive mixing, repeated rearrangement of the minor component enhances system homogeneity. In continuous mixing processes, composition uniformity at the emerging stream is directly related to the material residence time distribution. Blending of polymers can be performed in batch mixers, such as the Banbury mixer, or continuously in single or twin-screw extruders. Screw element design is an integral part of blending and requires the modeling of flow and mixing.
2.4.3.1. Deformation of LCP phase

It is generally accepted that viscosity ratio, blend composition, compatibility and flow fields are important parameters that govern fibrillation in blends [1, 30]. The main factors affecting blend morphology are the viscosities of the blend components and the interfacial tension between them. Taylor analyzed the deformation mechanism of spherical droplets in a flowing Newtonian liquid at low concentration of droplets and small deformations, as shown in Figure 2.9.

![Figure 2.9. Deformation of single droplet.](image)

To express extent of deformation, the following quantities are defined [168]:

\[
K = \frac{\eta_d}{\eta_m} \quad D = \frac{L - B}{L + B} \quad Ca = \frac{\eta_m a \dot{\gamma}}{\sigma}
\]  

(2.12)

where \(K\) is the viscosity ratio, \(\eta_d\) and \(\eta_m\) are the viscosities of dispersed and matrix phase, respectively; \(D\) is the extent of deformation, \(L\) is the length and \(B\) the width of the dispersed droplet; \(Ca\) is the Capillary number (hydrodynamic/interfacial stress), expressed in terms of initial droplet radius \(a\), interfacial tension \(\sigma\), and shear rate \(\dot{\gamma}\), where the interfacial stress is given by \(\sigma/R\).
At angle of orientation, $\alpha$, of $\pi/4$, Taylor showed that at very low capillary numbers where the interfacial stress effect dominates, the deformation $D$ can be expressed as follows [168]:

$$D = Ca\frac{19K + 16}{16K + 16}$$

(2.13)

On the other hand, when $Ca=1$ (interfacial and viscous forces are equally important) and the viscosity ratio $K$ is very large:

$$D = \frac{5}{4}K$$

(2.14)

As these relations were derived for small deformations, they can only be used to predict the onset of deformation of LCP droplets into fibrils, and not the final fibril diameter [169]. The deformation of droplets is enhanced when the size of droplets and the viscosity ratio of the matrix to the dispersed phase are large. The deformation of droplets is hindered when interfacial tension is large. While droplets remain spherical when the viscosity of the dispersed phase is greater than that of the matrix, they elongate when the dispersed phase viscosity is smaller leading to finer phase morphology.

In LCP/thermoplastic blends, fine fibrillar morphology is obtained when the viscosity of the thermoplastic matrix is greater than that of the LCP [169]. The interfacial adhesion between the LCP and the thermoplastic plays a greater role in fibril formation when the viscosities of the blends components under the given processing conditions are similar.

He et al. noted that the coalescence of the dispersed phase is not accounted for in Taylor’s deformation theory [170]. The coalescence and break-up of LCP particles is
hindered at low temperatures due to high viscosities of dispersed and continuous phases, even when the matrix viscosity is higher than that of the LCP.

Kenig extended Taylor’s theory to high deformations and added a power law expression [171]. As elongation rate increases, droplets are first elongated into long fibers, but are broken up back into droplets at high draw rates. For PC/LCP (Vectra) blends, this was observed to occur at above a DDR of 5, accompanied by a reduction in modulus of blends. The application of this modified Taylor’s theory showed that a minimum in interfacial tension occurs at DDR of 5, followed by a swift rise at higher DDR. The decrease in modulus was calculated theoretically by applying the rule of mixtures to PC/LCP blends.

Beery et al. illustrated the importance of viscosity ratio for LCP/thermoplastic blends by studying the morphology of extrudates at different shear rates giving very different viscosity ratios [172]. At low shear rates in 80/20 PC/LCP (Vectra) blends where the LCP viscosity was greater than that of PC, LCP phase stayed as spherical droplets, while fibrils were formed at higher shear rates where the PC viscosity was greater. Blends of LCP with PBT and Nylon 6 (PA6), for both of which the LCP viscosity is greater than that of the matrix, were also studied. While only short LCP fibers with large diameter were observed in blends with PBT, fine and homogenous fibril morphology was observed in blends with PA6, for which rapid break-up and coalescence of the LCP phase occurred.

Heino et al. studied the effect of LCP/PP viscosity ratio (0.1-3.6) on the morphology of their blends by employing different materials and processing conditions [173]. They found that LCP fibrils are created most readily when the viscosity ratio of
LCP to PP is between 0.5 and 1. The lubricating affect of LCP, leading to reduced melt viscosity, was most significant when the LCP viscosity was lower.

Kenig studied the rheology and morphology of blends of a LCP (Vectra A) with amorphous Nylon (AN), PC, PBT and PA6 [174]. AN has a greater viscosity than the LCP at shear rates above 50 s\(^{-1}\), while its blends with LCP has lower viscosity than that of the pure polymers, as determined by a capillary rheometer. 75/25 AN/LCP blends had fibrillar morphology and showed good interfacial adhesion. 80/20 PC/LCP blends showed fibrillar morphology at higher shear rates as PC had a lower viscosity than the LCP above a shear rate of 300 s\(^{-1}\). The interfacial adhesion was poor and the viscosity of PC/LCP blends were between that of the pure components. No fibrillation was observed in 75/25 LCP/PBT and 80/20 LCP/PA6 blends, for which the viscosity of the matrix polymer was lower than that of the LCP for the studied shear range (10-10000 s\(^{-1}\)).

Lee et al. studied the effect of adding silica fillers to blends of Rodrun LC5000 (80/20 HBA/PET) and PP on the fibrillation mechanism [175]. With the addition of silica to the matrix, its viscosity was increased, which led to improved fibrillation of the LCP phase.

Ajji et al. studied orientation development upon drawing of compression molded PBT/LCP (40/60 PET/PHB copolymer) blends [176]. Prior to drawing, no improvements in modulus were recorded and the LCP domains were spherical. The morphology changed to partially ellipsoidal LCP domains upon drawing at around 200\(^\circ\)C, leading to increased modulus with LCP content particularly at above 30 wt\% LCP concentration where the orientation was even greater than for pure LCP. At up to 30% LCP concentration, the LCP phase exhibited a dispersed droplet morphology in the PBT
matrix. Upon drawing of the moldings, the LCP phase indicated little orientation, and the modulus of drawn moldings was governed primarily by the orientation of the PBT phase. It was suggested that the orientation of the LCP phase is controlled by interfacial adhesion between PBT and LCP in this partially miscible system.

Qin et al. studied fiber spinning and hot stretching of PP/LCP (Vectra A950) blends. Fibers were spun at a take up speed of 60 m/min from an extruder. The as-spun fibers were then hot stretched in a drawing unit composed of a hot plate and two rollers. Two variations of the hot drawing process were employed. In the first, single stage drawing was performed at a feed rate of 6 m/min and fibers were stretched to the maximum draw down ratio (DDR) at a temperature of 150°C. In the second, the two stage process, fibers were first stretched partially at 130°C, and then stretched to maximum DDR at 160°C. In the blends, LCP fibrillation was observed above 5%, while a fibrous network structure was formed above 15% LCP concentration. While stiffness and strength were improved for the as spun fibers, fragmentation of LCP fibrils was observed for drawn fibers (single stage, 150°C), resulting in an aspect ratio of 10. Two-stage drawing process, first at 130°C and then at 160°C led to greater orientation and less LCP fibril breakup. In the first drawing stage, break up of LCP fibers did not take place due to low draw ratio and the easier deformation of the PP compared to LCP. Employing high temperatures in the second drawing stage increased the mobility of the LCP chains, reducing fiber breakage while achieving a higher overall draw ratio. Greater modulus and tensile strength were achieved in the two stage drawing process [177]. Higher temperatures allowed greater draw ratio in the single-stage process, while use of lower
temperature (120°C) in the first stage and higher temperature in the second stage of the two-stage process led to greater mechanical properties [178].

In studies of the effect of the LCP structure in PP/LCP blends employing different LCPs, it was found that Vectra A900 and Vectra B950 formed fibrils, while the more flexible Rodrun LC3000 formed short elongated ribbons during fiber spinning [179]. The greatest improvements in fiber tenacity were recorded for PP/Rodrun LC3000 blends, for which the interfacial adhesion to PP was better than in the blends with rigid Vectra LCPs which formed a connected network structure. These higher tenacity blends also had greater aspect ratio of LCP fibrils. Low interfacial adhesion led to longer LCP fibrils and was attained at high drawing temperatures. Reducing compressional forces on LCP fibrils, such as through the use of low drawing speeds, prevented LCP fibril break up upon drawing of blends [180]. Extensional flow after exiting from the die was responsible for the creation of uniform and long LCP fibrils in blends of LCPs with thermoplastics [181].

While elongational flows promote fibrillation, shear flow in extrusion can also lead to fibril formation when the viscosity ratio of the matrix polymer to the dispersed LCP phase is very large. He and Bu observed fibrillation in extrudates strands of 90/10 PES/LCP blends having a viscosity ratio of LCP to matrix of 0.01 but not in 90/10 PC/LCP blends having a viscosity ratio of 0.13 under only shear flow [182]. The coalescence of fibrils after extrusion through die was observed and found to accelerate the formation of fibrils. Fibrous LCP domains were still present after being at rest for 60 s in the extruder die due to the rigidity of the LCP phase.
Liang and Isayev studied the injection molding of drawn PP/LCP (Vectra A950) extrudate strands [183]. While elongated fibrils were observed in drawn extrudates, the aspect ratio of elongated LCP domains was much lower in injection molding. Especially at an LCP concentration of 50%, the strength and modulus of moldings was significantly less than those of the drawn extrudate strands. This suggested disorientation of oriented LCP domains during injection molding. It also showed that drawing leads to greater LCP fibrillation than fiber spinning in blends. Liang and Isayev also studied the effect of PP molecular weight on LCP morphology [75]. They observed improved deformation of the LCP phase in blends with PP having the greater molecular weight. This was observed to result in improved LCP droplet break-up and better mixing, in addition to the generation of LCP fibrils with smaller diameters.

Valenza et al. studied immiscible PPS/LCP (Vectra B950) blends, in which the viscosity of the PPS was greater than that of the LCP at temperatures above 320°C and high shear rates [184]. Partial fibrillation was only observed only when the PPS viscosity was greater. Microporosity was observed around the LCP fibrils and droplets. This was attributed to interfacial slip due to poor adhesion between PPS and LCP.

Isayev and Subramanian studied PEEK/LCP blends (Xydar SRT-300) for which the viscosity of LCP was greater than that of PEEK under processing conditions [185]. They observed ellipsoidal LCP droplets at up to 10% LCP content, resulting in slight improvement in mechanical properties. Phase inversion took place at high LCP concentrations, leading to generation of PEEK fibers in LCP matrix, which did not result in mechanical property improvements. It was concluded that the viscosity ratio is a critical factor for fibrillation. Decrease in the viscosity of the blends with up to 10% LCP
concentration was recorded at high shear rates, while severe degassing occurred in blends with greater than 25% LCP concentration. The latter impaired pressure measurements in capillary rheometer [186].

Mehta and Isayev studied immiscible PEEK/LCP (Vectra A950) blends where the viscosity of the polymer matrix was ten times greater than that of the LCP. They observed a synergistic effect leading to improvements in tensile stress and modulus above those of pure LCP in 70/30 PEEK/LCP blends. With LCP concentration above 10%, fibrillation was observed. This effect increased with LCP content, leading to stiffer and more brittle blends. In blends, the impact strength of the 10/90 PEEK/LCP blend was twice that of pure LCP. This was explained by the increased effective mechanical energy dispersion through high modulus fibrils with high aspect ratio, which inhibits crack propagation [187].

Joshi et al. developed an energy criterion for fibrillation in LCP/thermoplastic blends. According to this criterion, fibrillation occurs when the energy utilization per unit volume of the thermoplastic component is less than that of the LCP component in the blend [188]:

\[
\frac{\dot{E}_m}{E_d} = \frac{\dot{\gamma}_m \phi_m}{\dot{\gamma}_d \phi_d} < 1 \tag{2.15}
\]

where \( \dot{E}_i \) are the rates of energy utilization, \( \dot{\gamma}_i \) the shear rates, \( \phi_i \) the volume fractions, and \( \eta_i \) the viscosities of the phases, with \( m \) referring to the matrix and \( d \) to the dispersed phase [188].

When the energy consumed by the LCP phase is lower than that of the matrix, the LCP phase experiences a relatively higher shear rate resulting in the elongation of
spherical droplets and fibrillation occurs. The volume fractions, interaction of phases, and processing methods all affect fibrillation. The above fibrillation criterion was experimentally verified in blends of LCP with PP, PEN, HDPE and PC, and was found to be superior over the viscosity ratio criterion [188].

Addition of a third component to LCP/thermoplastic blends can promote fibrillation. Addition of a multiblock copolyesterether into polyarylate/Vectra A950 blends and addition of polysulfone into PPS/Vectra B950 blends were shown to improve fibrillation in blends and enhance interfacial adhesion. Through rheological studies, it was shown that the viscosity of the thermoplastic increased with the addition of the third component, improving LCP droplet deformation [189,190]. The multiblock copolyesterether added into polyarylate/Vectra A950 blends was miscible with polyarylate, and also improved the interfacial adhesion of polyarylate to the LCP phase [190].

Sun et al. found that the addition of a second LCP to a thermoplastic/LCP blend can improve fibrillation of the liquid crystalline phase. Through the addition of 60PHB/PET (X7G) to PBT/Vectra A blend, in which all components were phase separated, the orientation of the Vectra A fibrils in the blend was improved and finer fibrils were formed in the skin region [191]. This led to improvements in tensile strength and modulus [192]. Similar results were recorded with the addition of Rodrun LC5000 semiflexible LCP to polyarylate/Ekonol E 7000 blends, where addition of the second LCP enhanced compatibility [193].
2.4.3.2. Morphology Development in Fiber Spinning

Understanding theories behind the deformation of the LCP droplets to fibrils is critical to achieving in-situ composites with desirable results. The simplified Halpin-Tsai composite theory is often used to predict the modulus of unidirectional fiber-filled composites, $E_c$, based on the modulus of matrix, $E_m$, and filler, $E_f$, and volume fraction of filler, $\phi_m$ [194].

In this theory, it is assumed that fiber and matrix deform elastically and have the same Poisson ratio, and that there is no interfacial adhesion.

$$E_c = \phi_f E_f + (1 - \phi_f) E_m \quad (2.16)$$

The tensile strength ($\sigma$) for unidirectional fiber-reinforced composite is calculated as:

$$\sigma = \phi_f (1 - L_c / 2L) \sigma_f + (1 - \phi_f) \sigma_m \quad (2.17)$$

which, under the assumption of infinitely long fibers with length greater than a critical length ($L >> L_c$), simplifies to:

$$\sigma_c = \phi_f \sigma_f + (1 - \phi_f) \sigma_m \quad (2.18)$$

The modulus of unidirectional fiber composites in the transverse direction can also be determined as:

$$E = E_m \left(1 + 0.5 A \phi_f \right) \quad (2.19)$$

where

$$A = \frac{E_f / E_m - 1}{E_f / E_m + 0.5} \quad (2.20)$$
and $\phi_p$ is the packing factor, which is 0.82 for random packing [194]. Mehta and Deopura studied fibers of PET/LCP (PET/PHB copolyester) blends and confirmed fiber formation upon comparing the properties of blends with simplified composite theory. LCP fibrillation in fiber-spun blends was experimentally confirmed by WAXS. Lower values of the modulus at low LCP content were explained by phase separation in the blends, aggregation of LCP domains and small aspect ratio [195].

Using the aggregate model proposed by Norholt and van der Hout, and the Halpin-Tsai model, Lin and Yee derived a relation for the elastic modulus of fibers, including both rotation and elongation of aggregates upon drawing. Their theory employed the orientation of LCP fibers. Based on the modulus of a perfectly oriented LCP fibril, effect of varying orientation of fibrils with respect to the fiber axis was incorporated by introducing an average orientation factor. The theoretical calculations correlated well with experimental results for LCP reinforced PC, showing a positive deviation from experimental results at draw ratios below 10. It was concluded that the elastic modulus of LCP reinforced composites is dominated by the aspect ratio and molecular orientation of fibers, in addition to LCP content [196].

The upper and lower bound models of fiber reinforcement define the limits of predicted moduli of composites. The upper bound is defined by eq. 2.18. In the lower bound model, the fiber and matrix are connected in series, and the system is under constant stress [154]:

$$1/E = \phi_f / E_f + (1 - \phi_f / E_m)$$

(2.22)
In the Takayanagi model, a fraction of the reinforcing phase, $b$, is considered to be continuous [197]. This continuous phase is connected to the rest of the system in parallel, and the noncontinuous fraction of the reinforcing phase connects to that in series. This is given by the following equation [154]:

$$E = b\phi_f E_f + \left(1 - b\phi_f\right) \left\{ \frac{1}{(1-b)\phi_f} + \frac{1-\phi_f}{(1-b\phi_f)E_f + (1-\phi_f)E_m} \right\}$$

where the fraction of the continuous reinforcing phase in the system is given by $b\phi_f$. This model has been used to study reinforcement by LCP fibrils in blends of LCPs with flexible chain polymers [154, 202].

### 2.4.3.2.1 Agreement between experimental and theoretical results

Song and Isayev studied morphology development during fiber spinning of PET and PBT with LCP (18/82 PET/HBA, Rodrun LC5000) blends. The effects of temperature, velocity and strain rates on 60/40 polyester/LCP blends were studied based on Taylor’s theory, Kase and Matsuo fiber spinning model, and affine deformation theory. Taylor’s theory was found to be insufficient due to its applicability only to small deformations. The competition between fiber break-up and elongation was studied. The best results were obtained with the affine deformation theory. The aspect ratio of LCP fibrils in the 60/40 PBT/LCP blends was lower compared to that in PET/LCP blends, for which the viscosity ratio of LCP to the PBT and the PET matrixes was similar. The difference in aspect ratio of LCP fibrils, and hence deformation of LCP phase, was attributed to the partial miscibility between PBT and LCP [198].
Kyotani et al. studied extension of PET/LCP (Vectra A950) blends and found that orientation increases with extension ratio and LCP content in the blends [199]. Draw down ratio (DDR) of 80 gave maximum orientation. Fibers of PET/LCP blends containing 10 to 80% LCP were brittle, and had similar elongation at break (3%). At low DDR, spherical LCP droplets were observed in the spun fibers where as LCP fibrils were formed at high DDR. The Halpin-Tsai equation was used to explain the relation between the modulus and volume fraction of reinforcing species. Below 20% PET in blends, the observed modulus was less than that predicted by the Halpin-Tsai equation. This was due to the nonuniform and short fibrils of LCP in these blends, which acted as weak fracture points during tensile testing.

Lin and Yee developed a model to predict the draw down ratio dependence of the modulus of LCP fibril reinforced blends [200]. In their composite model, perfectly oriented LCP fibrils and randomly oriented chains are connected in series, for which the fraction of oriented chains increases while that of random chains decreases with drawing. A model to predict the longitudinal and transverse elastic moduli of the reinforcing LCP fibers was derived assuming that only affine extensional deformation of the fibers in the composite takes place during drawing. Modulus predicted by the model agreed well with the modulus of fibers spun from PC/LCP (Vectra B950) blends. The longitudinal elastic modulus increased continuously with LCP concentration, whereas it increased to reach an asymptotic value with DDR. DDR at which saturation of modulus occurred increased with LCP content. As LCP fibrils become almost continuous at high draw ratios, the mechanical properties approach the rule of mixtures for various LCP concentrations as
draw ratio is increased. The transverse modulus is insensitive to LCP content but drops slightly with draw ratio.

Northolt and van der Hout analyzed the elastic extension of oriented fibers of LCPs and formulated a theory, where the oriented fibers were represented as a series of polymer chain aggregates with uniform stress distribution throughout the fiber [201]. Under external stress, the aggregates are elongated and rotated around the fiber axis due to misalignment and shear deformation. It was found that the buildup of stress during fiber drawing is a function of initial crystallite orientation distribution and fiber modulus. The theoretical predictions of the modulus were confirmed by experiments on poly(p-phenylene terephthalamide) fibers.

Lee and Suh studied orientation-mechanical property relationship in extrusion of Vectra A950 using different diverging dies. They found that the tensile strength of LCP extrudates increased in all directions with increasing diverging angle of die and screw rpm, which led to increased elongational flow and shear stresses, respectively. They developed a model based on the Halpin-Tsai equation and the rule of mixtures to relate LCP concentration and the orientation of LCP fibrillar domains to the modulus determined experimentally for the extrudates of LCP. Global orientation of the LCP increased with increasing elongational flows, through the generation of higher aspect ratio LCP fibrillar domains. Thereby, LCP was shown to exhibit ellipsoidal droplet morphology at low orientation, and continuous fibrillar morphology at high orientation, which were controlled by varying angle of diverging die of the extruder and the flow rate [202].
Brostow et al. developed the island model based on experimental observations of PET/LCP (70/30 PHB/PET copolymer) blends, in which the PET was miscible with the PET component of the LCP [203]. Greatest improvements in the tensile strength, flexural modulus and impact strength were observed in blends containing 60 wt% of the PHB component. The LCP domains were seen as islands, which are not affected by forces, with the forces concentrated around the matrix surrounding the LCP domains. The preferred crack propagation was between the islands of LCP. With addition of a small amount of LCP, the mechanical properties were slightly reduced as LCP islands do not absorb any stress. At high LCP concentrations, LCP becomes the continuous phase.

2.5. Rheology of blends containing LCPs

Various empirical and semi-empirical relations were proposed to determine viscosity of homologous polymer blends [204, 205, 206]. Among these relations are the additive rule of mixtures, the log-additive rule, and free-volume additive rule, which have been found to portray miscible blends with varying levels of success. The log additive rule of mixtures is given by Eq. 2.24:

\[
\log \eta_{12} = \sum c_i \log \eta_i
\]  

(2.24)

where \(c_i\) are the weight fractions and \(\eta_i\) the viscosities of the phases.

The morphology of blends is governed by the volume fractions of the phases, the viscosity and elasticity ratios, processing techniques, and the miscibility of the phases [207]. LCPs are easily oriented into fibrillar domains and certainly are not simple mixtures and are not expected to follow the log additive rule of viscosity. The unique
properties of these materials require a detailed study of the rheological properties of their blends.

Particle size plays a large role in fibrillation of LCP blends. No deformation of the LCP phase can take place below certain particle size and strain, which are respectively governed by composition and processing conditions [208]. The molecular orientation is suppressed at low LCP concentrations, leading to shorter fibrils. There are thresholds of LCP concentration below which no fibrillation occurs and no network forming effect of fibrils is seen [209].

When there is strong interfacial attraction between the phases of a polymer blend, a positive deviation from the log additive rule of viscosity is observed [207]. On the other hand, weak interfacial adhesion between the phases leads to delamination and consequent reduction in viscosity of the blends, which manifest itself as a negative deviation from the viscosity rule presented in Eq. 2.24. Both positive and negative deviations from this rule can occur when there is significant morphological change in the blend with composition.

As the anisotropic LCP phase readily aligns in the flow direction, it reduces the melt viscosity and acts as a “processing aid” its blends with flexible chain polymers [38]. When LCP is the minor phase in blends, this processing aid effect can sometimes lead to a blend viscosity below that of the components.

Viswanathan and Isayev observed a significant reduction in the viscosity of a poly(phenylene oxide) (PPO)/polystyrene (PS) alloy upon the addition of LCP (Vectra A950), leading to its improved processibility [210]. The blends exhibited skin-core morphology with finely developed LCP fibrils in the skin.
Rheological measurements of LCP blends have been carried out in both capillary and rotational rheometers and can show differences. Important considerations for testing of LCP systems are summarized in this section with reference to literature.

In capillary rheometry, elongational flows dominate in the entrance region of the capillary [211]. These lead to greater anisotropy of the LCP phase. The phase morphology in the entrance region of the capillary is affected by the blend composition and entrance region length dependent on the L/D ratio of the die.

Cogswell and Wissbrun reviewed the rheological behavior of LCP/isotropic polymer blends obtained by capillary rheometry [41]. These blends generally exhibit a negative deviation from the additive rule of viscosity. Viscosity minima are observed when the viscosity of LCP dispersed phase is greater than or close to that of the isotropic polymer. When such a blend is subjected to elongational flow, incompatibility between phases leads to interfacial slip. In most cases, skin-core morphology is observed with the lower viscosity LCP migrating to the surface.

Tensile stresses relax along the length of the capillary, and fibrillar LCP domains change into droplets at high L/D [209,212]. Mehta and Isayev observed that fibrillar morphology in blends of PEEK/Vectra A950 created by capillary extrusion with short dies were more pronounced and exhibited higher aspect ratio as compared to longer dies [187]. Turek et al. attained greater modulus in PC/Vectra A950 blends by extrusion from shorter dies at higher DR [212]. Formation of short LCP fibrils in the converging section of the capillary takes place through elongation and coalescence of LCP droplets [187, 213]. Relaxation of LCP fibrils in long dies is easier due to longer residence time. Short fibrils combine to form continuous fibers in the skin at high shear rates, while recoiling
and break up of LCP domains takes place in the core. This leads to the formation of spherical and ellipsoidal LCP droplets, particularly in high L/D dies [213]. The rates of fibrillation and coalescence increase with LCP content in blends due to decreasing inter-particle distance. Interfacial tension is an important parameter in these blends. If it is too low, droplet deformation will occur but will be followed by fiber breakage. This would result in good dispersion, but shorter fibers [213].

Limtasiri and Isayev studied blends of LCP(HBA/HNA copolymer) with poly(phenylene oxide) (PPO). In these incompatible blends, the observed a viscosity reduction with increasing LCP composition. With increasing LCP content, fibrillar morphology was observed in the blend [214].

Beery et al. studied the capillary rheometry of PC/LCP (Vectra A950) blends, where the elongational viscosity of LCP was greater than that of PC [211]. While the entrance pressure drop was small for PC, it reached 50% of the total pressure for LCP. While it is clear that entrance corrections need to be made for the blends, development of a stable flow regime in the capillary during testing of LCP blends requires greater length of time due to processing in the nematic state of LCP. This would require the use of a series of long dies for applying the Bagley correction, which may not be practical in some cases.

Sukhadia et al. used two extruders to plasticize the components of the blend separately at optimum temperatures to avoid degradation, which were then joined together into a static mixer with 18 helical elements set between 225-240°C, where the blend ratio was adjusted by controlling the feed rate into the individual extruders [215]. Upon drawing fibers from the resulting blend, they obtained a continuous LCP (Vectra
A900 and B950) fibril morphology in blends with PET and PP, as opposed to the skin core morphology obtained by mixing in a single extruder. While droplets, formed by mixing in the single extruder, were elongated into fibers, the LCP in the dual extruder process was divided into layers and separated to form continuous fibrils in the static mixer set below the melting temperature of either component. The latter led to 50% improvement in mechanical properties over mixing in a single screw extruder. The DDR obtained following the novel dual extruder mixing was low due to temperature constraints and limited mechanical properties.

Crevecoeur and Groeninckx studied PS and miscible PS/PPE (polystyrene/poly-2,6-dimethyl-1,4-phenylene ether blend) as the matrix polymer in blends with two LCPs (Vectra A950 and Vectra B950) [216]. Upon comparing morphology of injection molding and spun fibers, they observed much finer fibrils with practically infinite aspect ratio in fibers, and chopped fiber morphology in injection moldings. The tensile strength and modulus of PS/Vectra A950 blend lied below the rule of mixtures for injection moldings and above the rule of mixtures for the as-spun fibers, due to the enhanced orientation of the LCP phase in fiber spinning. In the fiber spinning of their blends with LCP, both the brittle PS and the ductile PS/PPE were effectively reinforced by the LCP phase. The resulting LCP containing fibers were stiffer but more brittle.

While the flow of LCP blends in the capillary rheometer is complicated due to fibril formation and droplet break-up, uniform spherical droplets are present in rotational rheometry studies. Due to morphological differences and the inapplicability of Cox-Mertz rule in dynamic rotational rheometry, the results obtained from these methods are not expected to agree quantitatively. Unrelaxed stresses during sample loading in
rotational rheometers can contribute to error in measurements. In capillary rheometry, four subsequent passes of the same material may be required to obtain reliable measurements through homogenization of LCP structure and destruction of defects [166]. This is obviously not an option when a component in the blend is susceptible to thermal degradation.

2.6. Various blends containing LCPs

Compatibilization of wholly aromatic polyester thermotropic LCPs with thermoplastics were the main focus of this research. Blends of most thermoplastic polyesters readily undergo exchange reactions during melt processing. Some flexible LCP/polyester blends are partially miscible due to the similarity in chemical structure. Transesterification reactions can be induced in wholly aromatic liquid crystalline polymers and their blends with extended mixing and annealing, and in some cases with addition of catalysts.

The morphology development in LCP/polyester blends depends on the viscosity ratio and miscibility of polymers, processing conditions and LCP concentration in blends. The morphology in turn dictates the mechanical properties of these systems. Song and Isayev compared properties obtained in blends of PET, PEN, PBT and PET copolyester with LCP (PET/HBA copolymer). Improvement in the strength and modulus of blends was influenced primarily by the choice of the flexible chain polyester matrix [217].

A review of PET/LCP, PEN/LCP, PBT/LCP, and LCP/LCP blends is provided in this section, as they relate directly to the experimental studies presented.
2.6.1. Blends with poly(ethylene terephthalate)

PET is a commercially important polyester with a wide range of applications. Its processing, mechanical and thermal properties can be improved by blending with LCP. Various studies of PET/LCP blends from literature are presented in this section.

Narh et al. studied the correlation between mechanical properties and amount of dispersive mixing in 85/15 PET/LCP (Vectra A950) blends in an internal mixer (300cc Brabender batch mixer) [218]. Upon mixing at 75 rpm and 280°C for 3 minutes, they recorded 10-15% improvements in modulus and toughness over 30 and 60 rpm mixing with the remaining conditions being the same. 280°C was identified as the ideal temperature for mixing, as degradation of PET takes place above this temperature.

Through studies in several blends, it has been established that the LCP phase (Vectra A900, A950, Rodrun LC5000, and others) acts as a nucleating agent for PET [61, 93, 203, 219, 220, 221, 222, 223].

Seppala et al. studied the mechanical properties of injection molded blends of LCP (Vectra A950) with PET [93]. They found out that the addition of LCP made the blends stiffer but more brittle and that the tensile strength and modulus increased linearly with LCP content. An increase in heat deflection temperature (HDT) from 62°C for pure PET to 79°C for 50/50 PET/LCP was recorded. HDT of pure LCP was 154°C.

In PET/LCP (PET/PHB copolyester) blends, Sukhadia et al. observed break up of LCP into small droplets in a coat-hanger die with L/H of 35 [219]. In this die, LCP droplets are elongated and break up into smaller droplets stabilized by interfacial tension. If droplets are small, they do not yield to elongation or shear. Larger droplets are favored by shorter dies and result in higher capillary numbers, leading to fibrillation. At
temperatures less than 240°C where the viscosity of LCP is greater than that of PET, the
deformation of the LCP phase becomes difficult and fibrils are not formed. Below 35
wt% LCP in the blends, there was a quasi-Newtonian plateau up to shear rates of 500 s⁻¹.
While addition of 2% LCP increased the viscosity of the blend, incorporation of 20%
LCP decreased the viscosity. A partial miscibility of the LCP (PET/PHB copolyester)
with PET could have resulted in higher viscosity of blends, hindering the generation of
fibrils.

Mithal et al. studied the effect of PET viscosity on PET/LCP (Vectra A900)
blends [224]. While good mechanical properties were obtained with high intrinsic
viscosity PET, using low intrinsic viscosity PET in the blends led to poor fibrillation and
reduced properties. Modulus and strength increases with LCP addition, accompanied by a
decrease in elongation, were recorded. Upon heat setting of fibers, orientation of LCP
domains is perfected and thermally induced randomization take place. Heat treatment of
fibers increased tensile strength and modulus of LCP rich components.

Liang et al. studied melt spinning of PET/LCP (Vectra A900) blends and fibers
spun from them [221]. While the orientation factor increased by 10-20%, the crystallinity
of PET increased considerably. Upon annealing of fibers of 85/15 PET/LCP blends for
2.5 hours at 180°C, the tenacity and modulus were improved by 58% and 40%,
respectively. These improvements were attributed primarily to increased crystallinity
with annealing.

Joslin et al. studied fibers drawn from PET/LCP blends, for which chemical
structure of the LC block copolymer was tailored through the incorporation of para
connected rigid rod benzoic acid and flexible PBT segments [225]. In this liquid
crystalline block copolymer containing rigid segments, shortening the block size of flexible PBT segments was found to decrease the melting temperature due to increasing the number of defects in crystalline structure. Incorporation of longer rigid rod segments and less flexible spacers in LCP provides greater stiffness and dimensional stability of blends with PET, while use of long spacers does not result in distinguishable increase of interfacial adhesion. Blending 2.5 wt% of another LCP, poly(butoxyethoxy 1,4-phenylene terephthalate), with PET led to a reduction in melt viscosity of PET by 75% [226]. In blends of PET with a random liquid crystalline copolymer having a 60:40 ratio of oxyethylene-substituted hydroquinone to ethylene glycol, improvement in fiber modulus of 50% over pure PET at 5 wt% LCP concentration at a DDR of 5 was recorded. No change was found in the ultimate strength. Above 5 wt% concentration of the liquid crystalline copolymer, the fibers could not be drawn effectively and the modulus was reduced. While thermal analysis did not show interaction between the LCP and PET, some degree of adhesion was observed through SEM micrographs.

Melot and MacKnight studied blends of PET with Vectra A900, and LCPs synthesized by them [222]. One LCP has the following structure:

\[
\begin{align*}
\text{O} & \quad \text{C} \quad \text{O} \\
\text{C} & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \\
\end{align*}
\]

A more flexible LC copolymer, comprising of a block of three units having the above structure and three PET units in series, was also synthesized [222]. While all LCPs acted as nucleating agents for PET, the mechanism was different for Vectra A900 and the other synthesized LCPs. In the completely immiscible PET/Vectra blends, the nucleation took place at the blend polymer interface, and the crystallization rate increased with LCP
content as more interfacial area is created. On the other hand, some interactions were observed in blends of PET with the more flexible LCPs, although DSC studies indicated that they were immiscible. These blends exhibited a regular crystalline structure because nucleation begins around macrodomains of the LCP in the bulk. Consequently, the crystallization rate was greatly improved even at 1% of these LCPs. However, the crystallization rate was found to decrease at 20% LCP content due to agglomerations.

Lin et al. studied PET/LCP blends, in which the LCP was a block copolymer of \((\phi\text{COO})_3(\text{CH}_2)_4\text{OOC})_5—(\phi\text{COO}(\text{CH}_2)_4\text{OOC})_8\), where \(\phi\) refers to a benzene ring [223]. The blends were found to be miscible through the observation of a single \(T_g\) that shifted with increasing LCP content. Addition of up to 10% LCP led to higher crystallization temperatures and formation of finer crystals as LCP acts as a nucleating agent of PET. The crystallization of PET was not improved at greater LCP concentrations due to decreasing PET content. In this miscible blend system, dramatic reductions in viscosity, especially for blends with high MW PET, were recorded even at 2% LCP content. Unlike the interfacial slip and phase separation phenomena governing the viscosity minima in immiscible blends, the mechanism for the reduction of viscosity in these miscible blends was hypothesized to be due to the reduction of molecular entanglements of PET in the presence of rigid rod LCP molecules.

Joseph et al. studied blends of PET with 60/40 PHB/PET copolyesters [227]. Skin-core morphology was observed due to fountain flow in injection molding. Fibrils were observed at above 10 wt% LCP concentration, with the fibrils becoming more distinct and their diameters increasing with LCP concentration. A co-continuous morphology was observed in 50/50 blends.
Branciforti et al. blended PET with Vectra A950 and with Rodrun LC5000 in the presence of a compatibilizing agent. The compatibilizer (Lotader AX8900) was a random terpolymer of 67% ethylene, 25% acrylic ester, and 8% glycidyl methacrylate. The degree of orientation in blends with Vectra was higher than with Rodrun, due to its stiffer structure. The compatibilized blends had lower degree of orientation, suggesting improved interfacial adhesion, which led to restriction of chain mobility. The drop in orientation was greater than that in the PET/Vectra blend than it was in the PET/Rodrun blend. The size of LCP domains and diameter of fibrils decreased with addition of the compatibilizer [228].

Sharma et al. studied blends of PET with Vectra A900 and with 80/20 PHB/PET copolyester, prepared by melt blending in a twin screw extruder [229]. Wide angle x-ray diffraction (WAXD) studies have shown significant crystalline orientation in the blends upon extrusion, resulting in a fibrous microstructure.

2.6.2. Blends with poly(ethylene naphthalate)

Blends of PEN with different LCPs were studied in literature [228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238]. Findings of these studies on the rheological, thermal, mechanical and morphological properties of PEN/LCP blends are summarized in this section.

Kom et al. studied blends of PEN with a synthesized thermotropic LCP containing flexible butylenes/hexylene spacers in the main chain and triad aromatic ester in mesogenic unit, containing a naphthalate group [230]. LCP acted as nucleating agent for PEN and decreased the cold crystallization temperature ($T_{cc}$). Good interfacial
adhesion and 40-50 nm sized fibrillar LCP domains were observed at up to 10% LCP content in the blend. A similar decrease in T_{cc} with LCP content was observed in PET/LCP blends [239].

Kim et al. studied PEN/Rodrun LC5000 (80/20 PHB/PET) blends. LCP increased the crystallization rate and acted as nucleating agent in this system [232]. Dibutylindilaurate (DBTDL) transesterification catalyst increased viscosity of blends, improved mechanical properties, and interfacial adhesion upon melt blending at short residence times. Optimal catalyst concentration was predicted to be 500 ppm.

He et al. studied fibers spun from PEN/Vectra A950 blends obtained using a spinneret diameter of 1mm and take up speeds of 300-800 m/min [231]. At shear rates above 10 s^{-1}, PEN viscosity was observed to be higher than that of the LCP.

Kyotani and Saeed studied ternary PET/PEN/LCP (Vectra A950) blends. LCP acted as a processing aid by reducing viscosity of the blends [233]. A linear increase in modulus and strength of extruded strands of the blends was observed with increasing LCP content. Presence of LCP was found to have no effect on PET/PEN transesterification.

Gao et al. studied blends of PEN with a 73/27 HBA/HNA copolymer. LCP acted as a nucleating agent [234]. Crystallization of PEN improved with LCP content up to 1 wt% and leveled off thereafter. T_{g} of PEN/LCP decreases with LCP content. Size of PEN spherulites decreased with increasing concentration of LCP in blends, but the structure of PEN crystals was not affected.

Minkova and Magagnini studied PEN blended with Vectra A950 and a synthesized semiflexible LCP (polycondensate of PET (10 mol%), HBA (76.5 mol%),
terephthalic acid (6.75 mol%), 4,4’-dicydrocybiphenyl (6.75%) [235]. Addition of both LCPs decreased crystallization time of PEN. Role of LCP as a nucleation agent was more pronounced at 7 wt% concentration due to larger interfacial area created by the finer dispersion of LCP domains (0.2-0.5 µm). While nucleation rate of PEN increased, structure of PEN crystals was not affected in the presence of LCP.

Xie et al. studied blends PEN/LCP (Rodrun LC5000) blends [236]. They observed decrease in the tensile strength with up to 50 wt%, and no increase in the Young’s modulus up to 30 wt% LCP concentration was found. Slight improvements in tensile strength and modulus over the rule of mixtures at 70 wt% LCP concentration were recorded. Crystallization temperature of PEN was found to increase in the blends till 50 wt% LCP, acting as a nucleating agent [236, 237]. The crystallization temperature decreased at higher LCP concentrations due to steric hindrance [236]. The storage modulus from DMTA analysis was found to increase with LCP concentration, with highest values being at 70 wt% LCP, due to a synergistic effect caused by partial miscibility. SEM micrographs of injection moldings containing up to 30 wt% LCP showed oriented elliptical LCP droplets in the skin and LCP droplets in the core region. At greater LCP concentrations, the aspect ratio of LCP domains increased with formation of fibrils in the skin. The decrease in tensile strength of blends at low LCP concentrations was attributed to immiscibility and interfacial slip. Synergistic improvement in mechanical properties and storage modulus was observed at 70 wt% LCP concentration. This was attributed to transesterification reactions, which improved stress transfer between PEN and LCP phases.
Jang and Kim observed improvement in the tensile strength and flexural modulus of PEN/LCP (Vectra A950) blends [238]. The blends became stiffer and more brittle as the LCP content increased. A synergistic effect was recorded for injection moldings of 30/70 PEN/LCP blends, with tensile strength and flexural modulus increasing from 150 MPa and 5.8 GPa for pure LCP, to 201 MPa and 6.5 GPa for the blends, respectively. The heat of fusion increased from 0.4 J/g in pure LCP to 10 J/g in 30/70 PEN/LCP blends. X-ray diffraction studies showed an increase in the degree of orientation in the 30/70 blends. The fibrillar structure in the skin region became more uniform with increasing LCP content in the blends. The synergistic effect in 30/70 blends was due to fine fibrils with high aspect ratio. The interfacial attraction was found to be very low for all blends, as indicated by the presence of voids around LCP droplets in the core region. The blend became increasingly shear thinning with the addition of LCP [237]. While viscosity of 90/10 blends was much lower than that of pure PEN. Pure LCP had the highest viscosity. Fibrillar morphology similar to that of pure LCP was observed for 50/50 PEN/LCP extruded at 290°C in a capillary rheometer above a shear rate of 5000 s\(^{-1}\). Processing temperature was found to have significant impact on fibrillation. Thermal analysis with DSC showed that the \(T_g\) did not change. Heat deflection measurements revealed that LCP enhanced the dimensional and thermal stability of PEN.

2.6.3. Blends with poly(butylene terephthalate) (PBT)

PBT is more flexible than PET or PEN. It has lower \(T_g\), \(T_m\) and viscosity. Moreover, due to its flexible structure, greater miscibility is observed in its blends with LCPs. From this perspective, studying PBT/LCP blend literature is valuable.
Engberg et al. studied PBT/LCP (Vectra A950) blends [240]. The viscosity of the LCP is ten times greater than that of PBT and no fibrillation was observed at up to 38% LCP concentration. An increase in secant modulus was recorded above 38% LCP concentration. It was also found that the mechanical properties were highly dependent on orientation of the LCP phase and followed different patterns depending on whether fibrillation occurred or not.

Daragas et al. studied blends of PBT with a synthesized LCP having long flexible segments [241]. The blends were found to be partially miscible with up to 20% LCP content; crystallinity of the PBT phase decreased with LCP content.

Heino and Seppala found an increase in the tensile strength and modulus of PBT/LCP (Vectra A950) blends above 20% LCP content along with a decrease in ductility due to poor interfacial adhesion [242]. An improvement in fibrillation with increasing LCP content, viscosity ratio of matrix to LCP, and strain rate was recorded.

Paci et al. studied blends of PBT with liquid crystalline homo-polyester poly(biphenyl-4,4'-ylene sebacate) [243]. The melting and crystallization temperatures of PBT are found to decrease with LCP content, while the degree of crystallinity of PBT increases. The blends were found to be miscible above the smectic to isotropic transition temperature of the LCP and to undergo transesterification upon annealing at these temperatures.

Kimura and Porter studied the source of partial miscibility in PBT/LCP (60/40 poly(oxybenzoate) (POB)/PET copolyester) blends [244]. The blends prepared by solution precipitation were compression molded. NMR analysis showed no traces of transesterification. PBT was found to be compatible with the flexible PET phase of the
LCP, as observed by lower $T_g$ of this phase with increasing PBT concentration. The rigid POB phase was incompatible with PBT. Its $T_g$ was unaffected by the presence of PBT. No changes were observed in the crystallization behavior of PBT.

Pracella et al. observed that the rate of spherulite growth and overall crystallization of the PBT phase was reduced by the presence of LCP (poly (decamethylene 4,4’-terephthaloyldiroydibenoate)), which was miscible with the PBT [245]. The nucleation in pure PBT is athermal. Crystallization from heterogeneous nuclei is retarded in the presence of the mesophase, shifting the mechanism to homogenous, thermal nucleation resulting in less nuclei formation. With the incorporation of LCP into the PBT phase, induction time increases and melting point depression takes place. The strong dependence of the crystallization rate of PBT on LCP concentration is believed to be due to the high miscibility of the two components, which affects the nucleation mechanism.

2.6.4. LCP/LCP Blends

Blends of two or more LCPs have also been studied and offer insight into possibilities for the current study.

In particular, Stachowski and DiBenedetto blended three aromatic LCPs (K161, Vectra A950, Vectra RD501) were with two semiflexible LCPs based on PHB/PET (Rodrun LC3000, X7G) [157, 158]. It was found that the morphology and mechanical properties of blends were governed by the block structure of the LCPs, composition, viscosities and transesterification reactions, which were promoted in the presence of TBOT catalyst.
De Meuse and Jaffe also studied LCP/LCP blends. Blends of 73/27 HBA/HNA (Vectra A) with a copolyester of 50/25/25 HNA/TA/HQ are partially miscible and show two $T_g$’s in the whole concentration range. Blends of Vectra A with a copolyester of 57/41/1/1 HBA/HNA/TA/HQ (HQ: hydroquinone) were miscible in the whole composition range, revealing a single $T_g$ as predicted by the Fox equation. It is important to note that different LCPs based on HBA/HNA are miscible only at certain proportion of these components. Although inclusion of TA and HQ moieties into HBA/HNA is expected to affect molecular orientation and interaction with the other HBA/HNA blend, these blends are miscible [246].

Akhtar and Isayev studied blends of two thermotropic LCPs. The immiscible LCPs (Vectra A950 and Ultrax 4002) were found to produce self-reinforced composites in which one LCP enhances the molecular orientation of the other. The blends showed an extraordinary tensile strength and modulus at 50/50 concentration [12]. Ding and Isayev also studied blends of two LCPs (Vectra A950 and Ultrax 4003) [247], which were found to be partially miscible based on composition. The impact strength of these blends lied closer to that of the components. It should be noted that Ultrax 4002 is amorphous, and Ultrax 4003 is semi-crystalline with a melting point of 315°C [71].

Lee et al. studied melt spinning of fibers from blends of a wholly aromatic LCP (K161) with a semi-flexible LCP (PET/PHB60) in a capillary rheometer. The global molecular orientation remained constant above a certain DDR. Although orientation was insensitive to temperature, the fiber modulus was affected by this parameter. It was noted that when there was no relaxation of molecules following drawing, and the orientation of LCPs could be modeled by the rotation of rigid molecules in the nematic phase [248].
Kenig et al. studied blends of Vectra A (73/27 HBA/HNA) with a copolymer of 60/20/20 HNA/TA/acetoxy-acid aniline. The orientability parameter $\lambda$ was calculated according to the following equation:

$$\tan \phi = C \cdot DDR^{-\lambda}$$  \hspace{1cm} (2.25)

where $\phi$ is the average orientation angle, measured by WAXS, $C$ is a constant, and DDR is the draw ratio [249].

Parameter $\lambda$ was 0.35 for Vectra and 0.55 for the other copolymer. Blends of 25/75, 50/50, and 75/25 concentration had $\lambda$ of 0.55. The orientation enhancement in the blends was attributed to miscibility of the LCPs, which was determined through the observation of a single $T_g$ for the blends lying between the two components. It was suggested that orientation of miscible polymers can lead to increased packing. This was used to explain the synergistic improvements, much above the rule of mixtures, in the strength and modulus of 50/50 and 25/75 Vectra A/HNA/TA/acetoxy-acid aniline blends [249].

2.7. Ultrasound

Ultrasound is made of mechanical pressure waves like audible sound and propagates in media. Ultrasound can be generated using magnetostriction or piezoelectric properties of materials. Electric polarization induces mechanical stress in piezoelectric materials and can be employed to produce oscillations at a resonant frequency. The first piezoelectric material was quartz and today various ferroelectric ceramics are used, including barium titanate, lithium niobate and lead zirconate titanate, the latter of which is commercially used for generation of ultrasound transferred by horns to ultrasonic
cleaning baths. Calibrated ferroelectric materials are used to measure the intensity of ultrasound. Ultrasound generated by the ferroelectric materials is of a single frequency, commonly between 20-100 kHz, and have adjustable acoustic power [250].

Acoustic amplitude can vary greatly in the propagation direction, resulting non-uniform field topology. In the limit of a progressive planar or spherical wave, the acoustic intensity \( I \) and pressure \( P_A \) are related as shown below:

\[
I = \frac{P_A^2}{2\rho c}
\]

where \( \rho \) is the density of the medium, and \( c \) is the longitudinal wave speed or the speed of sound. Acoustic impedance is given as \( \rho c \) [250].

Cavitation is induced by oscillatory pressure and resulting in the formation of pulsating bubbles that grow and breakup through interaction with the medium and among themselves [251]. Nucleation of cavitation bubbles is expected to occur when the acoustic force exceeds the cohesive forces in the bulk. However, the presence of structural defects greatly reduces the required acoustic force for cavitation due to inhomogeneity of medium [250]. The forces required for cavitation in solids is much lower than their tensile strength due to weak points such as micro-inhomogeneities, crystal lattice defects and dislocations. Similarly in fluids, inhomogeneities in structure, usually in the form of micro bubbles, are nucleation sites for cavitation [251].

Studies of acoustic cavitation in solvents showed that frequencies between 20-500 kHz are effective for the generation of radicals in heterogeneous systems. While no cavitation occurs below a certain energy threshold, excessive energy can lead to generation of bubbles throughout the fluid to render the energy unavailable for reaction.
It was shown for solvent systems that increasing pressure hinders bubble initiation but increases the energy released on bubble collapse [250].

Ultrasonic treatment of polymers can be carried out in solution and in the melt state. Both batch and continuous ultrasonic treatment processes have been employed for treatment of polymers in the melt state. The ultrasonication of polymers in melt and solution has some similarities in their mechanism and effects.

High power ultrasound creates high amplitude alternating pressure and leads to cavitation [252, 4, 8]. The cavitation process is schematically shown in Figure 2.10. The acoustic cavitation can occur in liquid or solids. In liquids, ultrasonic oscillations create alternating tension and compression forces, known as the negative and positive halves of the pressure cycle, respectively [8]. These oscillating forces act primarily on bubbles, which then grow through expansion and contractions, reaching a size around 100-200 µm and goes into resonance with the ultrasonic field. Oscillations of bubbles during this resonance period release energy, which can overcome the energy of activation of chemical reactions. Upon reaching a critical size, the cavitation bubbles burst, generating localized hot spots with theoretically calculated pressures of ~1000-2000 bar and temperatures of ~5000K as well as very large instantaneous electrical fields in the order of $10^{11}$ V/m. In the ultrasonication of viscoelastic media, bubble collapse is generally not expected, and the fatiguing action of resonance of cavitation bubbles is commonly responsible for chain scission and generation of active sites [252, 4]. The amount of energy released is directly proportional to the ultrasonic pressure amplitude, which determines the strain of oscillations.
Cavitation also occurs in liquids free of bubbles when the acoustic pressure amplitude is greater than the hydrostatic pressure [250]. Voids are formed at locations of cohesive failure between molecules, which then act as micro bubbles and grow in size under the action of ultrasound. Defects in lattice structure and impurities such as filler lead to cavitation. The bursting of micro bubbles leads to formation of radicals and scission of macromolecular chains. Since micro voids are also generated by mechanical and thermal stresses, sheared polymers in an extruder have many sites of imperfection where cavitation takes place [252, 4].

Thixotropic viscosity reduction has been reported for polymers under ultrasonication, which takes place by cavitation when the pulsation and rupture of bubbles is hindered [253]. Ultrasound overcomes Van der Wall attraction forces and can also break macromolecular chains resulting in permanent viscosity changes. Gel formation in rubbers and irreversible viscosity decrease in various plastic matrices have been reported. The MW of macromolecules after prolonged sonication approaches a
minimum value. The MW of PS was found to be about $3 \times 10^4$ upon prolonged sonication in solution. The effect of ultrasound is greater on longer chains, and has been modeled by first order reaction kinetics. Mechanical or chemical degradation of polymers results in the creation of radicals at the ends of macromolecular chains, and hence radicals of two different polymers can react to form copolymers. Copolymer formation, branching and grafting of polymer chains also take place under sonication [252, 254]. In case of polymer blends, grafting can occur by reaction of ultrasonically generated radicals with C=C bonds [253]. The extent of reactions is dependent on residence time in sonication [251].

Ultrasonic treatment in the melt in a batch reactor has been studied by Shim et al. [255]. They studied bubble formation in the ultrasonic devulcanization of poly(dimethyl siloxane) in static conditions. It was found that greater ultrasonic power is consumed at higher applied pressure. The exact power consumed by breakage of specific bonds cannot be calculated as the imposed ultrasonic energy goes to breakage of bonds, heat dissipation in the rubber, power transmitted through the rubber and is eventually lost from the system [256]. Temperature of the sample is found to increase with duration of sonication, and is greater for thinner samples due to consumption of more energy at smaller gap. The number of bubbles increases steadily at first with nucleation but then decreases with coalescence of the bubbles. While initiation of bubble growth is greater under low pressure and low amplitude, coalescence is favored under high pressure and amplitude. It was found that a greater amount of main chain breakage than crosslinks occurs under static conditions as opposed to the more selective crosslink breakage under shear, as in continuous melt processing in an ultrasonic extruder [255].
The ultrasonic efficiency is lower under low pressure [257]. Through static ultrasonic treatment experiments in a batch reactor, it was shown that rubber sol is only created locally around ultrasonic cavitation bubbles. The gel fraction and crosslink density are lower in continuously devulcanized samples. The kinetic study of bubble formation and coalescence kinetics with dissolved gas as nucleation sites showed that the difference between ambient and ultrasonic pressures is the governing parameter. It was found that the rate of bubble formation increases with number of dissolved gas particles. Dissolved gas in rubber acts as nucleation sites for formation of bubbles, which can then coalesce through depressurization by ultrasound. Increase in ambient pressure also leads to an increase in ultrasonic pressure due to greater velocity of sound in denser media.

The pressure in ultrasonic treatment zone is reduced because of 1) heat generation by ultrasound, 2) shear thinning effect due to wave propagation in polymer melt, 3) reduction of friction between the horn surface and melt, and 4) polymer degradation [5].

In continuous melt processing in an ultrasonic extruder, pressure is lower at greater gap size [5]. Pressure is also lower when two horns are in operation, due to the interaction of ultrasound waves generated by the two horns. Decrease in gap size leads to higher power consumption. The total power consumption increases with 2 horns but it is not double that recorded during treatment with a single horn. This indicates that there is an interaction between the horns.

Interaction of horns can occur in multiple horn systems, which is verified by fluctuations in power consumption in the continuous ultrasonic extrusion process [5]. Thermo-mechanical degradation of polymer seen during ultrasonic treatment, leading to reduced viscosity. This is the acoustic cavitation effect, also seen in polymer solutions
during ultrasonic treatment. For the same ultrasonic amplitude, the strain amplitude is greater at reduced gap size (2 mm vs. 4 mm) and more degradation is observed in that case.

2.7.1. Theoretical models of the continuous ultrasonic extrusion process

Modeling of the effect of ultrasound on the polymer melt is a coupled problem for which both the flow of material in the ultrasonic die in the macromolecular level, and the molecular effects of ultrasound in the micromolecular level must be considered together [252, 258]. Flow is derived with a die-filling model where heat transfer effects include rate of viscous dissipation with flow, rate of ultrasonic dissipation by oscillatory deformation, and rate of energy consumption due to chain scission [252].

The growth of bubbles with ultrasonic cavitation put stress on macromolecular chains, chain scission taking place depending on the type of bond [252]. The maximum bubble diameter is a function of ultrasonic frequency and amplitude, hydrostatic pressure and elastic properties of the material. The forces acting on chains decrease with increasing distance from the bubble surface.

Simulation of the ultrasonic devulcanization process has been studied [252]. The calculation of velocity profile, temperature, hydrostatic and acoustic pressures allowed prediction of the rate of breakup of mono-, di-, and polysulfidic crosslinks. Discrepancy with experimentally data was attributed to the recombination of radicals to form new bonds, which could not be modeled. While theoretical calculations using viscoelastic model predicted that no bubble collapse occurs at high ambient pressure, devulcanization of rubber was observed, leading to the conclusion that bubble collapse is not a necessary
criterion for breakup of chains. Ultrasonic degradation occurs around pulsating cavitation bubbles.

The calculated effect of cavitation was found to depend largely on the viscoelastic nature of the material [252]. Comparison of results using pure elastic solid and linear or Rouse viscoelastic solid models showed that the violent collapse of bubbles does not occur as readily in viscoelastic solids. In Rouse solids at low ambient pressures, high amplitude oscillations occur around the cavitation bubbles and bubble collapse does not take place. The strain on chains is determined by acoustic pressure, which must be sufficiently high for degradation to take place. Decreasing gap size in the ultrasonic die leads to higher acoustic pressure and power consumption due to increase in ultrasonic strain. Static pressure decreases the compressibility of bubbly media and increases the power consumption of ultrasound, enhancing its effect of bond scission [259].

In the ultrasonic devulcanization of rubbers, the relative degrees of rupture of crosslinks and main chains were found to depend on the kind of rubber [252]. It was observed that the ultrasonic treatment of SBR, which is less thermally stable than PDMS, leads to greater main chain scission. Furthermore, particle filled rubber systems have greater ratio of main chain rupture to devulcanization since the filler particles act as imperfections where cavitation readily occurs. The reduction of chain mobility by filler particles further increases the degradation effect of ultrasound.

In the devulcanization of rubber, random crosslink scission, main chain scission, depropagation, radical transfer with chain scission, and first-order radical termination reactions take place simultaneously [252]. Although thermally induced chain scission and recombination reactions are stress dependent, it was assumed in the model that the rate
constants are the same for static and continuous ultrasonic treatment. It is seen that with increased exposure to ultrasound, degradation is accelerated by depopagation and radical transfer reactions because of heat buildup.

Isayev et al. developed a model to predict velocity, temperature and pressure fields during the continuous ultrasonic devulcanization process and the resulting gel fraction and degradation of matrix [260]. Assuming that main chains and crosslinks are broken independently, rate of bond cleavage is a function of bond strength and local stress concentration, collapsing cavities do not interact, and that devulcanization rate is governed by average residence time, rate of bond breakage was written as a first order reaction dependent on type of bond. Only bonds surrounding the bubble are taken to be in the active zone, determined by the hydrostatic and acoustic pressures and ultrasonic strain. The flow is coupled with cavitation and bond rupture using a die filling algorithm.

2.7.2. Compatibilization of polymer blends with ultrasound

Ultrasonic technology was found to be effective in the compatibilization of polymer blends during extrusion and in the creation of novel copolymers with enhanced properties and decreased interfacial tension in immiscible blends [252]. The action of ultrasound led to significant improvement in the mechanical properties of blends of PP/NR(natural rubber), PP/EPDM(ethylene propylene diene (M-class) rubber), HDPE/NR, HDPE/EPDM and HDPE/SBR(styrene butadiene rubber) blends. Tensile strength, elongation at break, Young’s modulus, toughness and impact strength were improved upon ultrasonic treatment at amplitudes of 6 and 10 µm in each of these blends.

In 2003, Isayev and Hong were issued a patent for the continuous ultrasonic
compatibilization of polymer blends and formation of copolymers with the said process, including the reaction of polyesters and copolyesters with ultrasound [9].

In NR/SBR blends, the crosslink density was lower than those of the devulcanized pure components, possibly due to lower level of unsaturation and chemical reaction between the components [257]. $M_n$ of NR and SBR were more than halved with ultrasonic treatment at 5 $\mu$m. However, the $M_n$ after ultrasonic treatment at 7.5 and 10 $\mu$m was higher than after treatment at 5 $\mu$m ultrasonic amplitude. This meant that chain scission took place with ultrasound and created reactive end groups, which then recombined to generate longer chains. Significant improvements in the tensile strength and elongation at break were explained by chain interchange reactions between NR and SBR. Ultrasonic treatment led to the formation of NR/SBR copolymer at the interface. The tensile modulus was not improved for NR/SBR blends, which was attributed to the lower crosslink density of the blend because of ultrasonically induced molecular degradation of the pure compounds [252].

Oh et al. studied the in-situ compatibilization of PP/NR blends [6]. The Young’s modulus, elongation at break and toughness of 50/50 and 75/25 PP/NR blends were significantly improved upon ultrasonic treatment. Sonochemical cleavage of polymers took place by ultrasonic treatment, and the created radicals reacted to form copolymers. The impact properties are significantly improved, signifying the formation of in-situ copolymer, which in turn reduces the interfacial tension between the phases. No significant differences in viscosity were observed between untreated and ultrasonically treated blends at short residence times. The viscosity decrease was observed at long residence times. The latter was due to the prevailing breakage of main chains under the
action of ultrasound. SEM images of annealed blends showed that the domain size of NR was much smaller in treated blends. The authors suggested that phase growth is hindered in treated blends due to the presence of copolymer at the interface. Since the copolymer allows greater adhesion between the phases, it became more difficult for the NR chains to diffuse and coalesce. Atomic force microscopy (AFM) images of cryo-microtomed blends showed that the PP/NR boundaries were very sharp in untreated samples (height of steps is 100 nm), while the treated blends did not exhibit delaminated regions (max step size 30 nm). Delamination occurred when the interfacial adhesion between the phases was low. Rougher PP/NR interfaces were observed in treated blends, also indicating good adhesion of the phases.

Measurement of root mean square (RMS) roughness from AFM phase images was carried out to detect the improvement in interfacial adhesion upon ultrasonic treatment of PP/EPDM blends [5]. As PP and EPDM had different thermal expansion coefficients, the surface topography changed to reveal peaks and valleys on the surface after cryomicrotomy. The measured RMS roughness will be less if the interfacial adhesion is greater, in which case the attraction between EPDM and PP restricts the different thermal expansions of phases of the blends. After treatment by 1 horn at 7.5 µm at 2 mm gap size, the RMS roughness of 50/50 blends decreased from 130 nm to 80 nm. IR spectra of 50/50 PP/EPDM blends after the extraction of PP showed the ethylene peak of EPDM phase only for ultrasonically treated samples. This confirmed the existence of copolymer in ultrasonically treated PP/EPDM 50/50 blends. Increase in modulus at 5% elongation was observed under certain treatment conditions and this increase was also greater when 2 mm gap size was used due to higher strain amplitude imposed by
ultrasound. The domain sizes of untreated and treated blends before annealing were about the same. However, after annealing, the domain size of treated blends was smaller; hence the treated PP/EPDM blends had more stable morphology after annealing.

Hong and Isayev studied blends of ultrasonically devulcanized ground tire rubber (GTR) and HDPE [261]. They found that ultrasonically treated GTR/HDPE blends had greater tensile and impact properties than GTR which was first devulcanized and then blended. This was attributed to improved interfacial adhesion through specific reactions between the phases of the incompatible blend caused by ultrasound. Impact properties of the blends were further improved by dynamic revulcanization, which led to a more uniform distribution of rubber particles with rough and porous surfaces.

Zhang et al. used ultrasonic extrusion to graft maleic anhydride onto several polyolefins and EPDM [262]. They were successful in inducing ultrasonically initiated functionalization reactions for HDPE, LLDPE (linear low density polyethylene) and EPDM but not PP. They observed excessive chain scission for PP. With ultrasonic energy less than 250 W, the recombination of macroradicals predominated degradation for HDPE. Grafting of MA onto EPDM also took place and the possible reaction scheme was demonstrated.

Feng and Isayev studied the in-situ compatibilization of PP/EPDM blends by ultrasound [5]. They observed significant improvements in the yield stress, tensile strength, elongation at break and toughness of 50/50 PP/EPDM blends treated at an ultrasonic amplitude of 7.5 μm over untreated blends for specimens prepared by compression molding, but not for injection molding. For injection molded specimens, they observed only a slight increase in the yield stress and tensile strength of the blends.
with ultrasound. Through SEM micrographs, they showed that the rubber domain size of untreated and ultrasonically treated compression molded specimens was larger than extrudate strands because of growth and coalescence during high temperature treatment. On the other hand, injection molded specimens had only slightly larger domain size than the extrudate strands, indicating coalescence and growth as a result of the high shear rates experienced in injection molding. Hence, new interfaces were generated between the two phases and the copolymer formed with ultrasonic treatment, resulting in less amount of copolymer in new interface. This suggests that shearing after ultrasonic treatment in extrusion or injection molding randomly displaces the copolymer formed. Shaping of the ultrasonically treated blend into desired articles with minimal shear mixing is ideal in order to keep in-situ formed copolymer at the interface. This is experimentally viable in the fiber spinning operation following extrusion.

Lin and Isayev studied the ultrasonic compatibilization of PP and PA6 (Nylon 6) blends and the effect of ultrasound on the pure polymers [263]. They observed increase in the complex viscosity of PA6 from 1400 Pa*s to 1850 Pa*s at an angular frequency of $1.19 \text{ s}^{-1}$ after ultrasonic treatment at an amplitude of 5 $\mu$m. At ultrasonic amplitudes of 7.5 and 10 $\mu$m, viscosity was reduced to below 1400 Pa*s. This was because of the simultaneous polymerization and degradation of PA6. IR spectra were unchanged and the reactions were classified as 1) polycondensation reactions between PA6 chains, and 2) radical reactions leading to some long-chain branches (LCB). In PP/PA6 blends, plots of storage vs. loss modulus fell on master curves irrespective of the use of ultrasound for both polymers. This led to the conclusion that ultrasound did not result in the formation of LCBs created by free radicals. Rather, ultrasound must have lead to polycondensation,
which takes place through ionic reactions. This has also been observed in polyamides in the ultrasonic treatment of polyurethane systems.

Vinogradov-Malkin plot can be used to determine changes in molecular weight distribution of polymers with ultrasound [263]. When all untreated and ultrasonically treated PA6 samples fall on the same master curve, the molecular weight distribution does not change. If chain scissions occur randomly, as under thermal degradation, the molecular weight is expected to broaden. Through experimental studies, it was concluded that the random chain scission of PA6 did not occur under ultrasonic treatment. Annealing of PA6 at 250°C for 10 minutes led to the same increase in viscosity. However, the residence time in ultrasonic treatment was 3 s and extrusion temperature was 230°C. Cole-Cole plots of PA6 samples annealed for 1 hour revealed that they do not fall on the same master curve, which indicated that branching or crosslinking take place with annealing. Nylon gelation under heat has been reported before. Hence, ultrasonic treatment leads to two competing reactions in PA6: polycondensation and mechanochemical degradation.

Ultrasonic treatment was shown to increase the melting temperature of both PP and PA6 [263]. Treatment at an ultrasonic amplitude of 5 µm was shown to increase the crystallinity of PA6 by 12% and that of PP by 5% over extruded but untreated polymers. The higher impact properties of PA6 and PP with treatment at an amplitude of 5 µm were attributed partially to higher crystallinity and more uniform crystal size.

The 60/40 PA6/PP blends treated at an amplitude of 7.5 µm showed 50% increase in impact energy over untreated blends [263]. The increase in the toughness and impact properties of these blends were probably due to the in-situ formation of a copolymer,
which increased the interfacial adhesion between the phases. Lin and Isayev summarized the reactions on the basis of sonochemistry and mechanochemistry and explained that the nature of polymers and reaction temperature play roles in copolymer formation. They didn’t observe further improvement in the mechanical properties of PA6/PP blends at higher residence times. Because highly reactive radicals do not have high selectivity during coupling reactions, complete compatibilization cannot be achieved.

2.7.3. Effect of ultrasound on particle filled polymers

The addition of fillers can amplify the effect of ultrasound, as seen in the increased level of devulcanization with the addition of carbon black (CB) filler to natural rubber (NR) [252]. Ultrasound also acts to break weak physical crosslinks between filler and polymer, as observed in precipitated silica filled PDMS. Filled rubber systems have worse mechanical properties upon revulcanization with increasing filler content. Due to reduced mobility of chains and increase in structural imperfections, the effect of ultrasound is increased in the presence of fillers.

Suetsugu and Sato observed dispersion of compacted nanosized agglomerates with an ultrasonic attachment having glass walls, attached to a twin screw extruder [264]. The dispersion of SiO₂, TiO₂ and ZnO₂ agglomerates were observed with respect to particle size using a hi-speed camera. Ultrasound caused expansion-contraction of agglomerates at amplitudes of 7-9 µm at a residence time of 0.3 seconds. The recorded period of particle expansion-contraction corresponded with the used frequency of ultrasound, 19 Hz.
Ultrasonic treatment of 80/20 HDPE/PS blend was performed during extrusion through a capillary die [265]. Reductions in apparent viscosity and die pressure were recorded with ultrasonic treatment, and were found to be more significant at low flow rates. The compatibility of HDPE/PS blends was improved through ultrasonic treatment, as indicated by greater uniformity of dispersion and particle size in addition to improved impact strength and elongation at break of the blends under some ultrasonic treatment conditions. The compatibilization by ultrasonic treatment of the blends is ascribed to the chain scission of the pure components and consequent recombination, resulting in the generation of copolymers. The presence of copolymer in the treated blends was inferred by the presence of the characteristic absorption peak of PS after extraction of the blend only in ultrasonically treated samples.

In ultrasonic treatment of EPDM/silica mixtures, the size of silica agglomerates was reduced upon ultrasonic treatment during extrusion and led to higher viscosities as compared to the untreated mixtures compounded under the same conditions [266]. This was because of increased surface area created by silica dispersion. A single horn ultrasonic extruder was also used to disperse silica agglomerates in EPDM matrix. Compared to internal mixing and milling, ultrasonic extrusion broke the silica particles down most effectively and viscosity did not decrease upon processing.

In treatment of CB filled NR, it was found that the effect of devulcanization increases with CB content [257]. CB can act as a polyfunctional radical acceptor inhibiting the recombination of broken chains. As filler particles also limit movement of polymeric chain, CB also increases the probability of chain scission.
Diao et al studied the devulcanization of silicone rubber and found that $M_w$ increases with ultrasonic treatment while $M_n$ decreases, due to the creation of branched chains [267]. The viscosity of devulcanized silicone rubber is greater than the virgin rubber because of higher gel fraction. The mechanical properties of revulcanized silicone rubber were found to be better than the virgin rubber.

Lapshin and Isayev used the ultrasound aided extrusion process to intercalate and partially exfoliate nanoclay (montmorillonite) in PP [268, 269]. At a residence time of 7-21 s in the ultrasonic treatment zone, they observed an increase in the basal spacing from 2.4 to 4.1 nm with ultrasonic treatment for 21 s at an amplitude of 10 $\mu$m at 4 mm gap. They commented that for a larger gap, the strain amplitude is lower even though the residence time is greater. The effect of ultrasound is consequently greater at smaller gap size. They identified two competing effects in the ultrasonic treatment process: intercalation, partial exfoliation of clay and degradation of polymer.

Swain and Isayev studied the ultrasonic assisted extrusion of HDPE/clay nanocomposites [270]. Reduction in pressure with the addition of clay to HDPE/Closite 20A nanocomposites was attributed to the reduction in friction between the HDPE/clay particles and the die wall. Increase of complex viscosity with ultrasound was seen at all clay concentrations. Ultrasonic treatment at 5 and 7.5 $\mu$m of HDPE with 10% clay concentration was observed to increase the complex viscosity. Treatment at an amplitude of 10 $\mu$m led to decrease in complex viscosity, which was explained by the degradation of the matrix.

Based on the findings presented in this section, the addition of inorganic catalyst particles to LCP/polyester blends could be expected to induce more effective ultrasonic
reactions by acting as defects where cavitation will be pronounced. The action of ultrasound could lead to greater catalyst efficiency, and effectively reduce concentration of catalyst and residence time required to obtain comparable compatibilization.

2.8. Conclusions of literature review

Thermotropic liquid crystalline polymers are commonly processed in the nematic state. In this mesomorphic state they form highly aligned fibrillar structures in thermoplastics, especially under elongational flow. LCP also acts as a processing aid in blends with flexible chain thermoplastics. The viscosity of these blends can be even lower than that of the components at low concentrations of LCP. The main advantage of flexible chain/LCP blends is the creation of in-situ or self-reinforced composites during processing.

Self-reinforced polymer composites containing LCPs exhibit extraordinary stiffness and strength. However, they are usually brittle due to poor miscibility in these blends. Interfacial adhesion in these blends is worse in the case of wholly aromatic LCPs, which also offer the greatest potential for improved mechanical properties of LCP/flexible chain thermoplastic blends due to their high stiffness. Numerous studies on improving the compatibility of these blends have been reviewed. While improvements in the ductility and stiffness were obtained in some cases, processes used were based on elaborate synthesis of tailored LCPs or block copolymers, melt mixing for prolonged times with and without the addition of catalysts, and multiple stage processing. A novel method for the in-situ compatibilization of aromatic LCP/flexible chain polyester blends involving continuous ultrasonic treatment in the melt state is suggested.
Application of ultrasonic energy to polymers leads to chain scission and generation of active sites. In polymer blends, copolymers can be formed by the recombination of active sites. In the case of polyester blends, recombination reactions are expected to occur by transesterification. The literature survey indicated that these reactions may occur in flexible chain/flexible chain, thermotropic/flexible chain, thermotropic/thermotropic polyester blends. It could be expected that transesterification reactions in these blends could be promoted by high power ultrasound. The aim of this study was to apply continuous ultrasonic extrusion process to these blends and to study the effect of processing conditions on their properties.

The process characteristics during ultrasonic extrusion of binary blends containing flexible chain and thermotropic polyester are to be studied in different ultrasonic extruder setups in order to elucidate the effects of ultrasonic treatment and identify conditions where improvement in properties of blends would occur with ultrasonic treatment. Rheological, structural, thermal, mechanical and morphological characterizations are the main methods used to probe the effect of ultrasound on these systems.
CHAPTER III
MATERIALS AND METHODS OF INVESTIGATION

In this chapter, the materials and experimental procedures employed in the current study are explained in detail. Binary blends of flexible chain and thermotropic polyesters were prepared in a single screw ultrasonic extruder. Other processing operations for preparation of samples included twin screw compounding, fiber spinning, injection and compression molding.

The characterization of untreated and ultrasonically treated pure materials and blends were performed through rheological, mechanical, thermal, mechanical, and spectroscopic methods. Rheological testing methods included dynamical rotational rheometry and capillary rheometry. Differential scanning calorimetry was the primary thermal characterization method. Thermal mechanical analyzer was also used to determine the second order phase transitions and dynamic mechanical properties of the polymers studied. Tensile testing was carried out on injection moldings and spun-fibers. Impact testing of injection moldings was also carried out. Spectroscopic methods used for structural identification of ultrasonically treated pure components and blends included Fourier transform infrared (FT-IR), nuclear magnetic resonance (NMR), and mass (matrix assisted laser desorption ionization time of flight, MALDI-TOF) spectroscopy. In addition, optical and barrier properties of some blends were studied.
3.1. Materials

Two liquid crystalline copolyesters and two flexible chain polyesters were chosen for studies of blending in ultrasonic extrusion. These materials behaved differently with ultrasonic treatment due to differences in their chemical structures. In addition, two transesterification catalysts were used in this study. The materials used are described in detail below.

3.1.1. LCPs

LCP1: Vectra A950, Ticona (Florence, KY), $T_m=280^\circ\text{C}$ [271]

![Chemical structure of LCP1](image)

Vectra® A950 is a wholly aromatic copolyester containing 73% HBA and 27% HNA. It was developed by Hoechst Celanese in 1985, and is currently marketed by Ticona. As discussed in section 2.1.2, this material was extensively studied in literature.

LCP2: Ultrax 4002, BASF (Ludwigshafen, Germany), $T_m=292^\circ\text{C}$

![Chemical structure of LCP2](image)

Ultrax 4002 is a 25:25:50 copolyesters of terephthalic acid (x), isophthalic acid (y) and dioxydiphenyl (z). LCP2 has also been the subject of many studies [27, 62, 12,
272, 273, 274, 275, 276]. It should be noted that $T_m$ indicated for both LCPs is the solid to nematic phase transition temperature.

3.1.2. Flexible chain polyesters

PET: Eastapak 7352, supplied by Eastman Chemical Company (Kingsport, TN)

I.V. = 0.74 dl/g, $T_m$=253°C

![PET structure]

PEN: VFR 40046, supplied by Shell Chemical Company (Houston, TX)

I.V. = 0.64 dl/g, $T_m$=275°C

![PEN structure]

The above polyester resins were chosen as their chemical structures are closely related. PEN is stiffer than PET due to the presence of the naphthalene group in the backbone. Moreover, PEN has greater melt viscosity than PET. These factors influenced properties of the studied LCP/thermoplastic polyester blends.

3.1.3. Transesterification catalysts

Tetrabutyl orthotitanate (TBOT, 97% reagent grade, Aldrich (St. Louis, MO)) has been identified as a promising transesterification catalyst [157, 158, 277] and will be used in melt processing of LCP/flexible chain polyester blends. TBOT is supplied by Sigma Aldrich. Its chemical structure is: $C_{16}H_{36}O_4Ti$
Another useful transesterification catalyst is antimony trioxide. Antimony is a typical catalyst used in the polycondensation step where glycolic esters combine to form polymers [109], and has also been used for transesterification reactions [156, 110]. Antimony trioxide was supplied by Fluka (Ronkonkoma, NY) at greater than 98% purity. Its chemical structure is: $\text{Sb}_2\text{O}_3$

3.2. Processing of polymer blends

In this section, the ultrasonic extruders are presented, followed by all processing operations used. These included twin screw compounding, fiber spinning, injection and compression molding. Before processing, materials were dried in a vacuum oven at a temperature of $120^\circ\text{C}$ for at least 24 hours to remove moisture.

3.2.1. Extrusion

The ultrasonic single screw extrusion process employing different designs used for treatment of components and blends, and twin screw extrusion used for preparation of masterbatches with catalyst are described in this section.

3.2.1.1. The ultrasonic extrusion process

Two different ultrasonic extruders were used in order to determine the effect of mixing on the properties of the blends and the extent of ultrasonic compatibilization. The first extruder was designed by the author and had a screw that extended after the
The extended screw provided mixing during and after treatment of polymer melt. Two separate screw configurations were used in this newly designed extruder. Isayev and coworkers designed the second ultrasonic extruder, which had a slit die in the ultrasonic treatment zone [6]. The screw configuration of the second extruder in this study was adapted later by Lapshin and Isayev [269]. Both are 1” single screw extruders (KL100, Killion, Houston, TX). These extruders are described in detail below.

The first ultrasonic extruder, henceforth referred to as SONIC1, had an extended barrel and a 33:1 screw. A schematic drawing (not to scale) of the ultrasonic extruder is shown in Figure 3.1

![Figure 3.1. Schematic drawing of the ultrasonic extruder with extended screw (SONIC1).](image)

Two different screw configurations were used in SONIC1. In both configurations, the screw diameter is 1” in the original extruder section. The screw diameter increases to
1.5” before the ultrasonic section and then decreases to 1.3” in the horn section to provide the 0.1” maximum gap for ultrasonic treatment. The diameter of the final section of the screw is 1”. In both screw configurations, a 5.38 cm long Union Carbide Mixer (UCM) was located 41.8 cm from the start of the screw. Also present in both screws was a 6.35 cm long Melt Star Mixer (MSM) located 7 cm after the first mixing section. Both of these mixing sections were before the ultrasonic treatment zone.

In the first screw, used in the processing of PET, LCP1, and their blends, an additional 6.35 cm long melt star mixing section was present at the discharge end of the screw after the ultrasonic treatment zone, as shown in Figure 3.2.

![Figure 3.2. 33:1 screw with two mixing sections before the ultrasonic treatment zone, and a melt star mixing section after it.](image)

In the second screw, the melt star mixing (MSM) section was replaced with conveying screw elements in order to reduce the extent of degradation caused by extrusion. This screw, shown in Figure 3.3, was used for processing of PEN, LCP2, PEN/LCP2 blends, and PET/PEN blends.

![Figure 3.3. 33:1 screw with two mixing sections before the ultrasonic treatment zone, and conveying screw flights after it.](image)

The ultrasonic zone, located at a distance of 73 cm from the feed end of the screw in both configurations of SONIC1, was preceded by a flightless section of the screw.
where a pressure transducer (P1) with a maximum pressure of 34.5 MPa (PT435A, Dynisco, Franklin, MA) was mounted onto the barrel. Pressure, barrel temperature and ultrasonic power consumption were recorded by a PC through a data acquisition system (DI-715-U, Dataq Instruments, Akron, OH). A schematic drawing of the ultrasonic treatment section of SONIC1 is shown in Figure 3.4, along with the position of the pressure transducer, P1. It should be noted that two identical flow channels are located between the screw and the barrel, with the bottom and top horns. The pressure transducer P1 is only mounted on the top side.

Figure 3.4. Schematic drawing of the ultrasonic treatment section of SONIC1.

The ultrasonic system was composed of two identical sets of 20 kHz power supplies of 6 kilowatt power capacity (2000bdc, Branson, Danbury, CT), fan cooled ultrasonic converters (Branson H.P. 101-135-124), 1:1 titanium boosters (Branson 101-149-096) and aluminum ultrasonic horns of 2.54x2.54 cm$^2$ cross section. The horns had tips with a radius of curvature of 18.4 mm. For all ultrasonic treatment experiments, both horns were operated simultaneously. The ultrasonic power imposed on the melt was controlled by adjusting the amplitude dials on the ultrasonic power supplies. Zero power
consumption of the horns was determined by measuring the power consumption with no material present below the horns, and is shown in Table 3.1.

Table 3.1. Zero power consumption of ultrasonic horns for SONIC1.

<table>
<thead>
<tr>
<th>Ultrasonic amplitude</th>
<th>Top</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>7.5</td>
<td>49</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>37</td>
</tr>
</tbody>
</table>

The amplitude at the tip of the horns was calibrated in air, and is shown in Figure 3.5.

![Ultrasonic amplitude calibration of horns for SONIC1.](image)

Figure 3.5. Ultrasonic amplitude calibration of horns for SONIC1.

The horns were mounted symmetrically onto the barrel. Streamlined relieves on the sides of the barrel in the ultrasonic treatment area guided the polymer melt to flow equally through the two channels of 2.54 mm (0.1 in) thickness between the ultrasonic horns and the screw. Polybenzimidazole (Celazole, PBI Performance Products Inc.,
Charlotte, NC) seals of 4 mm thickness were mounted in the barrel around the ultrasonic horns to prevent leakage of polymer melt.

The ultrasonic horns were cooled with water to prevent over heating of the ultrasonic system. Water flow rate was controlled with 2500 cm$^3$/min capacity flow meter (Key Instruments, Trevose, PA). In the treatment of PET, LCP1 and their blends, both horns were cooled with tap water at a flow rate of 1000 cm$^3$/min flow rate. In the treatment of PEN and its blends with LCP1, a flow rate of 300 cm$^3$/min was used to cool each horn to reduce pressure fluctuations in the extruder due to the higher melting point of PEN. In LCP2 and LCP1/LCP2 blends, a temperature controller unit (Sterltronic S8412-4, Stelco, Hamilton, Ontario, Canada) was used to regulate temperature of the horns by passing water at 80°C through them, enabling more accurate pressure readings through a constant temperature cooling source. The combined water flow rate to the horns was set at 2500 cm$^3$/min. The difference in water temperatures between delivery and return lines during the process was less than 2°C.

![Figure 3.6. Schematic drawing of conical die attached to SONIC1.](image)

The flow rate was varied to study the effect of residence time of the melt in the ultrasonic treatment zone. Under flood feeding conditions, screw speeds of 15 and 7 rpm
gave mass flow rates of 1 and 0.5 kg/hr, resulting in mean residence times of 7 and 14 s, respectively. A circular die of 2 mm diameter preceded by a converging circular section was attached to the end of the extruder. A schematic drawing of the die is shown in Figure 3.6. Melt exiting the die entered a room temperature water bath. Solidified polymer was then collected, dried, and subsequently pelletized in a grinder (WSL180/180, Weima, Fort Mill, SC).

![Extruder Diagram](image)

Figure 3.7. Extruder with slit die ultrasonic attachment (not to scale) [5]. From W. Feng and A. I. Isayev, Polymer, 45, 1207-1216. Copyright © 2004. Reprinted by permission of John Wiley & Sons, Inc.

A second ultrasonic extruder (SONIC2) with a slit die ultrasonic treatment attachment, shown in Figure 3.7, was also used to blend and ultrasonically treat 80/20 PET/LCP1 blends. The extruder was designed by Oh and Isayev [6]. It has a screw with special mixing elements, which was first used by Lapshin and Isayev [269]. This extruder had a 24:1 screw of 1” diameter with two mixing sections, as shown in Figure 3.9a. A
5.38 cm long UCM located at 41.8 cm from the start of the screw a 6.35 cm long MSM located 7 cm after the former were present, as shown in Figure 3.9b. Two square ultrasonic horns with cross sections of $38.1 \times 38.1 \text{ mm}^2$ were mounted in a rectangular slit die having dimensions of $157.5 \times 38.1 \times 4.0 \text{ mm}^3$. The gap between the ultrasonic horns was set at 4 mm, such that the horns were flush with the die, eliminating possible dead zones for flow in the ultrasonic treatment section. A schematic drawing of the flow channel at the ultrasonic treatment zone is shown in Figure 3.8.

Figure 3.8. Schematic drawing of flow channel in the ultrasonic treatment zone of SONIC2. From W. Feng and A. I. Isayev, Polymer, 45, 1207-1216. Copyright © 2004. Reprinted by permission of John Wiley & Sons, Inc.

A die having 4 holes with diameter of 3.175 mm was attached to the end of the slit die. Both horns were cooled with tap water at a flow rate of $1 \text{ cm}^3/\text{min}$ flow rate. A pressure transducer (PT) of maximum pressure 51.7 MPa (PT465XL, Dynisco) was placed in the slit die before the treatment zone at a distance of 21.6 mm from the front of the horn.
Figure 3.9. The screw used in SONIC2: (a) view of whole screw, (b) detailed view of the UCM and MSM mixing sections.

The ultrasonic system of SONIC2 had a frequency of 20 kHz and was comprised of a pair of a 3.3 kW ultrasonic power supplies (2000bdc, Branson), air cooled converters (CR-20, Branson), and 1:1 booster (Branson) connected to the above described ultrasonic horns. Zero power consumption of the horns was determined by measuring the power consumption with no material present below the horns, and is shown in Table 3.2.

<table>
<thead>
<tr>
<th>Ultrasonic amplitude (µm)</th>
<th>Top horn</th>
<th>Bottom horn</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>7.5</td>
<td>57</td>
<td>49</td>
</tr>
<tr>
<td>10</td>
<td>98</td>
<td>125</td>
</tr>
</tbody>
</table>

Figure 3.10. Ultrasonic amplitude calibration of horns for SONIC2.
The amplitude at the tip of the horns was calibrated in air, and the calibration chart is shown in Figure 3.10.

At a flood fed mass flow rate of 1 kg/hr, the mean residence time in SONIC1 was 4.8 minutes while that in SONIC2 was 4.5 minutes for the polyesters studied. While greater distributive and dispersive mixing was expected in SONIC1 due the extended length of the screw, greater polymer degradation could also result due to greater shear for longer time as compared to SONIC2. The MSM section of the screw after the ultrasonic treatment zone in SONIC1 was present in the processing of PET, LCP1 and their blends. For ultrasonic extrusion of PEN, LCP2, PET/PEN and PEN/LCP1, the MSM section on the screw after the ultrasonic treatment zone in SONIC1 was replaced with conveying screw flights. This modification was done to reduce polymer degradation induced by greater shear in the additional mixing section, which was observed in the processing of PET and PET/LCP1 blends.

3.2.1.2. Twin screw compounding

A twin screw extruder (Prism USA Lab 16, Thermo Electron, Waltham, MA), was used for compounding of LCP/TFBO and PEN/TFBO masterbatches. The twin screw extruder had two co-rotating screws fitted with shear intensive mixing elements. The screws, shown in Figure 3.11, had a diameter of 16 mm, and a length of 400 mm (L/D=25). A circular die of 3 mm diameter was fitted to the end of the extruder, and a 20 MPa pressure transducer was fitted onto the die. The feed throat was cooled with water at a flow rate of 1900 cm³/min with a 7500 cm³/min capacity flow meter (King Instrument Company, Garden Grove, CA). Pressure and torque were monitored by the extruder.
Figure 3.11. 24:1 shear intensive co-rotating screws of the twin screw extruder.

The barrel temperature was set at 285°C in all zones, except the rear zone, which was maintained at 235°C due to the water cooled feed throat. Water cooling minimized the evaporation of TBOT catalyst from the feed section of the extruder. The extruder screw speed was set at 200 rpm. This screw rpm allowed processing of pure PEN at a flow rate of 1 kg/hr without exceeding the maximum torque of the extruder.

The extrudate was collected in a water bath, and ground in a grinder (WSL180/180, Weima). A twin screw feeder (K2V-T20, K-tron, Pitman, NJ) of 11.2 kW power was used for feeding LCP and PEN pellets at high gear setting (3.2:1 gear reduction), calibrated for each polymer by weighing its output over 1 minute. The average standard deviation for the twin screw feeder was 2%, based on 5 measurements for feeding of PEN and LCP1 pellets. TBOT catalyst was fed using a syringe pump (NE-1000, New Era Pump System, Wantagh, NY) using at 24 ml syringe filled up to the 23 ml mark with TBOT liquid. The actual mass flow rate of TBOT in the syringe pump was calibrated by weighing the pump output every 5 minutes for 3 times. The percent standard deviation on syringe pump output was 1%. Two masterbatches were prepared, PEN with 2% concentration of TBOT, and LCP1 with 1.5% concentration of TBOT. For preparation of the PEN masterbatch, syringe pump feeding rate was set at 0.321 ml/min, which gave a flow rate of 20 g/hr, while the twin-screw feeder rate setting was 440 units, which gave a feed rate of 980 g/hr. For preparation of LCP1 masterbatch, the syringe
pump was set at 0.24 ml/min and yielded a mass flow rate of 14.8 g/hr of TBOT, while the twin screw feeder was operated at a setting of 443, yielding a flow rate of 985 g/hr for LCP1. For both masterbatches, the total flow rate including catalyst was 1 kg/hr.

The masterbatches were prepared for dilution in SONIC1. As degradation in the PEN masterbatch was expected, the amount of PEN to be compounded was selected such that this material would later be diluted by a ratio of 1:6.8 in SONIC1. However, there was excessive degradation in the PEN masterbatch, and this route of dilution was later abandoned, as described in CHAPTER VIII. LCP1 indicated significantly less change than PEN after compounding with TBOT. This material was chosen for preparation of TBOT catalyzed blends. 1214 g of LCP1/1.5% TBOT masterbatch was bag mixed with 4786 g of PEN for compounding SONIC1, yielding a final TBOT concentration of 0.3% in 80/20 PEN/LCP1 blend. The 80/20/0.3 PEN/LCP1/TBOT blend was processed in SONIC1 at a flow rate of 1 kg/hr without treatment and with treatment at ultrasonic amplitudes of 5, 7.5, and 10 µm. 1 kg of sample was collected for each condition.

3.2.1.3. Ultrasonic extrusion conditions

The extrusion conditions used for the processing of pure materials and blends in SONIC1 are shown in Table 3.3. In this table, extrusion temperature referred to the temperature setting for all zones except the rear zone, closest to the hopper, which was set at 260°C for all materials. The flow rate was calculated by weighing the extrudate in 1 minute intervals, and averaging 5 readings. The corresponding rpm for different materials, which showed some variation due to differences in melting behavior of materials and pellet shape, are shown in Table 3.3.

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Table 3.3. Extrusion temperatures and rpm in SONIC1.

<table>
<thead>
<tr>
<th>Homopolymers</th>
<th>Extrusion Temp (°C)</th>
<th>rpm, 1kg/hr feed rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>285</td>
<td>15</td>
</tr>
<tr>
<td>PEN</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td>LCP1</td>
<td>285</td>
<td>15</td>
</tr>
<tr>
<td>LCP2</td>
<td>300</td>
<td>15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Blends</th>
<th>Extrusion Temp (°C)</th>
<th>rpm, 1kg/hr feed rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/PEN</td>
<td>285</td>
<td>13</td>
</tr>
<tr>
<td>PET/LCP1</td>
<td>285</td>
<td>15</td>
</tr>
<tr>
<td>PEN/LCP1</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td>LCP1/LCP2</td>
<td>300</td>
<td>15</td>
</tr>
</tbody>
</table>

All materials were extruded without treatment and at ultrasonic amplitudes of 5, 7.5, and 10 µm. A residence time of 7 s was obtained in the ultrasonic treatment zone of SONIC1 at a flow rate of 1 kg/hr, under flood feeding conditions. In SONIC2, the residence time was 13 s for a mass flow rate of 1 kg/hr, which was achieved at a screw speed of 8 rpm for 80/20 PET/LCP1 blends under flood feeding conditions for the fixed gap thickness of 4 mm between the horns. The average ultrasonic power consumption was calculated after subtraction of zero power consumption of the top and bottom horns.

In addition to the conditions presented in Table 3.3, 80/20 PET/LCP1 blends were also processed in SONIC1 at a flow rate of 0.5 kg/hr to give a residence time of 14 s in the sonication zone at a screw speed of 7 rpm. 80/20 PET/LCP1 blends were also extruded in SONIC2 at the same temperatures as SONIC1 and at 1 kg/hr feed rate at a screw speed of 8 rpm.

The effect of ultrasound on PET, PEN, LCP1, and LCP2 homopolymers was studied. LCP1 was adopted as the minor component in the blends as the primary aim of this study was to improve the mechanical properties of thermoplastic resins by
incorporating LCP1 in blends. PET/LCP1 blends were studied in 90/10, 80/20, 70/30, and 60/40 weight ratios of PET to LCP1. PET/LCP1 blends were processed in both SONIC1 and SONIC2. The effect of TBOT and Sb$_2$O$_3$ catalyst addition was also studied in 80/20 PET/LCP1 blends. PEN/LCP1 blends were studied in 90/10 and 80/20 weight ratios of PEN to LCP1. PEN/LCP1 blends of higher concentrations of LCP1 were not processed since results on PET/LCP1 blend indicated compatibilization only in 90/10 and 80/20 compositions. This could be due to agglomeration of LCP1 domains at higher concentrations, and the consequently reduced available surface area for interfacial reactions [155]. PET and PEN were blended in a 50/50 weight ratio to demonstrate increased extent of transesterification by ultrasonic treatment. LCP1/LCP2 blends were prepared in 75/25, 50/50, 25/75 weight ratios in order to study reinforcement and effect of ultrasound in a blend of two LCPs.

The neat materials and blends which were ultrasonically extruded were subjected to further processing and consequent characterization, as explained in the following sections.

3.2.2. Reciprocating screw injection molding

The injection molding of LCP/thermoplastic blends provides both shear and elongational flow and results in skin-core morphology, with the generation of LCP fibrils in the skin and spherical or ellipsoidal LCP droplets in the core [63]. Effect of blend composition and ultrasonic intensity were determined by the testing and characterization of moldings made under the conditions described in this section.
Impact bars and dumbbell shaped mini tensile bars (63.50 x 9.53 x 1.52 mm$^3$, ASTM D 638-03) were injection molded simultaneously using a Van Dorn 55 HP-2.8F (Strongsville, OH) injection molding machine. Length of molded impact bars was double that in ASTM D 256-05 at 127 mm, while the width (12.70 mm) and thickness (3.18 mm) were in accordance with the said standard. The molded impact bars were cut into to equal pieces along the length and labeled as the gate and dead end, which were tested separately except for PET, LCP1 and their blends. The geometry of these samples with the location of notches is shown in Figure 3.12. It should be noted that notching was not performed in cases for which the recorded values were too low with notching.

![Figure 3.12. Preparation of DE and GE samples used for Izod impact testing.](image)

The injection molding conditions used for the pure materials and blends are shown in Table 3.4. Other molding parameters common to all materials were: rear zone temperature of 60°C (all other zones were kept at 285°C for all materials), a clamping force of 490 kN (55 tons U.S.), and a screw set speed of 120 rpm in the recovery stage. The injection molding process was injection speed controlled, which was maintained with less than the set maximum machine hydraulic pressure of 17.2 MPa. It should be noted that a mold temperature controller was not available during the molding of PET, LCP1,
and their blends and the mold remained at a temperature slightly above room temperature with continuous moldings. This is the reason why a mold temperature of 27°C was chosen in the later injection molding of the other materials, for which a mold temperature controller was present (M50-9-2-2, Stelco)

Table 3.4. Injection molding parameters for pure materials and blends, other parameters are described in the text.

<table>
<thead>
<tr>
<th>Materials</th>
<th>PET, LCP1, PET/LCP1</th>
<th>PEN, LCP2, PEN/PET, PEN/LCP1, LCP1/LCP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrel temperature</td>
<td>285</td>
<td>285</td>
</tr>
<tr>
<td>Mold temperature</td>
<td>Room temperature/ no control</td>
<td>27</td>
</tr>
<tr>
<td>Injection speed</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Holding pressure</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Holding time</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Cooling time</td>
<td>40</td>
<td>25</td>
</tr>
</tbody>
</table>

3.2.3. Piston driven injection molding

The use of a small sized injection molding machine was required under certain conditions. These included insufficient number of moldings for extra testing, or lack of large amount of material required for the use of the reciprocating screw injection molding process. The piston driven micro injection molding machine (Haake Minijet, Thermo Electron, Waltham, MA) was used to mold dumbbell shaped mini tensile bars (63.50 x 9.53 x 1.52 mm³) from dried pellets of virgin, untreated, and ultrasonically treated LCP1, and masterbatches of LCP1 and PEN compounded in the twin-screw extruder with TBOT. While all of these samples were used for DMA testing, moldings of LCP1/TBOT and PEN/TBOT masterbatches were used for both DMA and tensile testing.

The piston driven injection molding conditions were similar to those used for the reciprocating screw injection molding process. The barrel temperature was 290°C, and
mold temperature was 25°C. The mold was coated with a mold release agent (Frekote HMT2) before use. The barrel was filled with polymer pellets, leaving the top 2 cm empty, and the polymer was left to melt for 5 minutes. An injection pressure of 65 MPa was applied for 11 s. After waiting for 20 s, the mold was opened and the molding was removed. A second molding was made with the remaining material packed in the barrel immediately afterwards. The second molding of each batch was used for testing. Multiple batches of samples were molded with fresh material as required for testing.

3.2.4. Fiber Spinning

Fibers spun from LCPs and their blends possess extraordinary stiffness and strength due to high alignment of LCP fibrils in the machine direction under elongational flows [60, 67, 68, 76, 69].

Considering the possibility of disturbance of in-situ formed copolymer at the interface of immiscible polymers during shear intensive processing [5], a single stage spinning process was originally attempted. However, a continuous stream of high melt strength extrudate could not be obtained with ultrasonic treatment, which led to formation of voids and bubbles in the extrudate. The latter did not allow spinning at high draw down ratio. Hence, a two stage process was adopted for fiber spinning.

The pelletized and dried extrudate from the ultrasonic extruder was placed in a capillary rheometer (Rosand RH7, Malvern Instruments). Barrel temperature was set at 300°C for all materials for consistency and to obtain fibers with uniform thickness. Polymer pellets were manually packed into the barrel by slowly filling in 5 minutes. The top 7-8 cm portion of the barrel (total length 30 cm) was not filled in order to minimize
differences in time required to uniformly melt the polymer. Following the manual packing, the plunger was pushed down until a pressure of 0.5 MPa was developed just above the capillary. This was followed by 4 more minutes of melting and a second push of the plunger until the development of 0.5 MPa pressure. After 4 more minutes of waiting to facilitate equilibration of the melt temperature, the melt was extruded. The take up device (Model 12A5BEPM, B&B Motor&Control Corp, L.I.C., NY) consisting of 1:20 geared motor (130V DC, 186 W, 1.8 Amp) had electronically controlled variable speed (0-125 rpm), and produced 8.5 Nm torque. The distance from the exit of the capillary die to the motor shaft was 360 cm.

The diameter of barrel ($d_{\text{barrel}}$) was 15 mm, a capillary die having a length of 24 mm and a diameter ($d_{\text{die}}$) of 1.5 mm was used. Plunger speed ($v_{\text{plunger}}$) was constant at 10 mm/min. The diameter of take-up bobbin ($d_{\text{bobbin}}$) was 287 mm. The take up speed was controlled with the motor speed, which was set at 50, 85, and 125 rpm using a digital speed controller. Resulting draw down ratios (DDR) were 45, 76.5, and 112.5, respectively. The DDRs were calculated as follows:

$$DDR = \frac{v_{\text{take-up}}}{v_{\text{extrude}}} = \frac{\left[ d_{\text{bobbin}} \cdot \pi \cdot \text{rpm} \right]}{\left( \frac{d_{\text{barrel}}}{d_{\text{die}}} \right)^2 \cdot v_{\text{plunger}}} \quad (3.1)$$

The actual DDR obtained was confirmed by measurement of spun fiber diameter ($d_{\text{fiber}}$), which was consistent to within 10%, as calculated from the following equation:

$$DDR = \left( \frac{d_{\text{die}}}{d_{\text{fiber}}} \right)^2 \quad (3.2)$$
In addition, extruded fiber was collected without any motor take up at a distance of 5 cm from the die exit. The DDR of the as-extruded fibers was calculated from measure extrudate thickness and was close to 1 for high viscosity materials and ranged up to 6 for low viscosity materials. Details on specific conditions are presented in CHAPTER IX.

3.2.5. Compression molding

A compression molding press (Carver 4122, Wabash, IN) was used to prepare films for permeability and light transmission studies, and discs for rheological testing. For measurements of oxygen permeability, films of 220-250 µm thickness and 13 cm diameter were molded at 290°C for the pure materials and blends. Mirror finished aluminum plates of 3.18 mm thickness and aluminum sheets of 2.54 mm thickness were used together to achieve consistent moldings. Both the aluminum plates and sheets were coated uniformly with a high temperature mold release agent (Frekote HMT2, Henkel, Rocky Hill, CT) before use. A circular aluminum mold of a thickness of 2.54 mm was placed in between the aluminum sheets, which was then sandwiched between the aluminum plates. Polymer pellets weighing 3.0 grams were placed onto the cold mold in the middle of this sandwich structure. Following a heating time of 5 minutes with no load, force was gradually applied to give a total force of 5 tons for 5 minutes. The plates were then removed and cooled for 2 minutes by setting down over a steel surface and placing a steel weight over them. Using this procedure, smooth, transparent films having less than 7% variation in thickness were obtained for PET, PEN, and their blends.
For rheological testing, four discs of 2 mm thickness and 25 mm diameter were molded simultaneously at 280°C for each of PET, PET/LCP1 and PET/PEN blends, and at 300°C for PEN and LCP1. The mold and steel plates were sprayed with high temperature mold release agent (Frekote HMT2), and Kapton® polyimide film (Dupont) was placed between the preheated platens and the mold. Following preheating of pellets in the mold for 2 min, a force of 1 ton was applied for 50 s and released for 10 s for 3 consecutive times. After that, a force of 5 tons was applied for 2.5 min and released for 10 s, this time for two consecutive times. The hot metal plates and the mold were removed from the press and allowed to cool for 8 minutes. The discs were then removed from the mold.

3.3. Characterization of polymer blends

Mechanical, thermal, rheological, morphological, and spectroscopic methods were be used to characterize the effect of ultrasound and composition on the studied blends and their components.

3.3.1. Soxhlet extraction

For FT-IR and NMR spectra of blends, the polyester phase was extracted to obtain spectra of LCP1 and possible copolymer.

Good solvents for PET include phenols (m-cresol, o-chlorophenol), phenol/chlorinated hydrocarbon mixtures (phenol/tetrachloroethane), acetonylacetone, hot benzyl alcohol, and hot benzyl acetate among others [278, 279, 280]. Kyotani et al. used trifluoroacetic acid to remove PET component in PET/Vectra A950 blends and
study SEM and X-ray diffraction [281]. Song used boiling phenol to extract the PET phase in PET/LCP (Rodrun LC5000) blends and washed the remaining material with methanol [282]. Due to reduced health hazards associated with m-cresol as opposed to phenol, m-cresol (97%, Acros organics, Geel, Belgium) was used for extraction of the polyester phase in the blends with LCP1.

Cellulose thimbles of 43mm diameter and 123mm length (Catalogue no 2800432, Whatman, Piscataway, NJ) were used in the Soxhlet extraction setup. As cellulose absorbs moisture, thimbles were dried in a vacuum oven for 24 hours before use and for 48 hours after extraction, at a temperature of 110°C. After extraction for 48 hours in boiling m-cresol, the thimbles were washed with methanol (histological grade, Fisher Chemical, Fairlawn, NJ). The drying temperature was chosen to remove as much m-cresol (boiling point of 203°C) as possible during the drying, while avoiding decomposition of the cellulose thimble (decomposition temperature 120°C). Weight of dried thimble before extraction, and thimble+sample after extraction, were measured within 30 s of taking out from the vacuum oven, to limit moisture take up by the cellulose thimbles.

3.3.2. Rheological studies

Capillary and rotational rheometers were used for comparative rheological studies. The viscosity results on pure LCPs and polymer blends were not expected to correlate with steady state experiments. This is because of the presence of varying domains and complicated morphology in the blends and fibrillation of pure LCP. In the case of dynamic viscosity, this causes the inapplicability of Cox-Merz rule. In case of
capillary rheometry involving LCPs, correction for entrance and exit effects by the Bagley correction would require the use of a series of long capillaries, in which the flow in the capillary needs to be developed fully. The length of capillary required for fully developed flow is expected to be longer in LCPs due to shear and concentration dependant domain orientation in the nematic state. Rotational rheometry of PET/LCP1 blends was chosen in favor of steady-state measurements as PET degrades at the elevated temperatures of measurement (280°C) if tested for long times. In case of PEN/LCP1 blends, degradation can also be an issue for prolonged times, and testing in a capillary rheometer offers high level of reproducibility with less testing time. LCP2 was also susceptible to thermal and oxidative degradation and testing in a capillary rheometer was observed to improve reproducibility of results in comparison to rotational rheometry.

While dynamic rotational viscosity measurements were carried out for PET, PEN, LCP1, and PET/PEN, PET/LCP1 blends. The viscoelasticity of the LCP/polyester blends in the melt state will be measured using parallel plate rheometer in dynamic oscillatory shear mode. In order to increase the reproducibility of measurements, a stringent sample preparation and testing procedure is followed, aiming to accurately reproduce the thermo-mechanical history of samples. Since annealing of LCPs above their solid to anisotropic liquid transition temperature can lead to crystallization and affect rheological measurements, the duration of experiments needs to be short. Hence dynamic shear experiments were preferable to steady shear experiments, which take longer time to perform.

An Advanced Rheometric Expansion System (ARES, TA Instruments) was used in oscillatory shear mode with parallel plate geometry. Strain amplitude was fixed at 2%
and dynamic frequency sweep experiments with angular frequency, $\omega$, from 0.1 to 100 s$^{-1}$ was performed at 280°C for PET, PEN, PET/PEN, PET/LCP1 blends under nitrogen atmosphere. Pure LCP1 was tested in air as it did not degrade during testing. The complex viscosity, $|\eta^*|$, dynamic storage, $G'$, and loss, $G''$, moduli were obtained and used to determine structural changes that took place with ultrasonic treatment. Percentage error (standard deviation/average) in viscosity measurements was 5% for PET and blends, and 10% for LCP1.

A capillary rheometer (Rosand RH7, Malvern Instruments, Westborough, MA) was used to test the viscosity of PEN, and PEN/LCP1 and LCP1/LCP2 blends at a temperature of 300°C. A capillary die of $l/d=24$, and $d=1$ mm diameter was used. During the testing, pellets were packed slowly into the barrel in a total of 8 minutes, leaving the top 7-8 cm of the barrel empty. The uniform melting of material was facilitated by packing of melt at up to 0.5 MPa and waiting for 4 minutes, before repacking to 0.5 MPa and waiting a final 5 minutes, before finally starting testing from the low shear rate. Each test took a total time of around 40 minutes from the start of packing to the collection of data point at the highest shear rate. Shear rates were varied from 20 to 2900 s$^{-1}$ in 10 steps, which were equally spaced on a logarithmic scale. The apparent viscosity and apparent shear rates were obtained. Viscosity results had a percentage error of 10%.

To obtain flow curves, apparent shear rates were corrected using the Rabinowitsch correction [283]. Comparison of viscosity of blends of different compositions and treated at different amplitudes was made at the same apparent shear rate. The power law index, $n$, was calculated from the slope of a logarithmic plot of shear
stress, $\tau$, versus apparent shear rate, $\dot{\gamma}$, determined by quadratic least squares fitting.

Corrected shear rate, $\dot{\gamma}_c$, was calculated as:

$$\dot{\gamma}_c = \left( \frac{3n + 1}{4n} \right) \dot{\gamma}$$

(3.3)

3.3.3. Dynamic mechanical thermal analysis

In dynamic mechanical thermal analysis, viscoelastic properties of materials are measured as a function of time, temperature or frequency of oscillations at constant oscillatory strain. Modulus and damping data, which are sensitive to changes in molecular structure, were collected. Glass transition temperature is determined from peaks in loss factor tan $\delta$ ($E''/E'$), when it cannot be resolved through thermal studies [284]. It is noted that $T_g$ obtained from tan $\delta$ in DMTA measurements is generally higher than that obtained by a DSC [285].

A dynamic mechanical analyzer (Perkin Elmer Pyris Diamond DMA) was used to measure changes in the mechanical response ($E'$ and $E''$) of polymers PEN, LCP1, PEN/LCP1, and LCP1/LCP2 blends with temperature. Change in bulk miscibility of blends at different processing conditions was inferred by following shifts in tan $\delta$.

A 16 mm section was cut from both ends of the injection molded mini-dumbbell samples (63.50 x 9.53 x 1.52 mm$^3$). The grip ends were sanded before clamping onto the sample holder by screwing onto locking washers. The locking washers prevented slip of sanded samples from grips. DMA experiments were carried out in tension sinusoidal oscillation mode with an amplitude of 10 $\mu$m on samples having gauge length of 10 mm. The samples were heated from 20°C to 160°C at a rate of 2 °C/min with a data logging
rate of 1 point/second. Other DMA parameters were: a minimum force of 200 mN, a
tension gain of 15, a force amplitude of 4000 mN, an approved maximum deformation of
10000 µm (a machine safety parameter), and a position movement wait time of 8
seconds.

E’, E”, and tan δ were plotted against temperature to study the dynamic
mechanical properties of materials. Shifts in the modulus versus temperature behavior
were used to infer structural changes in the components and blends. The loss tangent (tan
δ) peak from DMA measurements were used to obtain the glass transition temperatures
(Tg) of materials. The accuracy of DMA temperature measurements was 1-2°C.

3.3.4. Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter (DSC, TA Instruments) was used to determine
the thermal behavior of materials at a heating rate of 10°C from room temperature to
300°C under N₂ atmosphere at a N₂ gas flow rate of 50 ml/min. Between 5-8 mg of
sample cramped in an aluminum hermetic pan was used in each case. Reference pans
were chosen to similar weight with no more than 0.2 mg difference between the empty
sample pans.

Two consecutive heating runs were performed. Between the heating runs, the
DSC cell was cooled at the same variable rate for all samples, by placing a reservoir
filled with 102 cm³ of water at a temperature of 11±1°C over it. This procedure provided
quenching at the beginning of the cooling cycle. The temperature versus time plot during
cooling of the DSC cell is shown in Figure 3.13.
Figure 3.13. Temperature vs. time curve for cooling the DSC cell.

The results of the second heating runs were reported to eliminate the processing thermal history. The crystallinity ($X_c$) was determined by subtracting the enthalpy of cold crystallization ($\Delta H_{cc}$) from the enthalpy of fusion ($\Delta H_f$), and dividing that by the enthalpy of fusion of the perfect crystals (140 J/g for PET [286], 103.4 J/g for PEN [287]). Glass transition ($T_g$), cold crystallization ($T_{cc}$) and melting ($T_m$) temperatures were recorded with an accuracy of ±1°C.

3.3.5. Scanning Electron Microscopy (SEM)

SEM is used for topographical, morphological, compositional and crystallographic studies [280, 288].

Morphology of injection moldings was studied with a Hitachi S-2150 SEM at a voltage of 20kV. Injection molded mini tensile bars of PET/LCP1 and PEN/LCP1 blends were cryogenically fractured in the center inside liquid nitrogen after waiting for 5 minutes for temperature equilibration. Micrographs were taken at both the core and skin regions of moldings. Brittle fracture could not be obtained in the center of the
LCP1/LCP2 mini tensile bars as LCP fiber pullout occurred during breaking, even after keeping for 30 minutes in liquid nitrogen. For study of LCP1/LCP2 morphology, a rectangular strip was cut from the gate section of injection molded mini tensile bars, and cryogenically fractured along the transverse direction, as shown in Figure 3.14. Fracture surface showed fibrils aligned parallel to the surface. Micrographs were taken at core region of fractured surface.

![Figure 3.14. Fracture of LCP1/LCP2 blends for SEM.](image)

Before imaging, all SEM sample were mounted onto aluminum sample holders with double sided conductive copper tape (3M, code 1182). Two thin strips of single-sided copper tape (3M, code 1181), were adhered to the sample at opposite edges, in order to increase conductivity along the sample and provide more secure mounting to the sample holder. The sample surfaces were coated with silver with thickness in the order of 10 nm using an Emitech K575X Peltier cooled Turbo Sputter Coater in one cycle. The sputter coating cycle parameters were: cleaning of oxidized target for 30 s at a current of 150 ma, Argon gas flash time of 25 s and bleed time of 20 s, no pump hold, and a sputter current of 55 milliamps for 60 s.

The morphology of fibers was studied with a field emission scanning electron microscope (JSM7401F, Jeol, Tokyo, Japan). Use of the field emission SEM allowed
obtaining high resolution micrographs at up to 50,000x magnification. Imaging was performed at a voltage of 10kV in SEI mode. For the preparation of samples, aluminum sample holders were first covered with double sided copper tape. Afterwards medium cure (15 minute grade) two part epoxy resin (Bob Smith Industries, Atascadero, CA) was mixed 1:1 and brushed on the sample holders with copper tape. After waiting for 10 minutes for partial hardening of epoxy resin, two undrawn fibers (DDR ≈ 1) and four fibers drawn at a DDR of 45 were embedded inside the epoxy and the sample holders were hung upside down with double sided adhesive tape (3M) for the epoxy to cure for 1 hour with the fibers sticking out. The samples were then sputter coated at the same conditions as the moldings. Skin-core morphology was not as distinct as in injection moldings, and micrographs from the core regions were reported.

3.3.6. Tensile Testing

Tensile testing is a means of assessing the modulus, strength and ductility of materials. The sample is uniaxially stretched and the length and load at given intervals are recorded [289].

An Instron 5567 tensile tester (Norwood, MA) was used to study the tensile properties of injection molded mini tensile bars following ASTM D 638-03. A 30 kN load cell was used for testing at a constant crosshead speed of 5 mm/min. Young’s modulus was obtained using an extensometer with 7.62 mm gauge length. For PET, and PET/LCP blends, tensile tests to obtain strength and elongation at break were carried out without an extensometer, which caused premature failure due to generation of stress concentration. A minimum of 6 samples were used for each test.
For testing of fibers, cardboard templates with a rectangular hole of 25 mm length in the center were used. Fibers were mounted tautly on the cardboard template parallel to the testing direction using extra thick cyanoacrylate glue (BSI, Atascadero, CA) and accelerator (Accelerator MH16, Mercury adhesives, Cumming, GA). After clamping the cardboard with the fiber glued to it using pneumatic grips, the sides of the cardboard parallel to the fiber mounted in the center were cut. As fibers were observed to break in away from the grips with no slip, interaction with the thick viscosity glue was ruled out and dependability of the fiber mounting method was demonstrated. A 100 N load cell was used for testing at a constant crosshead speed of 5 mm/min. In the testing of LCP1, single fibers were used. For the testing of PEN, PEN/LCP1 blend and LCP2, 4 fibers were mounted next to one another without any crossover and tested together. For testing of PET and PET/LCP1 blends, 10 fibers were mounted together. Multiple fiber testing was adopted in order to improve the accuracy of load reading by the load cell, and the number of fibers was set based on the load reading by the machine. A minimum of 5 samples were tested for each condition, and Young’s modulus, strength at yield, elongation at yield, elongation and break, and strength at break were determined when applicable to the materials.

3.3.7. Impact Testing

Injection molded impact bars, which were cut into two equal pieces labeled dead-end (DE) and gate-end (GE) to conform to the size specifications of ASTM D 256-05, were tested with an Izod impact tester (Testing Machines Inc., Ronkonkoma, NY). PET/LCP1 and PEN/LCP1 blends were too brittle with notching so they were tested
without notching, along with PEN and LCP1 for comparison. PET did not break without notching, and was tested with notching on the side away from the impact (reverse notching). PET/PEN blends and PEN were also tested with reverse notching. LCP2 and LCP1/LCP2 blends were tested with notching on side of the impact (forward notching).

In testing of DE specimens, the portion close to the mold end was held in the sample holder, while in the testing of GE sample, the portion close to the gate was clamped in the holder. The difference between the two sets of data was found to be statistically significant for LCP2 and LCP1/LCP2 blends, but was insignificant in case of PEN and PEN/LCP1 blends, for which results from the DE and GE samples were averaged.

Testing of PET/LCP1 and PEN/LCP1 blends were carried out with a 907 g load. Testing of unnotched PEN, LCP1, LCP2, LCP1/LCP2 blends, reverse notched PET, PEN, and 50/50 PET/PEN blends, and forward notched LCP2 and LCP1/LCP2 blends was carried out with a 4536 g load. Both unnotched and notched LCPs and their blends fractured by breakage of most LCP fibrils but either twisting out of the path of the hammer or flying out from the sample holder in most cases. Hence, the fracture was not as clean as in pure PET, PEN and their blends with LCP1.

3.3.8. Solid State NMR Spectroscopy

Solid state NMR spectroscopy was used to study presence of copolymer in 80/20 PET/LCP1 blends, without treatment and at an ultrasonic amplitude of 7.5 µm, from which the PET phase was extracted. The presence of alkyl groups of PET was compared.
$^{1}\text{H}$-$^{13}\text{C}$ cross-polarization (CP) magic-angle spinning (MAS) data were collected on a Varian Unity$^{\text{PLUS}}$ 200 (4.7 T) spectrometer (Palo Alto, CA) operating at 50.77 MHz for $^{13}\text{C}$ using a Doty Scientific VT CP-MAS wide bore probe. Samples were packed into 7 mm silicon nitride rotors using kel-F end caps and spun at a MAS rate of 5 kHz. The chemical shifts were referenced to hexamethylbenzene (HMB) (17.3 ppm; methyl). For each spectrum, 15680 transients were collected under continuous wave (CW) proton decoupling. Pulse widths of 5 $\mu$s were used for both nuclei with a recycle delay of 4 s and cross-polarization time of 2 ms.

3.3.9. $^{1}\text{H}$ solution NMR

NMR spectroscopy of 50/50 PET/PEN blends without and with ultrasonic treatment was performed to study extent of transesterification and average sequence length of PET and PEN blocks in their copolymer.

$^{1}\text{H}$ NMR spectroscopy of 50/50 PEN/PET blends was performed in a Varian VNMRS 500 MHz system (Palo Alto, CA). Parameters were: a pulse angle of 90°, a relaxation of 10 s, 32 scans, average time of 2.049 s, transform size of 32k, line broadening at 0.11 Hz, spectral width of 14 to -2, a temperature of 26°C, and spin of 20 Hz. Samples were dissolved in a 70/30 by weight mixture of deuterated chloroform and trifluoroacetic acid, and filtered through a 100 $\mu$m filter before transferring to NMR tubes (5 mm diameter and 203 mm (8") length).

In $^{1}\text{H}$ NMR of PET, PEN and their blends, the ethylenes from PEN are seen at 4.88 ppm, while those from PET occur at 4.78 ppm. The presence of copolymer is detected from the ethylenic protons in the PEN/PET copolymer located at 4.83 ppm. The
degree of randomness (DR), which is also defined as % transesterification, was calculated following Stewart et al. [111]. Repeats were run, and the standard deviation in percent transesterification was calculated as 0.2%.

3.3.10. Mass spectroscopy

Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectroscopy was performed in order to identify chemical changes occurring with ultrasonic treatment.

Mass spectroscopy identifies chemical structure by separating gas phase ions according to their mass to charge ratio (m/z) [290, 291]. The first step in this method is ionization of the sample to the gas phase. Ionization techniques are categorized into two, based on their effect on molecular structure. These are “hard” ionization, which generates fragment ions by breaking chemical links, and “soft” ionization, which ionizes molecules with minimal fragmentation [290,292]. Due to its applicability to high MW synthetic polymers and low degree of fragmentation [293], the soft ionization technique matrix assisted laser desorption ionization (MALDI) was adapted for this study.

MALDI mass spectroscopy employs a matrix, a small molecule containing chromophore for absorption of laser irradiation. The matrix also acts as a diluting and suspending medium for analyte molecules and limits interactions between them [293]. Matrix is mixed with the analyte molecules in solution and crystallized on the target probe by evaporation of the solvent. A high intensity short laser pulse initiates desorption and ionization of molecules of the matrix, which carry analyte molecules into the gas phase along with molecules of the matrix.
Ions produced by MALDI are commonly singly charged, and can be characterized by a time of flight (TOF) analyzer. The produced ions are transferred to the detector by a strong electric field. The different m/z species are separated as they take different times to travel to the detector [290]. A reflectron TOF analyzer can be employed to improve the separation of ions by increasing the path length travelled by ions through the introduction of an ion reflector [294]. TOF analyzer has theoretically unlimited mass detection capability and high ion transmission rate, rendering it ideal for studying synthetic polymers [294].

MALDI-TOF measurements were carried out on a Bruker Ultraflex III TOF/TOF (Bruker Daltonics, Inc., Billarica, MA), equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. All spectra were measured in the positive reflector mode. The instrument was calibrated prior to each measurement with an external standard PMMA.

For the preparation of samples of PET, PEN, and their blends, T-2-(3-(4-t-Butyl-phenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) matrix (20 mg/mL) in tetrahydrofuran (THF), and sodium-trifluoroacetic acid (NaTFA) cationizing agent (10 mg/mL) in THF were mixed in 1:1 ratio, and 0.5 µl of final mixture was deposited on microtiter plate wells (MTP 384-well ground steel plate). After the spots were dried, 0.5 µl of samples (10mg/ml) in 1,1,1,3,3,3,-hexa-fluoro-iso-propanol were printed on the top of the matrix and salt.

For preparation of samples of LCP1, PET/LCP1 and PEN/LCP1, the only suitable solvent was pentafluorophenol. Solution of 10mg/ml ratio was prepared. In order to dissolve the LCP1, the solutions were heated to 80°C and sonicated for 6 hours in an ultrasonic bath (Branson, Danbury, CT). DCTB matrix (20 mg/mL) in THF, and NaTFA
cationizing agent (10 mg/mL) in THF were mixed in 1:1 ratio, and 0.5 µl of the final mixture was deposited on microtiter plate wells. After the spots were dried, 0.5 µl of samples in pentafluorophenol were printed on the top of the matrix and salt. After drying, 0.5 µl of matrix/salt mixture was deposited on top of the samples, and let dry. The sample thus “sandwiched” between the layers of matrix improved ionization of samples and hence the resolution of MALDI-TOF spectra.

3.3.11. FT-IR Spectroscopy

FT-IR absorption spectra reveal the vibrational modes of bonds and are used to obtain information on the molecular structure of hydrocarbons. For polymers, transmission and attenuated total reflection (ATR) modes are commonly used [280]. Several researchers studied FT-IR spectra of systems involving Vectra A [228, 295, 296, 297, 298].

Rath et al. studied the changes in PEEK/LCP (Vectra A950) blends in the presence of polyphosphazene, which is miscible in both polymers. They identified shifts in the C=O stretching bands of both PEEK and the LCP, suggesting transesterification. The C=O stretching band of LCP was shifted from 1733 to 1722 cm\(^{-1}\). Other important absorption bands for Vectra A950 include the C-O-C symmetric stretching at 1149 cm\(^{-1}\), and the C-O-C asymmetric stretching at 1257 cm\(^{-1}\) [296]. The characteristic carbonyl absorption bands are at 1713 and 1728 cm\(^{-1}\) in PET and LCP, respectively. PET/HBA copolymers are expected to have carbonyl absorption peaks at 1713, 1728 and 1688 cm\(^{-1}\) [299].
The Nicolet 4700 FT-IR (Thermo Scientific, Waltham, MA) was used in attenuated total reflectance mode on films of blends prepared by compressing molding of extruded pellets. The single reflectance diamond crystal ATR module (DuraScope, SensIR Technologies, Danbury, CT) was capable of studying the 200-3000 cm\(^{-1}\) frequency range. 32 scans at a resolution of 2 cm\(^{-1}\) were averaged and the effect of ultrasonic treatment on LCP/polyester blends was analyzed.

3.3.12. Oxygen permeability

Oxygen permeability of PET, PEN and their blends were determined using compression molded films by means of an oxygen permeation analyzer (Model 8000, Illinois Instruments, Johnsburg, IL) in accordance with ASTM D 3985-95. Circular films having a diameter of 10 cm were cut from compression moldings having thickness in the range of 215-250 \(\mu\)m and clamped in the testing chamber following the application of silicon vacuum grease around film circumference for sealing. Oxygen and nitrogen gas pressures were both set at 0.345 MPa. Purge level was set at 1 units. Tests were run until equilibration of oxygen transmission rate (OTR), which took 20 hours for PET films, 40 hours for films of PET/PEN blends, and 60 hours for PEN films. OTR was measured in units of cm\(^3\)/m\(^2\)/day and converted into permeability coefficient (P) by multiplying with film thickness and dividing that by pressure of O\(_2\) gas. P was reported in units of cm\(^3\)*mm/m\(^2\)/day/0.1 MPa.
3.3.13. Optical transmission

The transmission of compression molded films of untreated and ultrasonically treated PET, PEN, and 50/50 PET/PEN was measured. Measurements were carried out in the wavelength range from 800 to 200 nm, which encompasses ultraviolet, visible, and near infrared range (UV-VIS-NIR). The readings were performed in a UV-3600 UV-VIS-NIR Spectrophotometer (Shimadzu, Columbia, MD). The wavelength range of measurements was from 800 to 200 nm.

The Beer-Lambert law was used to correct % transmittance for differences in sample thickness [300]. Absorbance (A) is related to % transmittance through:

\[ A = 2 - \log_{10} \%T \]  

(3.4)

where absorbance is given by the multiplication of \( \varepsilon \), molar absorbtivity, \( b \), sample thickness, and \( c \), molar concentration of chromophore, which can be expressed as:

\[ A = \varepsilon \cdot b \cdot c \]  

(3.5)

As absorbance is zero for a sample of zero length, sample thickness, \( b \), is directly proportional to absorbance. The Beer-Lambert law can be used to calculate the thickness dependence of absorbance for a sample of the same material, in which the absorptivity of chromophore and its concentration are the same. Using the measured thickness of moldings, dependence of % transmittance can be removed by correcting data for thickness of 230 \( \mu \text{m} \), which was the average thickness of compression molded films of PET, PEN and their 50/50 blend (section 6.10).

The average transmittance in the visible light range [300] was calculated by averaging transmittance in the range of 750-450 nm. The absorption cutoff wavelength for UV-light was also observed from the transmittance data. This wavelength for PEN
films is expected to be 380 nm, rendering this transparent polymer useful in UV barrier film applications [301]. Molar concentration of chromophore determines the required sample thickness for the absorption of the same fraction of light, according to Beer-Lambert law [300]. Therefore, blends of PEN with other polymers, such as PET, could be used to tailor UV blocking properties to a required thickness [302].
CHAPTER IV
PET/LCP1 BLENDS

The effects of composition, residence time, and ultrasonic extruder setup on the rheological, thermal, mechanical, and morphological properties of ultrasonically extruded PET/LCP1 blends are discussed in this chapter.

4.1. Introduction

PET is a widely studied commercial polyester with good mechanical properties. Blending PET with LCP produces in-situ reinforced composites with high stiffness and strength. These blends are commonly immiscible and therefore are generally brittle. It is possible to improve the mechanical properties of PET/LCP blends by compatibilization. A literature survey of PET/LCP blends was provided in section 2.6.1.

Ultrasonic treatment was studied as a novel alternative to conventional compatibilization methods of these blends. Results on PET/LCP1 blends are presented in this section.

4.2. Process characteristics

PET was blended with LCP1 (73/27 HBA/HNA copolymer) in two different ultrasonic extruders (described in section 3.2.1.1). SONIC 1 was used to extrude the neat materials, and 90/10, 80/20, 70/30, 60/40 PET/LCP1 blends. The screw with the melt star
mixing section (MSM) after ultrasonic treatment, shown in Figure 3.2 was used for extrusion of PET, LCP1 and their blends.

The effect of double residence time in the ultrasonic treatment zone (14 s vs. 7 s) was studied in 80/20 PET/LCP1 blends processed in SONIC1. An ultrasonic extruder with a shorter screw and different ultrasonic treatment zone geometry (SONIC2) was also used to study 80/20 PET/LCP1 blends at a residence time of 7 s in the ultrasonic treatment zone.

The barrel temperature in the ultrasonic treatment zone ($T_{ultra}$), the melt temperature at the connection of the original extruder barrel to the ultrasonic attachment ($T_{melt}$), and extruder torque were recorded. The results are listed in Table 4.1. The standard deviation of the recorded temperatures was 3$^\circ$C. The percent standard deviation (standard deviation/average), in torque readings was 10%.

As can be observed from Table 4.1, there was little variation in $T_{ultra}$ with ultrasonic amplitude and from sample to sample in SONIC1. In SONIC1, the melt temperature was higher than the set temperature in all cases except in the extrusion of 80/20 PET/LCP1 blends at a flow rate of 0.5 kg/hr. This indicated that there was more shear heating during extrusion at a flow rate of 1 kg/hr due to the higher rpm. While no increase in temperature was recorded with ultrasonic treatment of the blends, it should be noted that the melt temperature transducer was mounted before the treatment zone.

The barrel temperature in the ultrasonic treatment zone of SONIC2 was observed to be much lower than the set temperature of 285$^\circ$C without the application of ultrasonic energy, as shown in Table 4.1. As the set temperature could not be achieved, the resulting pressure and torque values were also very high. The high pressure lead to leakage of
polymer melt in the barrel to ultrasonic attachment connection and untreated sample could not be extruded, and hence was not studied.

Table 4.1. Temperature at ultrasonic treatment zone, melt temperature, and extruder torque measured during processing of PET/LCP1 blends.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Ultrasonic Amplitude (μm)</th>
<th>T_{ultra}(°C)</th>
<th>T_{melt}(°C)</th>
<th>Torque (Amp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET 1kg/hr in SONIC1</td>
<td>0</td>
<td>284</td>
<td>289</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>284</td>
<td>290</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>285</td>
<td>289</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>286</td>
<td>292</td>
<td>1.6</td>
</tr>
<tr>
<td>90/10 PET/LCP1 1kg/hr in SONIC1</td>
<td>0</td>
<td>285</td>
<td>292</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>285</td>
<td>292</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>285</td>
<td>293</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>287</td>
<td>292</td>
<td>1.6</td>
</tr>
<tr>
<td>80/20 PET/LCP1 1kg/hr in SONIC1</td>
<td>0</td>
<td>284</td>
<td>287</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>284</td>
<td>288</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>285</td>
<td>288</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>286</td>
<td>289</td>
<td>2.5</td>
</tr>
<tr>
<td>80/20 PET/LCP1 0.5 kg/hr in SONIC1</td>
<td>0</td>
<td>284</td>
<td>283</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>284</td>
<td>285</td>
<td>1.7</td>
</tr>
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<td>7.5</td>
<td>285</td>
<td>285</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>285</td>
<td>283</td>
<td>1.5</td>
</tr>
<tr>
<td>80/20 PET/LCP1 1kg/hr in SONIC2</td>
<td>0</td>
<td>272</td>
<td>276</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>279</td>
<td>276</td>
<td>8.1</td>
</tr>
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<td>7.5</td>
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<td>6.1</td>
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<td>276</td>
<td>8.8</td>
</tr>
<tr>
<td>70/30 PET/LCP1 1kg/hr in SONIC1</td>
<td>0</td>
<td>286</td>
<td>289</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>286</td>
<td>291</td>
<td>3.4</td>
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<td>286</td>
<td>291</td>
<td>3.2</td>
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<td></td>
<td>10</td>
<td>288</td>
<td>291</td>
<td>2.5</td>
</tr>
<tr>
<td>60/40 PET/LCP1 1kg/hr in SONIC1</td>
<td>0</td>
<td>286</td>
<td>288</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>286</td>
<td>293</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>287</td>
<td>293</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>288</td>
<td>292</td>
<td>2.2</td>
</tr>
<tr>
<td>LCP1 1kg/hr in SONIC1</td>
<td>0</td>
<td>284</td>
<td>284</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>284</td>
<td>288</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>285</td>
<td>288</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>285</td>
<td>287</td>
<td>3.8</td>
</tr>
</tbody>
</table>

As can be observed from Table 4.1, the inefficient heating in SONIC2 was the shortcoming of this extruder and is the reason why it was not used in further studies.
However, with ultrasonic treatment, the temperature in the treatment zone was closer to the set point, leading to stable extrudate under these conditions. The melt temperature, on the other hand, was substantially lower than in SONIC1, which would change the effect of ultrasound in this extruder due to the different viscosity of the melt during treatment.

The torque reading is correlated with the temperature of polymer melt, and was higher at lower melt temperatures, as can be observed from Table 4.1. Reduced torque recorded at ultrasonic amplitude of 10 µm for PET and 90/10, 70/30, and 60/40 PET/LCP1 blends is a result of thixotropic and permanent reductions in viscosity with treatment, as well as a possibly higher melt temperature after sonication. An increase in torque was recorded at an amplitude of 7.5 µm for PET, and is in agreement with the viscosity results that will be discussed in section 4.3. The torque for 80/20 PET/LCP1 blends was not observed to change with amplitude of treatment at a flow rate of 1 kg/hr. In SONIC1, the torque for 80/20 blend lied lower at a flow rate of 0.5 kg/hr and was observed to decrease at an amplitude of 10 µm, indicating possible degradation of polymer melt at this amplitude. The torque was highest during the extrusion of pure LCP1. The torque during processing of 60/40 and 70/30 PET/LCP1 blends was also observed to be higher than that of PET, and lower LCP1 concentration blends in SONIC1. This could be due to the close proximity of the solid to nematic transition temperature of LCP1 (280°C [271]) to the set processing temperature. As a result, the viscosity of LCP would be higher than that of PET in the initial sections of the extruder, and this could account for the greater torque in the presence of LCP1 during processing at the set temperature of 285°C.
Figure 4.1 shows the ultrasonic power consumption as a function of LCP1 concentration at different ultrasonic amplitudes for a flow rate of 1 kg/hr in SONIC1. This figure also shows variation of the ultrasonic power consumption with amplitude for 80/20 PET/LCP1 blend at a flow rate of 0.5 kg/hr. Ultrasonic power consumption increased with ultrasonic amplitude, due to increased strain amplitude imposed on the melt. It also increases with flow rate, due to increased pressure acting on the melt. With the addition of LCP1, it goes through a maximum at certain LCP1 concentration depending on ultrasonic amplitude. This maximum is most prominent for 80/20 and 70/30 PET/LCP1 blends, processed at a flow rate of 1 kg/hr and ultrasonic amplitudes of 7.5 μm and 10 μm signifying a greater effect of ultrasound under these conditions. The higher ultrasonic power consumption observed in some blends could be due to the increased number of defect sites available for acoustic cavitation at the interface of
immiscible polymers. The morphology of the blend and the nature of the pure components affect acoustic cavitation [263] and resulting power consumption.

Figure 4.2. Pressure before ultrasonic treatment zone at different ultrasonic amplitudes (µm) versus LCP1 concentration during extrusion at 285°C at a flow rate of 1 kg/hr (solid symbols) and for 80/20 PET/LCP1 blend at a flow rate of 0.5 kg/hr (open symbols). Values shifted along abscissa for clarity.

Figure 4.2 shows the pressure before the ultrasonic treatment zone of SONIC1 as a function of LCP1 concentration for different ultrasonic amplitudes at a flow rate of 1 kg/hr. This figure also shows the pressure values obtained for 80/20 PET/LCP1 blend at a flow rate of 0.5 kg/hr and different amplitudes. As expected, pressure is lower at the lower flow rate. For each blend composition, the pressure is found to decrease with increasing ultrasonic amplitude. Therefore, there is a possibility for increased output in extrusion with the application of ultrasonic energy at lower extruder power consumption. Acoustic cavitation in the melt results in both permanent and thixotropic changes, with thixotropic changes recovering after passing through the ultrasonic treatment zone. The
pressure reduction in ultrasonic extrusion could also be due to a possible slip of polymer melt along the surface of the horns [7]. In case of polymer degradation with ultrasonic treatment, thixotropic and permanent reductions in viscosity are complementary effects. On the other hand, when recombination of polymer chains and homopolymerization is promoted by ultrasonic treatment, permanent effect of sonication can result in increased viscosity. In this case, thixotropic and permanent effects of ultrasonication compete to determine the net change in pressure. Homopolymerization of PET occurs by polycondensation reactions, which give off water as the reaction proceeds. Water formed as a byproduct, which cannot be removed during ultrasonically-aided extrusion, is expected to act as defect sites that promote greater ultrasonic cavitation in the treatment zone and thereby amplify the effect of ultrasonic treatment.

Concerning the effect of LCP1 concentration on pressure, the presence of a maximum and a minimum pressure is noted depending on LCP1 concentration and ultrasonic amplitude. The high pressure recorded for pure LCP1 is due to its high viscosity, as shown in Figure 4.4a and b. At an amplitude of 10 µm, the pressure continuously increases with concentration. At other amplitudes there is a non-monotonous variation of the pressure with LCP1 concentration due to variation of the effect of ultrasound at different blend compositions. Such a variation of pressure can be attributed to the sensitivity of pressure to the melt temperature during extrusion. As previously stated, possible temperature variation in the melt under the ultrasonic horns could not be directly measured. Tap water at a constant flow rate of 1000 cm³/min was used to cool the horns, still the temperature of horns and subsequently of the melt could increase with increasing ultrasonic power consumption. Moreover, in order to avoid
excessive degradation of PET, the processing temperature (285°C) was chosen relatively close to the solid to nematic phase transition temperature of the LCP1 (280°C [271]). In this temperature region, the sensitivity of viscosity to temperature is most pronounced, and therefore the processing temperature may contribute to the complexity of the observed pressure variation.

Figure 4.3 shows the change in power consumption and pressure with amplitude of ultrasonic treatment for 80/20 PET/LCP1 blends in SONIC2. The ultrasonic power consumption in this extruder was observed to be higher than in SONIC1 for 80/20 PET/LCP1 blends. While the higher power consumption values in SONIC2 could indicate that the effect of ultrasound is more pronounced, the thixotropic vs. permanent changes cannot be gauged from pressure. Different power consumptions between the two extruders at the same residence time of melt could be due to different geometries of the treatment zone, and differences in the ultrasonic components.

![Figure 4.3. Change in ultrasonic power consumption and pressure before the ultrasonic treatment zone with amplitude of treatment for PET/LCP1 blends processed in SONIC2.](image)

As also indicated in Figure 4.3, the pressure in SONIC2 was lower than that in SONIC1. The first reason for the lower pressures in SONIC2 is that the pressure transducer was located closer to the die exit in SONIC2 as compared to that in SONIC1. The ultrasonic power consumptions were observed to be similar at amplitudes of 7.5 and 10 µm. Since the die immediately follows the sonication section in SONIC2, there was shorter time for recovery of acoustic effects before exiting the die, as compared to that in SONIC1, in which another mixing screw section follows the sonication zone. The sharper drop in pressure with ultrasonic amplitude observed in SONIC2 could be due to a more pronounced thixotropic effect by possible interaction of horns [5].

4.3. Rheology

Rheological measurements were performed under dynamic conditions, in contrast to steady-state conditions that require longer testing time. This was done in order to avoid PET degradation and to reduce changes in LCP texture during testing [17]. Figure 4.4a and Figure 4.4b show the complex viscosity of the blends without and with treatment at different ultrasonic amplitudes at a flow rate of 1 kg/hr varies with increasing LCP1 concentration at frequencies of 1 s\(^{-1}\) and 100 s\(^{-1}\), respectively. In this section, virgin refers to PET and LCP1 which were compression molded into discs and tested without any other processing for comparison of their rheological behavior with the extruded materials. In contrast to the maximum relative error of 5% in viscosity for samples of pure PET and the PET/LCP1 blends, an error of 10% was recorded for samples of pure LCP1. Similar variations in LCP1 viscosity measured by rotational rheometry have been documented by other researchers [17,42]. This was attributed to the proximity of the testing temperature
to the nematic transition temperature of LCP1 [42], differences in sample texture due to
the presence of oriented domains [17,42] and the inability to completely remove residual
normal stresses at the start of testing [34]. No noticeable changes in the viscosity of LCP1
with ultrasonic treatment were observed from the dynamic viscosity measurements in this
study.

Figure 4.4. Complex viscosity at different ultrasonic amplitudes versus LCP1
concentration at frequencies of (a) 1 s$^{-1}$, and (b) 100 s$^{-1}$, at a flow rate of 1 kg/hr (solid
symbols) and 0.5 kg/hr 80/20 PET/LCP1 blend at a flow rate of 0.5 kg/hr (open symbols).
While the pressure during extrusion was observed to decrease with ultrasonic amplitude, it can be seen from Figure 4.4b that the viscosity of pure PET as well as 90/10, 80/20 and 60/40 PET/LCP1 blends at a flow rate of 1 kg/hr was higher at a frequency of 100 s\(^{-1}\) after treatment at an amplitude of 7.5 µm. Similar observations can be made in Figure 4.4a for pure PET and 90/10 PET/LCP1 blend at a shear rate 1 s\(^{-1}\). The observed increase of viscosity of the PET and PET/LCP1 blends after their ultrasonic treatment is opposite to the pressure reduction with the increase of ultrasonic amplitude (Figure 4.2). The latter clearly indicates that thixotropic and slip phenomena are the dominating factors in pressure reduction with ultrasonic amplitude during extrusion. The pressure data of Figure 4.2 and the rheological data of Figure 4.4a and Figure 4.4b show that ultrasound has a complex effect on the pressure and viscosity changes in PET/LCP1 blends. The effect of ultrasound on polymer blends depends on the ultrasonic amplitude, nature of components, blend composition and extent of chemical changes [263].

It is known that high intensity ultrasound leads to chain scission in long chains polymers [250]. It is also documented that this can lead to the formation of lower molecular weight species, as well as high molecular weight fractions and copolymers through the generation of active sites by chain scission and subsequent recombination reactions [251, 4]. These effects of ultrasound were reviewed in greater detail in section 2.7.2. The above mentioned increase of viscosity of PET and PET/LCP1 blends at an ultrasonic amplitude of 7.5 µm points toward the recombination of chains, which leads to molecular weight buildup, probably through polycondensation reactions in PET and copolymerization at the interface of PET/LCP1 blends in the melt state. On the other hand, pure PET and all of the blends are found to exhibit the lowest viscosity following
ultrasonic treatment at an amplitude of 10 µm, indicating a reduction in molecular weight by permanent chain scission at this high amplitude. These findings suggest that ultrasonic amplitude and residence time control the competition between chain scission and molecular weight buildup in this system [251].

Comparing the viscosity of PET at frequencies of 1 s⁻¹ (Figure 4.4a) and 100 s⁻¹ (Figure 4.4b), it is seen that they are nearly the same since PET exhibits Newtonian behavior. On the other hand, the LCP1 phase exhibits strong shear thinning behavior [1, 41, 43]. This explains why the viscosity of the blends at ω = 100 s⁻¹ is lower at higher concentrations of LCP1 in the blends. It was also seen that the viscosity of the 90/10 and 80/20 PET/LCP1 blends is less than that of the pure components. This is due to the action of LCP1 as a flow modifier [1, 39, 43]. Evidently, orientation of the LCP1 phase in the flow direction reduces melt viscosity, as observed in both capillary and rotational rheometry experiments [43].

With reference to Figure 4.4b, it can be seen that the viscosity of untreated 80/20 PET/LCP1 blends is higher at the lower flow rate of 0.5 kg/hr. This indicates that the polymer degradation during extrusion is less at lower flow rate. This mechanically induced degradation could be due to the presence of shear intensive mixing sections on the screw. It was also seen that the viscosity of 80/20 PET/LCP1 blend processed at a flow rate of 0.5 kg/hr and treated at an ultrasonic amplitude of 10 µm is slightly higher than that of the same blend treated at 7.5 µm. This behavior in viscosity is different than that observed at a flow rate of 1 kg/hr. The observed increase in viscosity at a flow rate of 0.5 kg/hr and at an ultrasonic amplitude of 10 µm indicates formation of high molecular weight components through chemical reactions in the melt. Moreover, the difference in
viscosity with processing at different flow rates signifies that ultrasound of given amplitude affects the same material differently depending on the residence time in the ultrasonic zone [6]. Ultrasonic treatment results in degradation of polymer chains leading to generation of reactive species. In polyester blends, polycondensation reactions can lead to further polymerization. Additionally, recombination of hydroxyl and carboxyl terminal groups through interchange reactions can lead to formation of copolymers [101, 103]. As ultrasonic treatment promotes recombination reactions [251, 4], it could lead to polycondensation and transesterification reactions in PET, LCP1 and their blends. This is supported by the observed increases of viscosity of PET and PET/LCP1 blends after ultrasonic treatment at an amplitude of 7.5 µm. It should be noted that similar reactions were observed in PA6 and PA6/PP blends during their ultrasonic treatment, leading to an increase of mechanical properties and viscosity [263].

Figure 4.5. \( G' \) versus \( G'' \) for PET/LCP1 blends without (filled symbols) and with (open symbols) ultrasonic treatment at an amplitude of 7.5 µm at a flow rate of 1kg/hr.
Cole-Cole plots [303] provide important rheological information and can be used to determine structural changes in materials [304, 305, 306]. Figure 4.5 is a plot of $G'$ versus $G''$ for PET, LCP1 and their blends without ultrasonic treatment and with ultrasonic treatment at an amplitude of 7.5 µm. It is seen that the viscoelasticity of the blends increases with LCP1 concentration. Ultrasonic treatment of pure PET causes $G'$ to increase more than $G''$, such that $G'$ vs. $G''$ plot of the treated PET lies above that of the untreated, showing the increased elasticity of the treated PET. This correlates well with the observed increase in viscosity of PET after ultrasonic treatment, suggesting that ultrasonically induced homopolymerization reactions take place in the melt. In PET/LCP1 blends, both $G'$ and $G''$ at a fixed circular frequency were observed to increase with ultrasonic treatment indicating the occurrence of structural changes in blends. However, the increase in $G'$ was less than that in $G''$, such that the curves of $G'$ versus $G''$, as shown in Fig. 5, lie lower for ultrasonically treated blends indicating the decreased elasticity of treated blends. In contrast to observed changes in PET and PET/LCP1 blends, the ultrasonic treatment of pure LCP1 did not result in any noticeable changes to values of the storage and loss moduli. This indicates the rheological measurements employed are not sensitive enough to detect structural changes in LCP with ultrasonic treatment.

Figure 4.6 compares the viscosity behavior of 80/20 PET/LCP1 blends at a flow rate of 1 kg/hr in SONIC1 and SONIC2. The blends treated in SONIC2 exhibited slight shear thinning behavior with treatment at amplitudes of 5 and 7.5 µm, while the blends treated in SONIC1 show significant shear thinning behavior. The viscosity of these blends at the higher shear rates is higher after treatment in SONIC2, typically
experienced in the injection molding process for preparation of specimens for tensile testing. Greater viscosity ratio of matrix to the LCP facilitates greater deformation of the LCP phase and finer fibrillation [1, 30, 169, 188] as explained in section 2.4.3.1. Therefore, injection molding of 80/20 PET/LCP treated in SONIC2 would be expected to be stronger than those treated in SONIC1. Also, the viscosity of 80/20 PET/LCP in SONIC2 is greater with treatment at an amplitude of 7.5 µm than it is at an amplitude of 5 µm, indicating that PET homopolymerization also occurred in SONIC2 at an amplitude of 7.5 µm. Figure 4.6 also shows that 80/20 PET/LCP treated at an amplitude of 10 µm in SONIC2 is highly shear thinning and exhibits the lowest viscosity at high shear rates among samples treated in SONIC2. The differences in the shear thinning behavior of ultrasonically treated blends signify structural changes with sonication. Due to its lower viscosity at high shear rates (typically experienced in injection molding), viscosity ratio of matrix to LCP would be lower in 80/20 PET/LCP treated in SONIC2 at an amplitude of 10 µm. Based on role of viscosity ratio on LCP fibrillation [30, 169, 188], this blend would be expected to have larger sized LCP1 domains in injection moldings.

It can also be observed from Figure 4.6 that the 80/20 PET/LCP1 blend ultrasonically treated at an amplitude of 10 µm in SONIC2 has a higher viscosity than that in SONIC1. This indicates less degradation of PET phase in SONIC2 as compared to SONIC1. The 80/20 PET/LCP1 blend ultrasonically treated at an amplitude of 10 µm in SONIC1 exhibits a Newtonian plateau. This could be due to the low viscosity of PET with treatment at this amplitude in SONIC1 and less significant effect of LCP1 orientation due to the reduced viscosity ratio of matrix to LCP1, and consequently less pronounced shear thinning behavior.
Figure 4.6. Complex viscosity vs. frequency for 80/20 PET/LCP1 blends at 1kg/hr feed rate, in SONIC1 (filled symbols), and in SONIC2 (open symbols).

Figure 4.7a and b show the storage and loss moduli, respectively, of 80/20 PET/LCP1 blends at a flow rate of 1 kg/hr in SONIC1 and SONIC2. Figure 4.7a shows that the storage modulus of 80/20 PET/LCP1 blends without treatment and with treatment at ultrasonic amplitudes of 5 µm, and 7.5 µm in SONIC1, and at 10 µm in SONIC2, lie close to each other and exhibit a lower slope against shear rate than the other conditions. The said conditions with higher G’ values and lower slope are also those that exhibit greater shear thinning behavior. The storage modulus of PET/LCP1 treated at 10 µm in SONIC1 is the lowest, also indicating severe degradation of PET under this condition. As seen from Figure 4.7b, the loss modulus is highest for the 80/20 PET/LCP1 treated at an amplitude of 7.5 µm in both SONIC1 and SONIC2. The lowest loss modulus was observed for the blend treated at 10 µm in SONIC1.
Figure 4.7. Moduli versus frequency for 80/20 PET/LCP1 blends at 1kg/hr feed rate: (a) storage modulus, (b) loss modulus, in SONIC1 (filled symbols), and in SONIC2 (open symbols).

Figure 4.8 is a Cole-Cole plot comparing 80/20 PET/LCP1 blends treated in SONIC1 and SONIC2. The 80/20 PET/LCP1 blends without treatment and with treatment at ultrasonic amplitudes of 5 µm, and 7.5 µm in SONIC1, and at 10 µm in
SONIC2 have the greatest G’ and G” values, and lower slope than at the other conditions. These conditions are also those that exhibit highly shear thinning behavior, as seen from Figure 4.6. The blends treated at 10 µm in SONIC1, and at 5 and 7.5 µm in SONIC2 exhibit the lower elasticity, with the former being the lowest. Differences in the Cole-Cole plots of 80/20 PET/LCP1 blends indicate that significant structural changes took place with ultrasonic treatment and these changes were different with ultrasonic amplitudes in SONIC1 and SONIC2.

![Figure 4.8](image)

Figure 4.8. Storage modulus vs. loss modulus for 80/20 PET/LCP1 blends at 1kg/hr feed rate, in SONIC1 (filled symbols), and in SONIC2 (open symbols).

4.4. Extraction of PET phase

PET phase was extracted from 80/20 PET/LCP1 blends processed in SONIC1 at a flow rate of 1 kg/hr without treatment and with ultrasonic treatment at an amplitude of 7.5 µm for FT-IR and solid state NMR with the intent of studying the presence of their copolymer. The extraction results of the blends are shown in Table 4.2. The 80/20
PET/LCP1 blend treated at an amplitude of 7.5 µm at a flow rate of 1 kg/hr in SONIC1 was chosen since rheological characterization indicated the greatest viscosity increase with ultrasonic treatment at this condition.

Table 4.2. PET phase extraction results for 80/20 PET/LCP1 blends processed in SONIC1 at a flow rate of 1 kg/hr, without and with ultrasonic treatment at an amplitude of 7.5 µm.

<table>
<thead>
<tr>
<th>Amplitude (µm)</th>
<th>W_{bd} (g)</th>
<th>W_{ad} (g)</th>
<th>W_{be} (g)</th>
<th>W_{t} (g)</th>
<th>W_{ae} (g)</th>
<th>X(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm</td>
<td>6.348</td>
<td>6.104</td>
<td>10.000</td>
<td>8.362</td>
<td>2.259</td>
<td>22.6</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>5.946</td>
<td>5.702</td>
<td>10.005</td>
<td>7.825</td>
<td>2.122</td>
<td>21.2</td>
</tr>
</tbody>
</table>

In Table 4.2, \( W_{bd} \) is the weight of thimble before drying, \( W_{ad} \) is weight of thimble after drying, \( W_{be} \) is the weight of sample placed in the thimble, \( W_{t} \) is the weight of sample and thimble together after extraction and drying, \( W_{ae} \) is the weight of sample after extraction, obtained after subtraction of \( W_{ad} \) from \( W_{t} \). The amount of unextracted material remaining in the thimble (X) was expressed as a percentage after dividing weight of sample after extraction (\( W_{ae} \)) with the weight of sample before extraction (\( W_{be} \)).

The amount of material that could not be extracted appears to be more than 20% after extraction from 80/20 PET/LCP1 blends, both without and with ultrasonic treatment at an amplitude of 7.5 µm. As the blend contains 20% LCP1, an amount greater than this would indicate the presence of unextracted PET or not completely dried thimble. The discrepancy could be due to physically bound PET remaining inside thimble, presence of possible PET/LCP1 copolymer, or m-cresol that could not be removed completely by drying. The thimble still smelled of m-cresol after drying so it is likely that some m-
cresol that did not evaporate affected the results. The accuracy of these measurements was low and they did not provide conclusive results.

4.5. Fourier transform infrared (FT-IR) spectroscopy

An attempt was made to determine copolymer formation using the FT-IR studies by comparing FT-IR spectra of untreated and ultrasonically treated PET, LCP1, and blends, without and with extraction of PET phase.

Figure 4.9 shows the FT-IR spectra of PET (a), untreated 80/20 PET/LCP1 after extraction of PET phase (b), 80/20 PET/LCP1 ultrasonically treated at an amplitude of 7.5 µm after extraction of PET phase (c), and LCP1 without ultrasonic treatment. All of these materials were processed in SONIC1 at a flow rate of 1 kg/hr.

No differences in the FT-IR spectra PET and LCP1 were observed without and with ultrasonic treatment. The spectra of untreated PET and LCP1 were shown in Figure 4.9a and Figure 4.9d, respectively, are also representative of PET and LCP1 that were ultrasonically treated at different amplitudes. The FT-IR spectra of 80/20 PET/LCP1 blends from which the PET phase was extracted had the same spectra as LCP1, both without treatment (Figure 4.9b), and with ultrasonic treatment at an amplitude of 7.5 µm (Figure 4.9c). While this was in contrast to the seemingly incomplete extraction of PET phase shown in Table 4.2, it indicated that either the discrepancies in measured weights of extracted samples presented in section 4.4 were due to residual solvent after drying, or that ATR FT-IR was not sensitive enough to pick up small concentrations of PET in the extracted blend. This would also indicate that the formation of a small amount of PET/LCP1 copolymer may not be observable in ATR FT-IR of PET/LCP1 blends.
FT-IR spectroscopy of 90/10 PET/LCP1 blends from which the PET phase was not extracted were performed on both untreated and ultrasonically treated samples. These spectra are shown in Figure 4.10a-c. The spectra of 90/10 PET/LCP1 blends were a combination of PET and LCP1 spectra shown in Figure 4.9a and d, respectively. The spectra of 90/10 PET/LCP1 blends did not indicate the formation of new peaks or shift in existing peaks with ultrasonic treatment.
Figure 4.10. FT-IR spectra of 90/10 PET/LCP1 blends, (a) without treatment, with treatment at an amplitude of (b) 7.5 µm, and (c) 10 µm.

The FT-IR spectra of 80/20 PET/LCP1 blends without extraction of PET phase were shown in Figure 4.11, without treatment in SONIC1 at a flow rate of 1 kg/hr (a), with treatment at an amplitude of 7.5 µm in SONIC1 at a flow rate of 1 kg/hr (b), and 7.5 µm in SONIC1 at a flow rate of 0.5 kg/hr (c), 10 µm in SONIC1 at a flow rate of 1 kg/hr (d), 7.5 µm in SONIC2 at a flow rate of 1 kg/hr (e). The spectra of 80/20 PET/LCP1 was also a combination of PET and LCP1 spectra shown in Figure 4.9a and d, respectively. All spectra shown in Figure 4.11a-e were identical with respect to position of peaks, and
indicated no new peaks. The differences in structure of blends processed under different conditions could not be identified by FT-IR analysis.

![FT-IR spectra of 80/20 PET/LCP blends](image)

Figure 4.11. FT-IR spectra of 80/20 PET/LCP1 blends (a) without treatment in SONIC1 at a flow rate of 1 kg/hr, (b) with treatment at an amplitude of 7.5 µm in SONIC1 at a flow rate of 1 kg/hr, and (c) 7.5 µm in SONIC1 at a flow rate of 0.5 kg/hr, (d) 10 µm in SONIC1 at a flow rate of 1 kg/hr, (e) 7.5 µm in SONIC2 at a flow rate of 1 kg/hr.

FT-IR studies of PET/LCP1 blends indicated no noticeable changes in the absorption spectra of the blends after ultrasonic treatment. In particular, no shift of peaks and no new peaks were detected in the FT-IR spectra. It is probable that the ester groups of LCP1 and its copolymer with PET overlapped and/or the amount of the copolymer was too small to be detected by this method.
4.6. Solid State NMR Spectroscopy

Solid state NMR spectroscopy is a more sensitive method than FT-IR spectroscopy for structure identification and can provide a better fingerprint of structural groups present. In the copolymerization of PET and LCP1, the following transesterification product, identified as HBA/HNA-co-PET, was expected:

\[
\text{HBA/HNA} \quad \text{PET} \quad \rightarrow \quad \text{HBA/HNA-co-PET}
\]

Figure 4.12. Structure of PET/LCP1 copolymer expected to be formed by transesterification reaction of PET and LCP1.

Determination of chemical differences between the pure polymers and their copolymer can be very difficult even with solid state NMR when the reaction product closely resembles the pure components. This could also explain why FTIR spectra of unextracted PET/LCP1 blends discussed in section 4.5 did not show any differences.

If all physically bound PET phase was completely extracted from the PET/LCP1 blend, and if there were not copolymers present, solid state NMR spectra would only indicate the LCP1 phase, and would not show any alkyl groups, as they are not present in LCP1. However, presence of alkyl groups in extracted PET/LCP1 blends, from which the PET phase was extracted, suggested otherwise.
Figure 4.13 and Figure 4.14 show the solid state NMR spectra taken after extraction of PET phase from 80/20 PET/LCP1 blends processed in SONIC1 at a flow rate of 1 kg/hr, without ultrasonic treatment, and with ultrasonic treatment at an amplitude of 7.5 µm, respectively. In these spectra, peaks identified with “*” are spinning side bands which appear at a frequency of 5 kHz at either side of the strong peaks. The peak at 61.93, appearing in both without and with ultrasonic treatment at an amplitude of 7.5 µm, is due to alky groups. This suggests either presence of residual physically bound PET, or PET chemically attached to LCP1, both without and with treatment.

As \textsuperscript{1}H-\textsuperscript{13}C cross-polarization was used to intensify the signal of the observed alky groups, direct quantification of the amount of each chemical structure present cannot be made. However, both spectra were collected with equal parameters, and for the same number of scans from powder packed in the same way into the rotors. This suggests that comparing the relative intensities of the peaks based on their areas might provide some insight to the extent of transesterification taking place in these blends. When the area under the strong aromatic groups of LCP1 (130.78, 176.74 ppm) were normalized to 100, the area under the alkyl peak at 61.93 ppm was 2.38 without treatment, and 4.28 with treatment at an amplitude of 7.5 µm. While some of the alkyl groups present could be due to remaining physically bound PET, the higher area under the alkyl peak for ultrasonically treated blend suggested the presence of greater physically or chemically bound PET due to ultrasonic treatment.
Figure 4.13. Solid state NMR spectrum after extraction of PET phase in untreated 80/20 PET/LCP1 blends processed in SONIC1 at a flow rate of 1 kg/hr.
Figure 4.14. Solid state NMR spectrum after extraction of PET phase in 80/20 PET/LCP1 blend ultrasonically treated at an amplitude of 7.5 µm in SONIC1 at a flow rate of 1 kg/hr.
While the presence of more than 20% residue after extraction suggested that some level of PET may have been left physically bound to LCP1, the greater amount of weight recorded could also be due to presence of unevaporated solvent. The fact that the recorded weights of unextracted portion of the blends were less in the case of ultrasonically treated 80/20 PET/LCP1 suggested that a lower amount of PET would be registered in its NMR spectra. On the contrary, the relative area of peak from PET alkyls was more in the ultrasonically treated blend. This suggests that the differences in measured weights after extraction were probably due to presence of m-cresol, which could not be completely removed from the extraction thimbles. FT-IR spectra also did not indicate presence of PET at any of its characteristic wavenumbers after extraction from blends. It appeared highly probable that most, if not all of the PET alkyls observed in solid state NMR spectra of 80/20 PET/LCP1 blends were due to PET chemically bound to LCP1. Results indicated presence of copolymer and/or physically embedded PET increased with ultrasonic treatment at an amplitude of 7.5 µm.

4.7. Mass spectroscopy

Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectroscopy of PET, LCP1, and their 80/20 blend was performed in order to investigate structural changes and the presence of copolymer with ultrasonic treatment.

Structural changes in PET with ultrasonic treatment at amplitudes of 7.5 and 10 µm were identified in section 6.6. The formation of new end groups and changes in the relative intensities of peaks from different species were identified in that section. In this section, MALDI-TOF spectra of LCP1 without and with treatment at amplitudes of 7.5
and 10 µm in SONIC1 at a flow rate of 1 kg/hr is shown. In addition, spectra of 80/20 PET/LCP1 blend in SONIC1 without treatment and with treatment at an amplitude of 7.5 µm at a flow rate of 1 kg/hr, and at an amplitude of 10 µm at a flow rate of 0.5 kg/hr are shown.

The MALDI-TOF mass spectra of LCP1 were complicated as it is a 73/27 block copolymer of hydroxybenzoic acid (HBA) and hydroxy naphthoic acid (HNA). MALDI-TOF mass spectra of LCP1 were studied in literature [307, 308]. According to Somogyi et al., the dominant series in LCP1 mass spectra is multiple oxybenzoyl (B) and oxynaphthoyl (N) units terminated on one end by an acetyl group and on the other by a Na+ complexed aromatic carboxylic acid group, as shown below [307]:

\[
\text{H}_2\text{C} - \left[ \text{O} \right]_b - \left[ \text{O} \right]_n - \text{Na}^+ \]

The molecular weights of LCP1 species were calculated as \((120.02*b + 170.04*n + 83.01)\), where \(b\) and \(n\) define the number of HBA and HNA units present in the copolymer, respectively.

Mass spectra of LCP1 in the m/z range of 980-2100 for LCP1 without and with ultrasonic treatment at amplitude of 7.5 and 10 µm are shown in Figure 4.15. The change in the relative intensity of mass spectra peaks and formation of some new peaks indicated that molecular rearrangements occur with ultrasonic treatment in the melt state. In depth analysis of end groups was complicated due to the copolymer structure of LCP1. The structural changes indicated by mass spectra occurred in-situ, due to high power ultrasonic treatment of the melt for an average residence time of 7 s. Ultrasonic treatment
could have led to generation of active sites through chain scission, and their recombination [6]. It should be noted that these changes could also be accompanied by formation of new end groups by polymer degradation. Randomization of HBA/HNA copolymers is expected to occur through interchange reactions including transesterification [145, 146].

Figure 4.15. Mass spectra of LCP1 in the m/z range of 980-2100 without and with ultrasonic treatment at amplitude of 7.5 and 10 µm. Increases and decreases in relative intensity of peaks are shown as (+) and (-), respectively. The presences of peaks not observed at other conditions are shown by (*).
Figure 4.16. Mass spectra of untreated and ultrasonically treated LCP1 in the m/z range of 1400 to 1750. Increased relative intensity of peaks (+), and the presence of peaks not observed at other conditions (*) are shown.

Mass spectra of LCP1 in the m/z range of 1400-1700 for LCP1 without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm are shown in Figure 4.16. The peaks labeled were not part of the A series (multiple oxybenzoyl (B) and oxynaphthoyl (N) units terminated on one end by an acetyl group and on the other by a Na+ complexed aromatic carboxylic acid group). These peaks indicated the formation of nontrivial structures, which are difficult to identify due to the complexity of the copolymer blend.
Figure 4.17. MALDI-TOF mass spectra of 80/20 PET/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm at a flow rate of 1 kg/hr, and at 10 µm at a flow rate of 0.5 kg/hr.

MALDI-TOF mass spectra of 80/20 PET/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm at a flow rate of 1 kg/hr, and at 10 µm at a flow rate of 0.5 kg/hr are shown in Figure 4.17. The mass spectra of 80/20 PET/LCP1 treated at an ultrasonic amplitude of 10 µm at a flow rate of 0.5 kg/hr exhibited greater intensity and new peaks, indicating greater PET degradation and copolymerization. PET/LCP1 copolymerization was shown more clearly in Figure 4.18.
Figure 4.18. MALDI-TOF mass spectra of (a) LCP1 0 µm at 1 kg/hr, (b) 80/20 PET/LCP1 blends without treatment, and (c) with ultrasonic treatment at 10 µm at a flow rate of 0.5 kg/hr, (d) PET 0 µm at 1 kg/hr, (e) PET 10 µm at 1 kg/hr.

Figure 4.18a-e shows the mass spectra of LCP1 0 µm at 1 kg/hr (a), 80/20 PET/LCP1 blends without (b), and with ultrasonic treatment at 10 µm at a flow rate of 0.5 kg/hr (c), PET 0 µm at 1 kg/hr (d), PET 10 µm at 1 kg/hr (e), all of which were processed in SONIC1. These peaks labeled in the 80/20 PET/LCP1 blends (b) and (c) indicate the presence of copolymers of PET and LCP1. These peaks were not present in untreated or ultrasonically treated pure PET and LCP1. Therefore, these new peaks observed in blends indicated formation of new species due to chemical reactions between
PET and LCP1. It should be noted that the number and intensity of new peaks was higher in the 80/20 PET/LCP1 blend treated at an amplitude of 10 µm at 0.5 kg/hr. The latter indicated enhanced copolymerization reactions at the greater residence time of 14 s in the ultrasonic treatment zone. In polyester blend, these interchange reactions are expected to take place by transesterification [101]. Mass spectroscopy is more sensitive to chemical changes than ATR FT-IR, which could not detect copolymer formation not only in the PET/LCP1 blend (section 4.5), but also in the PET/PEN blend (section 6.4), for which transesterification was clearly shown by $^1$H NMR (section 6.5).

4.8. Thermal analysis

Differential scanning calorimetry (DSC) studies of PET, and PET/LCP1 blends were performed to observe thermal changes in components and their blends following ultrasonic treatment. The melting endotherm for LCP1 appeared around 280°C, but its glass transition temperature ($T_g$) could not be determined using DSC. The second heating curve, run after cooling at the same rate to remove time-temperature history, was taken as basis for all measurements. For PET, $T_g$, the melting temperature peak ($T_m$), and percent crystallinity ($X_c$) are shown in Table 4.3. $X_c$ was determined after subtraction of PET cold crystallization enthalpy from the melting enthalpy and normalized with respect to PET content in the blends.

As seen from Table 4.3, no significant change in the melting point of PET occurred with blending or with ultrasonic treatment. There was also no significant change in the $T_g$ of PET phase upon blending with LCP1, and also with ultrasonic treatment. The $T_g$ of LCP1 phase (107°C as determined from the loss tangent peak in DMA, shown in
Figure 7.7) could not be observed in the DSC. The lack of change in $T_g$ of PET phase would point toward the immiscibility of PET/LCP1 blends without and with ultrasonic treatment. However, the $T_g$ of LCP1 could not be detected by DSC. Therefore, conclusions concerning miscibility of this system cannot be drawn based on DSC.

Table 4.3. Glass transition temperatures, crystallinity, and melting temperature of PET in DSC second heating runs for PET/LCP1 blends. All results are in SONIC1 at a flow rate of 1 kg/hr, except 80/20 PET/LCP1 in SONIC2 at a flow rate of 1 kg/hr, and 80/20 in SONIC1 at a flow rate of 0.5 kg/hr, as indicated.

<table>
<thead>
<tr>
<th>PET 2nd heating runs</th>
<th>$T_g$ (°C)</th>
<th>$X_c$ (%)</th>
<th>$T_m$ (°C)</th>
</tr>
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<tr>
<td>Virgin</td>
<td>77.3</td>
<td>0.4</td>
<td>249.7</td>
</tr>
<tr>
<td>0 µm</td>
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<td>76.4</td>
<td>22.3</td>
<td>251.4</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>77.0</td>
<td>21.6</td>
<td>252.2</td>
</tr>
<tr>
<td>10 µm</td>
<td>75.4</td>
<td>26.4</td>
<td>252.7</td>
</tr>
<tr>
<td>90/10 PET/LCP1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 µm</td>
<td>77.1</td>
<td>21.4</td>
<td>250.8</td>
</tr>
<tr>
<td>5 µm</td>
<td>77.1</td>
<td>23.0</td>
<td>250.7</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>77.2</td>
<td>25.2</td>
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<td>10 µm</td>
<td>77.0</td>
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<td>28.9</td>
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<td>32.2</td>
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</tr>
<tr>
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<td>31.0</td>
<td>252.2</td>
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<tr>
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<tr>
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</tr>
<tr>
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<td>78.5</td>
<td>23.5</td>
<td>251.3</td>
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<tr>
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<td>80/20 PET/LCP1 0.5 kg/hr R.T.</td>
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<td>78.3</td>
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<td>10 µm</td>
<td>78.9</td>
<td>33.9</td>
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<tr>
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</tr>
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<td>78.3</td>
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</tr>
<tr>
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<td>38.3</td>
<td>251.5</td>
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Figure 4.19 shows the heat flow as a function of temperature during second heating in DSC for PET without and with ultrasonic treatment.

![Heat Flow vs. Temperature Curves](image)

As seen from Table 4.3 and Figure 4.19, the crystallinity of virgin PET was much lower than the PET that passed through the extruder. Shorter polymer chains crystallize faster as there is more chain mobility at lower molecular weights [318]. The increase in crystallinity of PET with processing was a result of molecular weight reduction of PET during processing as indicated by viscosity measurements. With ultrasonic treatment at an amplitude of 7.5 μm, the cold crystallinity peak of PET shifted to higher temperature and increased in intensity as compared to that of untreated PET. This signified that crystallization of PET treated at 7.5 μm took place slower, and could infer a lower degree of crystallization during its cooling prior to this second DSC scan. This is due to creation...
of longer PET chains that crystallize slower after ultrasonic treatment at an amplitude of 7.5 μm. Creation of higher molecular weight species was also indicated by the higher viscosity of 80/20 PET/LCP1 blends treated at an amplitude of 7.5 μm in SONIC1, as discussed in section 4.3. With treatment at an amplitude of 10 μm, the PET cold crystallization peak shifted to lower temperature, indicating its faster crystallization. The latter is a result of reduced molecular weight of PET due to ultrasonic treatment with treatment at 10 μm.

![Figure 4.20](image.png)

Figure 4.20. Heat flow vs. temperature curves during second heating in DSC for 90/10 PET/LCP1 in SONIC1 without and with ultrasonic treatment.

Figure 4.20 the heat flow as a function of temperature during second heating in DSC for 90/10 PET/LCP1 blend without and with ultrasonic treatment. The glass transition of 90/10 PEN/LCP1 treated at an amplitude of 10 μm broadened as compared

186
to the blend without treatment and with treatment at amplitudes of 5 and 7.5 µm. This could indicate a partial miscibility of 90/10 PEN/LCP1 blends with treatment at 10 µm.

Figure 4.21 shows the heat flow as a function of temperature during second heating in DSC for 80/20 PET/LCP1 blends processed in SONIC1 at flow rates of 1 kg/hr and 0.5 kg/hr without and with ultrasonic treatment.

Figure 4.21 shows the heat flow as a function of temperature during second heating in DSC for 80/20 PET/LCP1 blends processed in SONIC1 at flow rates of 1 kg/hr and 0.5 kg/hr without and with ultrasonic treatment. As can be observed from Table 4.3, the crystallinities of 80/20 PET/LCP1 blends processed at 1 kg/hr were around 30%. Cold crystallization peaks for these blends were absent. This showed that crystallization of 80/20 PET/LCP1 blends processed at 1 kg/hr took place during cooling alone. On the other hand, cold crystallization peaks were observed for 80/20 PET/LCP1 blends processed at 0.5 kg/hr. It should be noted that the screw speed for this condition was 7
rpm (a flow rate of 0.5 kg/hr) as compared to 13 rpm (a flow rate of 1 kg/hr). This indicated that mixing could be poorer with processing at 0.5 kg/hr, leading to reduced dispersion of LCP1 domains in the PET matrix. Therefore, instead of LCP1 acting as nucleation sites for crystallization of PET like in the case of better dispersed LCP1 domains, undeformed larger LCP1 domains would hinder crystallization of the blend. This accounts for the lower crystallinity of PET/LCP1 processed at a flow rate of 0.5 kg/hr.

In 80/20 PET/LCP1 blends processed at a flow rate of 0.5 kg/hr, the duration of ultrasonic treatment is longer, and ultrasonically induced degradation and copolymerization reactions are expected to be more significant [6]. Therefore, the change in viscosity ratio of LCP1 to the matrix, which affects the dispersion of LCP1 domains, is also greater at a flow rate of 0.5 kg/hr (shown in section 4.3). PET crystallinity in blends increases when it undergoes degradation with ultrasonic treatment. On the other hand, crystallinity is reduced as degradation of PET with treatment hinders LCP1 deformation and limits nucleating agent capacity of LCP1. The crystallinity of these blends is determined by these competing effects.

Figure 4.22 shows the heat flow as a function of temperature during second heating in DSC for 80/20 PET/LCP1 blends processed in SONIC2. The cold crystallization peak of blend treated at an amplitude of 7.5 µm was broader and longer, indicating its reduced crystallinity during cooling as compared to the blend treated at an amplitude of 5 µm. This could be due to creation of higher molecular weight PET species with treatment at an amplitude of 7.5 µm in SONIC2. 80/20 PET/LCP1 treated at an amplitude of 10 µm had no cold crystallization peak, indicating its greater crystallization
during cooling. This could be due to degradation of PET at this condition. The small endotherm centered around 100°C in the heat flow vs. temperature curve could be due to residual water that could not be completely removed by drying. The T_g of blend treated at 10 µm was more diffuse.

![Graph showing heat flow vs. temperature curves during second heating in DSC for 80/20 PET/LCP1 in SONIC2 with ultrasonic treatment.](image)

Figure 4.22. Heat flow vs. temperature curves during second heating in DSC for 80/20 PET/LCP1 in SONIC2 with ultrasonic treatment.

The heat flow as a function of temperature during second heating in DSC for 70/30 PET/LCP1 blends is shown in Figure 4.23. The cold crystallization exotherms of 70/30 PET/LCP1 blends was small or could not be observed, depending on ultrasonic amplitude. The increased crystallinity at 30% LCP1 composition indicated that LCP1 acted as a nucleating agent for PET at high concentration. This could be due to the frozen in fibrous microdomains of LCP1 present in the extrudate that act as nucleation sites for PET [1, 61, 93, 166, 215, 216].
Figure 4.23. Heat flow vs. temperature curves during second heating in DSC for 70/30 PET/LCP1 in SONIC1 without and with ultrasonic treatment.

Figure 4.24. Heat flow vs. temperature curves during second heating in DSC for 60/40 PET/LCP1 in SONIC1 without and with ultrasonic treatment.
The DSC second heating heat flow as a function of temperature for 60/40 PET/LCP1 blends is shown in Figure 4.24. The cold crystallization exotherms of 60/40 PET/LCP1 blends was small, and disappeared with treatment at an amplitude of 10 µm. However, blends exhibited high crystallinity, as can be observed from Table 4.3, due to nucleating agent effect of LCP1. The highest crystallinity of blend treated at 10 µm, also shown in Table 4.3, indicated degradation of PET phase in the blend at this amplitude.

Figure 4.25 compares the heat flow versus temperature curves during DSC second heating for PET and its blends with LCP1 without and with ultrasonic treatment at an amplitude of 10 µm.
increased upon ultrasonic treatment at an amplitude of 10 µm, due to degradation of PET. The onset of the melting endotherm of PET was slightly shifted to lower temperatures with increasing LCP1 concentration in the blends, signifying the nucleating agent effect of LCP1 in the blends.

4.9. Mechanical properties

Figure 4.26a and Figure 4.26b, respectively, show the tensile strength and Young’s modulus as functions of LCP1 concentration in PET/LCP1 blends processed in SONIC1, without and with treatment at different ultrasonic amplitudes, and at flow rates of 1 kg/hr and 0.5 kg/hr for 80/20 PET/LCP1 blend. In this section, virgin refers to PET and LCP1 which were injection molded into specimens for testing without any other processing for comparison of mechanical properties with materials that were extruded before injection molding. In general, the blends become stronger and stiffer with the addition of LCP1. Slight improvements in the tensile strength of 80/20 PET/LCP1 blends and Young’s modulus of both 80/20 and 70/30 PET/LCP1 blends were recorded at an amplitude of 7.5 µm and a flow rate of 1 kg/hr. However, ultrasonic treatment at an amplitude of 10 µm leads to a significant decrease in the tensile strength and Young’s modulus at all concentrations of PET/LCP1 blends. This indicates that ultrasonic degradation of polymer melt prevails at high ultrasonic intensity. Ultrasonic treatment at an amplitude of 5 µm was not found have significant effect on the mechanical properties of the blends. It follows that there is a critical ultrasonic amplitude below which changes in molecular structure are not substantial as to have a prominent effect on mechanical properties.
Figure 4.26. Mechanical properties of PET/LCP1 blends treated at different ultrasonic amplitudes versus LCP1 concentration: (a) tensile strength, (b) Young’s modulus, at a flow rate of 1 kg/hr (solid symbols) and 0.5 kg/hr 80/20 PET/LCP1 blend at a flow rate of 0.5 kg/hr (open symbols). Values shifted along abscissa for clarity.

Tensile strength and Young’s modulus of 80/20 PET/LCP1 processed at a flow rate of 0.5 kg/hr in SONIC1 were lower than those processed at a flow rate of 1 kg/hr, as seen from Figure 4.26a and b, respectively. This could be due to poor dispersion of LCP1 domains in the blends at a flow rate of 0.5 kg/hr, which would result from lower shear
rates experienced at the lower screw speed of 7 rpm as opposed to that of 13 rpm at a flow rate of 1 kg/hr.

Figure 4.27a and Figure 4.27b show the toughness and unnotched impact strength, respectively, as functions of LCP1 concentration in PET/LCP1 blends without and with treatment at different ultrasonic amplitudes and at flow rates of 1 kg/hr and 0.5 kg/hr for 80/20 PET/LCP1 blend at a flow rate of 0.5 kg/hr (open symbols). Values shifted along abscissa for clarity.

Figure 4.27. Mechanical properties of PET/LCP1 blends treated at different ultrasonic amplitudes versus LCP1 concentration: (a) toughness, (b) unnotched Izod impact strength, at a flow rate of 1 kg/hr (solid symbols) and 0.5 kg/hr 80/20 PET/LCP1 blend at a flow rate of 0.5 kg/hr (open symbols). Values shifted along abscissa for clarity.
80/20 PET/LCP1 blend. It should be noted that the toughness values reported were determined without an extensometer, as it created a defect at the location it was clamped onto the tensile specimen following necking in PET. As PET did not break without notching, impact data is not available for comparison with the blends. The blends generally become more brittle with the addition of LCP1, owing to weak interfacial adhesion between PET and LCP1. However, improvements in the toughness of 90/10 PET/LCP1 blend with ultrasonic treatment at an amplitude of 10 µm, and in the impact strength of 80/20 PET/LCP1 blend at an amplitude of 7.5 µm show that ultrasonic treatment can reduce brittleness of these immiscible blends, suggesting that the effect of copolymerization in the melt is greater than the degradation of PET under these conditions. On the other hand, ultrasonic treatment at an amplitude of 10 µm led to significant reductions in the toughness of blends containing above 20 wt% LCP1, and in the impact strength of all blends. The latter was due to degradation of the PET matrix as indicated by the previously discussed decrease in viscosity with treatment at this amplitude. Apparently, chain scission is the prevailing effect during ultrasonic treatment of these blends at this high amplitude. The lack of improvement in PET/LCP1 blends containing high concentrations of LCP1 with ultrasonic compatibilization could be due to the higher mechanical properties of these blends, which leaves less room for incremental improvement with compatibilization [113]. However, the recorded improvements in some mechanical properties of blends with ultrasonic treatment at certain amplitudes indicate that there is a competition between chain scission and recombination.

Toughness and unnotched impact strength of 80/20 PET/LCP1 processed at a flow rate of 0.5 kg/hr in SONIC1 were lower than those processed at a flow rate of 1
kg/hr, as seen from Figure 4.27a and b, respectively. This could be due to poor dispersion of LCP1 domains in this condition as a result of lower screw speed.

The observed improvements in the tensile properties of the ultrasonically treated blends are partially due to homopolymerization of the pure PET, as indicated by an increase of its viscosity after ultrasonic treatment at an amplitude of 7.5 µm, shown in Figure 4.4. Improvements in mechanical properties with ultrasonic treatment at certain amplitudes could also possibly be related to transesterification reactions, leading to improved adhesion between PET and LCP1 as seen from the SEM micrographs presented in section 4.10.

Figure 4.27a and b also demonstrate that 80/20 PET/LCP1 processed at a feed rate of 0.5 kg/hr have greater toughness and impact strength following ultrasonic treatment at an amplitude of 10 µm, as opposed to 7.5 µm. This result is consistent with the increased viscosity recorded for this blend treated at an ultrasonic amplitude of 10 µm in contrast to 7.5 µm (Figure 4.4), indicating that high molecular weight species are evidently formed and compatibilization of the blend is achieved through possible esterification/transesterification reactions in the melt due to sonication.

The mechanical properties of 80/20 PET/LCP1 blends at a flow rate of 1 kg/hr in SONIC1 and SONIC2 are summarized in Table 4.4. Comparing the tabulated results, it is seen that the impact strength, strength, Young’s modulus, toughness, and elongation at break are higher for both untreated and ultrasonically treated samples in SONIC2 than in SONIC1. This could be due to the shorter screw and less degradation of PET phase in SONIC2. It can also be seen from Table 4.4 that all measured mechanical properties for 80/20 PET/LCP1 blends ultrasonically treated at an amplitude of 10 µm are significantly
higher for SONIC2, and do not show a drastic reduction over the untreated blend as observed in SONIC1. However, the increase in impact strength, strength, and toughness observed for 80/20 PET/LCP1 blends treated at an amplitude of 7.5 µm in SONIC1, which were discussed previously, are not seen with treatment in SONIC2. Apparently, the effects of the two ultrasonic extruders are different. This could be due to differences in ultrasonic horn setup and extruder geometry, and in actual melt temperatures, as discussed in section 4.2 on process characteristics.

Table 4.4. Impact strength, ultimate strength, Young’s modulus, toughness, and elongation at break of 80/20 PET/LCP1 blends in SONIC1 and SONIC2 at a flow rate of 1 kg/hr, without, and with ultrasonic treatment at different amplitudes.

<table>
<thead>
<tr>
<th>Amplitude</th>
<th>0µm</th>
<th>5µm</th>
<th>7.5µm</th>
<th>10µm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Impact strength (J/m)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SONIC1</td>
<td>364 ± 30</td>
<td>353 ± 24</td>
<td>480 ± 15</td>
<td>143 ± 14</td>
</tr>
<tr>
<td>SONIC2</td>
<td>-</td>
<td>678 ± 72</td>
<td>710 ± 44</td>
<td>673 ± 43</td>
</tr>
<tr>
<td><strong>Strength (MPa)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SONIC1</td>
<td>79.7 ± 1.8</td>
<td>82.8 ± 2.4</td>
<td>91.4 ± 6.5</td>
<td>48.5 ± 2.6</td>
</tr>
<tr>
<td>SONIC2</td>
<td>-</td>
<td>105.6 ± 1.0</td>
<td>107.4 ± 2.0</td>
<td>97.6 ± 2.5</td>
</tr>
<tr>
<td><strong>Young’s modulus (GPa)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SONIC1</td>
<td>3.7 ± 0.2</td>
<td>3.6 ± 0.1</td>
<td>3.8 ± 0.2</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>SONIC2</td>
<td>-</td>
<td>4.6 ± 0.1</td>
<td>4.6 ± 0.1</td>
<td>4.1 ± 0.1</td>
</tr>
<tr>
<td><strong>Toughness (MPa)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SONIC1</td>
<td>5.6 ± 0.5</td>
<td>5.9 ± 0.4</td>
<td>6.7 ± 0.2</td>
<td>2.6 ± 0.8</td>
</tr>
<tr>
<td>SONIC2</td>
<td>-</td>
<td>11.0 ± 1.0</td>
<td>10.8 ± 0.7</td>
<td>9.5 ± 1.1</td>
</tr>
<tr>
<td><strong>Elongation at break (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SONIC1</td>
<td>15.1 ± 1.6</td>
<td>14.3 ± 0.4</td>
<td>14.8 ± 0.8</td>
<td>11.5 ± 1.9</td>
</tr>
<tr>
<td>SONIC2</td>
<td>-</td>
<td>16.8 ± 0.7</td>
<td>16.7 ± 0.5</td>
<td>15.9 ± 0.8</td>
</tr>
</tbody>
</table>

While processing of 80/20 PET/LCP1 blends in SONIC2 resulted in less degradation, no beneficial effect of sonication was observed in SONIC2. As both good and bad effects of ultrasonic treatment were observed with processing in the newly designed SONIC1, it appeared to be a better choice than processing in SONIC2 for studying the effects of ultrasound on blends. The increased degradation in SONIC1 could
be overcome by redesigning the screw for the SONIC1. The final mixing screw element in SONIC1 was replaced with screw flights for studies of other blends, and pure components other than PET and LCP1, as described in section 3.2.1.1.

To identify the changes occurring in the structure of ultrasonically treated blends, it is also important to analyze the morphological changes taking place with sonication of the blends. It is seen that ultrasonic treatment leads to a higher viscosity matrix (PET). This should enhance the fibrillation of the LCP1 and improve mechanical properties through the generation of stronger in-situ-reinforced composites. In fact, it is known that matrix polymer having high viscosity typically enhances LCP1 fibrillation in blends [1, 159, 162, 181]. The effect of ultrasonic treatment on morphology of PET/LCP1 blends will be discussed in section 4.10.

Table 4.5. Mechanical properties of untreated and ultrasonically treated LCP1 with the error indicating 95% confidence intervals.

<table>
<thead>
<tr>
<th>LCP1</th>
<th>Virgin</th>
<th>0 µm</th>
<th>5 µm</th>
<th>7.5 µm</th>
<th>10 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate strength (MPa)</td>
<td>243±7</td>
<td>262±7</td>
<td>251±8</td>
<td>273±16</td>
<td>262±6</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>8.9±0.3</td>
<td>9.4±1.1</td>
<td>9.1±0.4</td>
<td>10.0±0.5</td>
<td>10.8±0.8</td>
</tr>
<tr>
<td>Toughness (MPa)</td>
<td>8.6±0.3</td>
<td>7.9±0.9</td>
<td>8.8±1.1</td>
<td>9.0±1.6</td>
<td>8.8±1.3</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>6.0±0.2</td>
<td>5.1±0.5</td>
<td>5.4±0.5</td>
<td>5.4±0.7</td>
<td>5.5±0.7</td>
</tr>
<tr>
<td>Impact strength (J/m)</td>
<td>3100±430</td>
<td>3310±600</td>
<td>3600±1040</td>
<td>4390±1090</td>
<td>3710±750</td>
</tr>
</tbody>
</table>

Table 4.5 shows the effect of ultrasonic treatment on the average values of the toughness, impact strength, ultimate strength, Young’s modulus and elongation at break of LCP1, with the strain determined using an extensometer for all measurements, along with error at 95% confidence intervals. Improvements in mechanical properties were recorded particularly after ultrasonic treatment at an amplitude of 7.5 µm. An average tensile strength of 273 MPa was achieved for LCP1 treated at an amplitude of 7.5 µm.
signifying an improvement over the tensile strength of 244 MPa for as-received sample, and 262 MPa for sample extruded without ultrasonic treatment. The higher tensile strength reported above for as-received sample in comparison with the value provided by manufacturer [271] is due to the increased relative thickness of the highly oriented skin region in injection molded mini tensile bars of the present study in comparison with the standard tensile bars of LCP1 of previous studies [64, 65]. Average recorded impact strength of pure LCP1 was 3710 J/m after ultrasonic treatment at an amplitude of 7.5 µm in contrast to the impact strengths of 3301 J/m and 3600 J/m for the as-received and untreated samples, respectively. Although experimental error should not be disregarded, improvements in the tensile and impact properties of LCP1 were recorded especially with ultrasonic treatment at an amplitude of 7.5 µm. It should be noted that in studies related to prolonged annealing on LCP, other researchers identified solid state polymerization and removal of critical flaws in crystal structure as the causes of increased tenacity of LCP fibers [1,51,52,53,54,55]. As opposed to heat treatment, the improvements observed in the present study could possibly be due to ultrasonically induced homopolymerization reactions in LCP1. It occurs in the melt state at very short residence times, as was observed in the ultrasonic treatment of other polymers [4, 5]. Although dynamic rheological studies did not indicate changes in the viscosity and dynamic properties of LCP (Figure 4.4, Figure 4.5), this does not preclude that ultrasonic treatment does not cause rearrangements in molecular structure of LCP1 through chain scission and recombination reactions. In fact, MALDI-TOF mass spectroscopy (section 4.7) showed structural changes in LCP1 with ultrasonic treatment at amplitudes of 7.5 and 10 µm.
4.10. Morphology

Injection moldings of LCPs are strongly anisotropic and exhibit skin-core morphology [60]. In general, the skin thickness covers a substantial fraction of the injection molded mini tensile bars [64]. Similar to LCP, SEM micrographs of PET/LCP1 moldings also revealed skin-core morphology. In these moldings, the core region contained spherical LCP1 droplets and the skin region of substantial thickness shows highly elongated LCP1 fibrils of various diameters.

The main factors affecting blend morphology are composition, viscosities of the blend components and the interfacial adhesion between them. It is governed by Taylor’s droplet deformation criterion [94], which was presented in section 2.4.3.1. Although this criterion was derived for small deformation of Newtonian fluids containing low concentration of droplets, it can be used to estimate the onset of deformation of LCP droplets into fibrils [198].

Accordingly, Eq. 2.13 can be used to calculate droplet deformation in cases of low shear stress occurring in the region close to the centerline in injection molding. In this region, the core morphology is determined by capillary number which is related to interfacial tension between the LCP1 and PET phases. Therefore, it is expected that in compatibilized blends a greater deformation of the dispersed phase would occur. On the other hand, when interfacial and viscous forces are equally important (Ca=1) and the viscosity ratio K is very large, Eq. 2.14 applies.

While the final fibril diameter cannot be predicted because of the constraint of small deformations for which the criteria was derived, it is clear that the droplet deformation is enhanced when the size of droplets is large and the viscosity ratio of the
dispersed LCP1 phase to the PET matrix is small. It should be noted that the viscosity ratio in the fibrillation criteria presented above is based on steady state viscosities of dispersed and matrix phases. Also, Cox-Merz rule is not applicable to LCP and PET/LCP1 blends, but it is applicable for PET phase. The complex viscosity of LCP is typically higher than its steady state viscosity \[43\]. Therefore, the value of viscosity ratio \(K\) is expected to be lower, thus creating more favorable conditions for LCP fibrillation in blends. In addition, since viscosity of PET is shown to increase with ultrasonic treatment at an amplitude of \(7.5 \, \mu m\), the value of \(K\) would further decrease, leading to enhancement of LCP fibrillation. Although, strictly speaking, one cannot make quantitative calculations of the aspect ratio of fibrils using the complex viscosity data, qualitative discussions based on Taylor’s criterion are still valid and support the morphological observations.

In addition to Taylor’s deformation criterion, the energy-based LCP fibrillation criterion developed by Joshi et al. \[188\] can be used to understand deformation of LCP component in the blends. This criterion was presented in Eq. 2.10. It indicates that fibrillation occurs when the energy utilization per unit volume of the thermoplastic component is less than that of the LCP component in the blend. Accordingly deformation is favored when the fraction of LCP1 is high and LCP1 to PET viscosity ratio \((K)\) is lower.

Summarizing the above discussion of LCP fibrillation criteria, it is expected that greater deformation of LCP1 droplets should occur in blends having a) high LCP1 content, b) low viscosity ratio of LCP1 to the matrix, c) high interfacial adhesion between the matrix and LCP1. Therefore, in LCP1/thermoplastic blends, fine fibrillar morphology
may be obtained when the viscosity of the thermoplastic matrix is higher than that of the LCP1. For PET/LCP1 blends, the viscosity of PET is lower than that of the LCP1 for the range of $\omega = 1$-100 s$^{-1}$ (Figure 4.4). Since LCP1 is highly shear thinning and PET exhibits Newtonian behavior, it is expected that at high shear rates encountered during injection molding the viscosities of the two components could be closer with LCP1 viscosity still being higher than that of PET. The viscosity of PET was shown to increase with ultrasonic treatment at an amplitude of 7.5 $\mu$m. Therefore, the deformation of LCP1 phase by PET is expected to be greater in blends ultrasonically treated at an amplitude of 7.5 $\mu$m. Moreover, due to compatibilization effect by possible copolymer formation during ultrasonic treatment, deformation of the LCP1 phase in ultrasonically treated blends is expected to be greater.

Figure 4.28. SEM micrographs of 90/10 PET/LCP1 blends obtained in SONIC1 at a flow rate of 1 kg/hr, (a) untreated core region, (b) core region treated at an ultrasonic amplitude of 7.5 $\mu$m, (c) untreated skin region, (d) skin region treated at an amplitude of 7.5 $\mu$m (d).
The following observations of blend morphology provide some experimental evidence of the occurrence of the above discussed effects. In particular, Figure 4.28 shows the SEM micrographs of the skin and core regions of 90/10 PET/LCP1 blends without (a, c) and with (b, d) ultrasonic treatment at an amplitude of 7.5 µm. In core and skin regions, LCP1 droplets and fibrils were observed, respectively. In the absence of ultrasonic treatment, the surface of LCP1 droplets in the core region is smooth, indicating little interaction with PET. On the other hand, the blend treated at an amplitude of 7.5 µm showed hairy structures on the surface of LCP1 droplets in the core region, indicating improved adhesion between the PET and LCP1 phases.

The surface of LCP domains in the core region of injection molded 90/10 PET/LCP1 blends can be observed in greater detail by comparing Figure 4.29a, without treatment, and Figure 4.29b, with ultrasonic treatment at an amplitude of 7.5 µm. While LCP domains were “bald” without treatment, they appeared “hairy” with ultrasonic treatment, indicating improved interfacial adhesion.

![SEM micrographs of 90/10 PET/LCP1 blends obtained in SONIC1 at a flow rate of 1 kg/hr. (a) untreated core region, (b) core region treated at an ultrasonic amplitude of 7.5 µm, indicating “bald” and “hairy” LCP domains without and with ultrasonic treatment, respectively, at 10,000x magnification.](image)

Figure 4.29. SEM micrographs of 90/10 PET/LCP1 blends obtained in SONIC1 at a flow rate of 1 kg/hr, (a) untreated core region, (b) core region treated at an ultrasonic amplitude of 7.5 µm, indicating “bald” and “hairy” LCP domains without and with ultrasonic treatment, respectively, at 10,000x magnification.
Figure 4.30. SEM micrographs of core regions of PET/LCP1 blends obtained in SONIC1 at a flow rate of 1 kg/hr, (a) 80/20 untreated, (b) 80/20 treated at an ultrasonic amplitude of 7.5 µm, (c) 70/30 untreated, (d) 70/30 treated at an ultrasonic amplitude of 7.5 µm.

Figure 4.30 shows SEM micrographs of the core regions of 80/20 and 70/30 PET/LCP1 blends without (a, c) and with (b, d) ultrasonic treatment at an amplitude of 7.5 µm. The average droplet size of LCP1 in the core of injection moldings is seen to decrease with increasing LCP1 concentration in the blends. This is consistent with the droplet deformation criterion of Eq. 4. Moreover, the surface of LCP1 droplets in the core of blends containing 20 and 30% LCP1 exhibits hairy structures without and with ultrasonic treatment. However, the size of LCP1 droplets in the core was lower in blends ultrasonically treated at an amplitude of 7.5 µm, in contrast to those without treatment. Smaller LCP1 droplets in the core of ultrasonically treated blends (Figure 4.30b and d), and the presence of hairy structures in ultrasonically treated blend containing 10% LCP1
(Figure 4.28a) affirm that deformation of the LCP1 phase and its compatibility with PET matrix are improved with ultrasonic treatment.

![Figure 4.31](image)

Figure 4.31. SEM micrographs of PET/LCP1 obtained in SONIC1 at a flow rate of 1 kg/hr and treated at an ultrasonic amplitude of 10 µm, (a) core region of 90/10, (b) core region of 80/20, (c) skin region of 90/10, (d) skin region of 80/20.

Figure 4.31 shows SEM micrographs of core and skin regions of 90/10 (a, c) and 80/20 PET/LCP1 (b, d) blends processed at a flow rate of 1 kg/hr and treated at an ultrasonic amplitude of 10 µm. Hairy structures on the surface of LCP1 droplets were observed in the core (Figure 4.31a and b). The latter indicated improved interfacial adhesion between PET and LCP1. Also, almost no fibrils were seen in the skin region of both blends (Figure 4.31c and d). Instead small LCP1 droplets were observed in both skin and core regions. In 90/10 PET/LCP1 blend, LCP1 droplets in skin and core regions were smaller than those in 80/20 blend. Evidently, these small LCP1 droplets in the skin were
created by break up of LCP1 fibrils. However, the stresses generated by ultrasonically treated PET matrix of reduced viscosity at an amplitude of 10 µm were unable to effectively deform these large LCP1 droplets into fibrils.

![SEM micrographs of 80/20 PET/LCP1 blends in SONIC1 ultrasonically treated at an amplitude of 7.5 µm at different residence times under ultrasonic horns. (a) 7 s (1 kg/hr flow rate), core region. (b) 14 s (0.5 kg/hr flow rate), core region. (c) 7 s (1 kg/hr flow rate), skin region. (d) 14 s (0.5 kg/hr flow rate), skin region.](image)

Figure 4.32. SEM micrographs of 80/20 PET/LCP1 blends in SONIC1 ultrasonically treated at an amplitude of 7.5 µm at different residence times under ultrasonic horns. (a) 7 s (1 kg/hr flow rate), core region. (b) 14 s (0.5 kg/hr flow rate), core region. (c) 7 s (1 kg/hr flow rate), skin region. (d) 14 s (0.5 kg/hr flow rate), skin region.

SEM micrographs of Figure 4.32 provide a comparison of the morphology of 80/20 PET/LCP1 blends ultrasonically treated at an amplitude of 7.5 µm and flow rates of 1 kg/hr (a, c) and 0.5 kg/hr (b, d). It should be noted that the injection molding conditions dictating final blend morphology were the same in both cases. At a flow rate of 0.5 kg/hr, dispersion in the blend is expected to be poorer than that at a flow rate of 1 kg/hr. Furthermore, the extent of homopolymerization and copolymerization reactions...
induced by ultrasound is greater at the longer mean residence time of 14 s at a flow rate of 0.5 kg/hr in contrast to 7 s at a flow rate of 1 kg/hr, as shown by MALDI-TOF in section 4.7. Comparing Figure 4.32a and b, it is seen that LCP1 droplet sizes in the core are larger indicating poor LCP1 droplet deformation at a flow rate of 0.5 kg/hr corresponding to a mean residence time of 14 s. This is due to the fact that the viscosity of PET at high amplitude and long residence time is significantly reduced due to PET degradation. At the same time, copolymerization may take place at this processing condition leading to improved interfacial adhesion causing hairy structures on LCP1 droplet surfaces, as indicated in Figure 4.32b. Micrographs of the skin regions reveal that the numerous LCP1 fibrils seen at a mean residence time of 7 s (Figure 4.32c) are replaced by fewer fibrils and large undeformed LCP1 droplets at a residence time of 14 s (Figure 4.32d). Clearly, the extent of deformation and number of LCP1 fibrils in the skin region of moldings are lower for the blend obtained at the longer residence time in ultrasonic treatment zone. These results indicate that while ultrasonic treatment improves the interfacial adhesion of PET/LCP1 blends through in-situ compatibilization, its effect on the viscosity of the matrix determines the extent of LCP1 phase deformation.

Figure 4.33 shows the morphology of 80/20 PET/LCP1 obtained at a flow rate of 1 kg/hr in SONIC2. The LCP1 droplets in the core and fibers in the skin observed at amplitude of 7.5 µm, Figure 4.33a and Figure 4.33b, respectively, are smaller in size than the LCP1 droplets and fibers observed at an amplitude of 10 µm, Figure 4.33b and Figure 4.33d, respectively. As the viscosity of 80/20 PET/LCP1 blends was also observed to decrease at an amplitude of 10 µm, increase in LCP1 domain size was expected due to decrease in viscosity ratio of the matrix to the LCP1, and consequently poor LCP1
domain deformation. Moreover, LCP1 droplets with treatment at ultrasonic amplitudes of both 7.5 µm (Figure 4.33a), and 10 µm (Figure 4.33b), were not observed to be hairy. In contrast, LCP1 droplets at 10 µm showed poor interfacial adhesion to the PET matrix, as evident from the voids around the LCP1 droplets, apparent as dark circles seen in Figure 4.33b.

Figure 4.33. SEM micrographs of 80/20 PET/LCP1 obtained at a flow rate of 1 kg/hr in SONIC2, (a) core region treated at an amplitude of 7.5 µm, (b) core region at an amplitude of 10 µm, (c) skin region at an amplitude of 7.5 µm, (d) skin region at an amplitude of 10 µm.

In summary based on morphology of 80/20 PET/LCP1 blends treated in SONIC2, ultrasonication in this extruder did not lead to visible improvements in interfacial
attachment between PET and LCP1, and also resulted in degradation of PET matrix at an amplitude of 10 µm. It has also been suggested in literature that high extent of compatibilization can inhibit LCP fibrillation and lead to bad mechanical properties [132, 134].

4.11. Conclusions

PET/LCP1 blends become stronger, stiffer and more brittle with the addition of LCP1. The blends exhibited greater shear thinning behavior with increased LCP1 content. The viscosity of 90/10 PET/LCP1 blends was below those of its components indicating that LCP1 acted as a processing aid. After ultrasonic treatment at an amplitude of 7.5 µm, PET and PET/LCP1 blends showed an increased viscosity and changes in storage vs. loss modulus behavior. This increased viscosity is an indication of the occurrence of homopolymerization of PET and copolymerization of blends at a short residence times of ultrasonic treatment.

LCP1 acted as a nucleating agent in 70/30 and 60/40 PET/LCP1 blends. Crystallinity of PET and blends increased with ultrasonic treatment at an amplitude of 10 µm, indicating PET degradation at this amplitude. No change in T\textsubscript{g} of PET or blends was observed with ultrasonic treatment. A decrease in crystallinity of 80/20 PET/LCP1 blends was recorded with treatment at an ultrasonic amplitude of 7.5 µm in SONIC1, indicating its higher MW than that of the untreated blend.

Solid state NMR results indicated greater binding of PET to LCP1 in 80/20 PET/LCP1 blends treated at an amplitude of 7.5 µm in SONIC1. MALDI-TOF mass spectroscopy studies showed the creation of new structural groups of PET and LCP1 by
their ultrasonic treatment. Mass spectra of 80/20 PET/LCP1 blends confirmed the presence of in-situ formed copolymer. The extent of copolymerization was observed to increase with duration of ultrasonic treatment.

Mechanical properties of LCP1 increased with ultrasonic treatment at an amplitude of 7.5 μm. Chemical changes in LCP1 with ultrasonic treatment were shown by MALDI-TOF. The ultimate strength, Young’s modulus, toughness and impact strength of 80/20 PET/LCP1 blend treated at an amplitude of 7.5 μm in SONIC1 and the toughness of 90/10 PET/LCP1 blend treated at an amplitude of 10 μm were improved due to improved LCP1 fibrillation and interfacial adhesion with ultrasonic treatment at a residence time of 7 s, as indicated by morphological studies.

In 90/10 PET/LCP1 blends, the presence of hairy structures on the surface of LCP1 droplets, indicating interfacial adhesion, were observed with ultrasonic treatment at amplitudes of 7.5 and 10 μm, but not without treatment. Without ultrasonic treatment, sizes of the LCP1 droplets and fibrils, respectively, in the core and skin regions of molding were reduced with increasing LCP1 content in the blends. Hairy structure on the surface of LCP1 droplets in moldings of untreated and treated 80/20 and 70/30 PET/LCP1 blends in SONIC1 were also observed. Such structures were more pronounced in 80/20 blends treated at an ultrasonic amplitude of 7.5 μm and a mean residence time of 14 s in SONIC1. In this blend, large size hairy droplets and reduced fibrillation of LCP1 were observed.

Processing of 80/20 PET/LCP1 blends in SONIC2 led to reduced degradation of blend. This caused greater fibrillation due to greater viscosity ratio of PET to LCP1 and
resulted. However, ultrasonic treatment in SONIC2 was not observed to introduce any beneficial effects.

The change in PET to LCP1 viscosity ratio and the compatibilization of PET/LCP1 blends through ultrasonically induced homopolymerization, copolymerization and degradation reactions determined the morphology and mechanical properties. The amplitude and duration of ultrasonic treatment are decisive factors in the improvement of mechanical properties of these blends. Processing in SONIC1 was shown to improve interfacial adhesion and fibrillation behavior of PET/LCP1 blends in the melt state at a residence time of 7 s. Further refinement of processing conditions could allow one to achieve greater enhancements in the performance of LCP1, and its blends with PET.
CHAPTER V
PEN/LCP1 BLENDS

The effects of composition on the rheological, thermal, mechanical, and morphological properties of ultrasonically extruded PEN/LCP1 blends are discussed in this section.

5.1. Introduction

PEN is a commercial aromatic polyester with greater rigidity than PET due to the naphthalene ring in its backbone. PEN has many advantages over PET, including superior mechanical properties and thermal stability [309]. While it has greater cost than PET, it could be more suitable for blending with LCP due to its higher viscosity and processing temperature. A literature survey of PEN/LCP blends was provided in section 2.6.2.

While PET/LCP1 blends, studied in CHAPTER IV, had promising results including indications of greater copolymer formation with ultrasonic treatment, enhanced LCP phase deformation and interfacial attachment under certain conditions, and improvements in mechanical properties of LCP1 and some PET/LCP1 blends, the process had certain shortcomings. The primary issue in processing PET/LCP1 blends was the extensive degradation of PET phase following extrusion at the minimum temperature that permits the processing of blends containing LCP1. Due to reduced viscosity of degraded PET after passing through the extruder without treatment, the deformation of LCP1
phase was limited. This also limited the improvements in mechanical properties of blends with the addition of LCP1.

PEN has greater rigidity and is expected to be more resistant to degradation by extrusion and ultrasonic treatment. Hence, PEN was chosen as another matrix material in blends with LCP1, with the aim of creating in-situ reinforced PEN/LCP1 blends. In studies on ultrasonically treated PET/LCP1 blends, beneficial effects of treatment were observed only at 90/10 and 80/20 concentrations. The enhanced effect of ultrasonic compatibilization could be due to the greater surface area of the dispersed LCP1 phase available at low LCP1 concentrations for interchange reactions. As greater effect of ultrasound was also expected at low concentrations of LCP1 also in PEN/LCP1, only 90/10 and 80/20 PEN/LCP1 blends were studied.

5.2. Process Characteristics

In processing of PEN/LCP1 blends, the extruder SONIC1 was used. The screw design was modified, and the melt star mixing section at the end of the screw, after the ultrasonic treatment zone, was replaced with screw flights. The screw used in this study was shown in Figure 3.3. Details on the extrusion setup can be found in section 3.2.1.1. As significant degradation of PET was observed in the study presented in CHAPTER IV, this modification was aimed to reduce thermo-mechanical degradation during extrusion. While the original additional mixing section used in PET/LCP1 blends was used to homogenize the melt following sonication, it also induced high shear, which could in turn lead to extended degradation. As the polymer is subjected to further mixing and
homogenization, the additional mixing section, thought to be responsible for some of the degradation, was replaced with screw flights for this study.

Initially an extrusion temperature of 285°C (285 °C in all zones, except the feed zone at 260°C) was attempted for extrusion of PEN. However, pressure instabilities occurred, indicating incomplete melting of PEN at this temperature. Therefore, extrusion of PEN, and PEN/LCP1 blends was carried out at 300°C. In order to provide a basis for the comparison of process characteristics with PEN and the blends, LCP1 was also extruded at a temperature of 300°C. However, characterizations of LCP1 obtained at these processing conditions were not made. Data reported for LCP1 are based on results obtained with extrusion at 285°C in SONIC1 with the additional mixing section at the end of the screw at a flow rate of 1kg/hr, and hence the same as those for LCP1 presented in CHAPTER IV.

The barrel temperature at the ultrasonic treatment zone ($T_{\text{ultra}}$), the melt temperature at the connection of the original extruder barrel to the ultrasonic attachment ($T_{\text{melt}}$), and extruder torque were recorded. The results are listed in Table 5.1. The maximum standard deviation on the recorded temperatures was less than 2°C. The percent standard deviation (standard deviation/average), in torque readings was 10%.

It can be observed from Table 5.1 that the barrel temperature was kept at 300°C in all conditions except LCP1 without ultrasonic treatment. In extrusion of LCP1 at 300°C, the barrel temperature in the ultrasonic treatment fell short of the set point. This could be due to the lower viscosity of LCP1 and reduced shear heating during its processing at these conditions compared to PEN and the blends, resulting in less heat dissipation which could not complement the heaters sufficiently to heat the large ultrasonic barrel
attachment to the set temperature. The melt temperatures measured at the extruder barrel to ultrasonic attachment connection indicated lower values than the set point for all cases. This explains why a lower set point of 285°C did not allow stable extrusion of PEN and the blends. In each case, except processing of LCP1, the melt temperature in the treatment zone was observed to go up slightly with ultrasonic treatment. The lower than set melt temperatures could be due to a heater with reduced efficiency. Nevertheless, the variations in melt temperature from sample to sample were considered acceptable for extrusion.

Table 5.1. Temperature at ultrasonic treatment zone, melt temperature, and extruder torque measured during processing of PEN/LCP1 blends.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Amplitude (µm)</th>
<th>$T_{ultra}$ (°C)</th>
<th>$T_{melt}$ (°C)</th>
<th>Torque (Amp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN</td>
<td>0</td>
<td>299</td>
<td>287</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>289</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>289</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>300</td>
<td>292</td>
<td>2.0</td>
</tr>
<tr>
<td>90/10 PEN/LCP1</td>
<td>0</td>
<td>299</td>
<td>279</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>300</td>
<td>281</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>283</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>300</td>
<td>283</td>
<td>1.8</td>
</tr>
<tr>
<td>80/20 PEN/LCP1</td>
<td>0</td>
<td>301</td>
<td>289</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>300</td>
<td>290</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>293</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>292</td>
<td>2.2</td>
</tr>
<tr>
<td>LCP1</td>
<td>0</td>
<td>293</td>
<td>286</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>286</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>287</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>286</td>
<td>1.5</td>
</tr>
</tbody>
</table>

It can be observed from Table 5.1 that the torque during extrusion was the highest for PEN, and lowest for LCP1, with the blends lying in between. The torque for PEN was observed to decrease substantially with treatment at amplitudes of 7.5 and 10 µm, indicating its degradation at these conditions. Torque for the blends also decreased with ultrasonic treatment, and was lowest at an amplitude of 10 µm. No change in torque of
LCP1 was observed with ultrasonic treatment, since the torque was already low for LCP1 due to its low viscosity in the nematic state.

Figure 5.1. Ultrasonic power consumption vs. ultrasonic amplitude for PEN/LCP1 blends (values shifted along abscissa for clarity).

Figure 5.1 shows the average net power consumption of the two ultrasonic horns after the subtraction of zero power consumption, determined with the horns in air, as a function of ultrasonic amplitude. Ultrasonic power consumption increases with ultrasonic amplitude in all samples. The power consumption was observed to be highest for LCP1, while that of PEN and blends were similar.

Figure 5.2 shows the pressure before the ultrasonic treatment zone as a function of ultrasonic amplitude for PEN/LCP1 blends. LCP1 was observed to have the lowest pressure, in agreement with the lower extruder torque for LCP1 in comparison to PEN and the blends. The pressure for untreated PEN and untreated blends were very similar. In general, pressure is expected to decrease with ultrasonic treatment. Changes in
pressure with ultrasonic treatment are a combination of thixotropic and permanent changes, as well as possible slip of polymer melt along the solid surface of the horn. This phenomenon was explained in detail in the ultrasonic extrusion process characteristics of PET/LCP1 blends, section 4.2.

![Graph showing pressure before the ultrasonic treatment zone vs. ultrasonic amplitude for PEN/LCP1 blends (values shifted along abscissa for clarity).](image)

Figure 5.2. Pressure before the ultrasonic treatment zone vs. ultrasonic amplitude for PEN/LCP1 blends (values shifted along abscissa for clarity).

As acoustic cavitation in the melt results in both permanent and thixotropic changes in viscosity [9]. The pressure reduction in ultrasonic extrusion could also be due to a possible slip of the polymer melt along the surface of the horns [7]. In case of polymer degradation with ultrasonic treatment, thixotropic and permanent reductions in viscosity are complementary effects. With increasing amplitude of ultrasonic treatment, the pressure for PEN decreased rapidly. The decrease in pressure was less at amplitudes of 5 and 7.5 µm in PEN/LCP1 blends. The difference in the effect of ultrasonic treatment on pressure indicated that greater degradation could be occurring in PEN at the same amplitude of treatment, and that LCP1 interacts with PEN and changes the behavior of
blends under sonication. The pressure of ultrasonically treated 90/10 PEN/LCP1 blends did not decrease monotonically with amplitude, and was highest at an amplitude of 7.5 \( \mu \text{m} \). The latter indicated that the properties of 90/10 PEN/LCP1 blend could be affected nontrivially upon treatment at an amplitude of 7.5 \( \mu \text{m} \).

5.3. Rheology

Capillary rheometry at a temperature of 300\(^\circ\)C was used to determine the viscosity of untreated and treated PET/LCP1 blends. Figure 5.3a and b show the apparent viscosity of PEN/LCP1 blends without and with ultrasonic treatment at apparent shear rates of 105 s\(^{-1}\) and 957 s\(^{-1}\), respectively. Apparent shear rates were used in order to plot the data together for comparison. Viscosities at both low (Figure 5.3a) and high (Figure 5.3b) shear rates were plotted to compare shear thinning behavior of the blends. It can be observed by comparing Figure 5.3a and b that PEN exhibits close to Newtonian behavior, while LCP1 is highly shear thinning. The PEN/LCP1 blends exhibited mildly shear thinning behavior.

It can also be observed from Figure 5.3a and b that the viscosity of virgin PEN is higher than extruded PEN. This showed that PEN degraded during extrusion. On the other hand, little change in the viscosity of LCP1 is observed with ultrasonic treatment. The viscosity of LCP1 treated at an amplitude of 10 \( \mu \text{m} \) was only slightly less than that in the other conditions.
Figure 5.3. Apparent viscosity vs. concentration for PEN/LCP1 blends at different ultrasonic amplitudes at apparent shear rates of (a) $105 \text{s}^{-1}$, (b) $957 \text{s}^{-1}$. Lines connecting data to pure LCP1 are drawn for convenience.

It is important to note that the viscosity ratio of PEN to LCP1 is greater than the viscosity ratio of PET to LCP1, which was presented in section 4.3. Therefore, greater deformation of the LCP1 domains is expected in PEN/LCP1 blends than that observed in PET/LCP1 blends. However, the viscosity of PEN was shown to decrease rapidly with amplitude of ultrasonic treatment, indicating that LCP1 domain size could increase in treated blends. On the other hand, PEN/LCP1 blends did not indicate any reduction in viscosity at amplitudes of 5 and 7.5 $\mu$m, as shown in Figure 5.3a and b. Hence, there exist substantial differences in the effects of ultrasound on pure PEN and PEN/LCP1 blends. While PEN was observed to degrade with all amplitudes of treatment, no reduction in viscosity was observed for its blends with LCP1, except at an amplitude of 10 $\mu$m. These
observations indicate that the degradation occurring in neat PEN is hindered in the presence of LCP1. Since the ultrasonic power consumption is the same in pure PEN and the blends, it is likely that some of the ultrasonic energy is consumed in recombination reactions.

5.4. Thermal analysis

Differential scanning calorimetry (DSC) studies of PEN and PEN/LCP1 blends were performed to observe thermal changes following ultrasonic treatment. The melting endotherm for LCP1 appeared at 280°C, but its glass transition temperature ($T_g$) could not be determined using DSC. The second heating curve, run after cooling at the same rate to remove time-temperature history, was taken as basis for all measurements. For PEN, $T_g$, the melting endotherm maximum temperature peak ($T_m$), crystallization temperature ($T_{cc}$), and percent crystallinity ($X_c$) are shown in Table 5.2. $X_c$ was determined after subtraction of PEN cold crystallization enthalpy from the melting enthalpy and normalized with respect to PEN content in the blends.

It was observed from Table 5.2 that the glass transition temperature of PEN decreased by 4°C with ultrasonic treatment at amplitudes of 7.5 and 10 µm, in comparison to virgin PEN. $T_g$ was also observed to decrease with treatment at an amplitude of 10 µm for 90/10 PEN/LCP1 and 80/20 PEN/LCP1 blends, by 2.5°C and 3.6°C, respectively, compared to the untreated blends. The decrease in $T_g$ of PEN and its blends with LCP1 indicated degradation with ultrasonic treatment at the specified amplitudes. No reduction in the $T_g$ of the blends was observed with treatment at an amplitude of 7.5 µm, in contrast to the decrease in PEN. This indicated the stabilizing
effect of LCP1 against ultrasonic degradation in PEN/LCP1 blends, and signified that ultrasound affects the components and blends differently. The fact that same ultrasonic power consumption was recorded at an amplitude of 7.5 µm for PEN and the blends pointed out to the possibility of structural changes in the blends in addition to chain scission.

Table 5.2. Glass transition temperature ($T_g$), cold crystallization temperature ($T_{cc}$), crystallinity ($X_c$) and melting temperature ($T_m$) of PEN in DSC second heating for PEN/LCP1.

<table>
<thead>
<tr>
<th>DSC 2nd heating runs</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$X_c$ (%)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Virgin</td>
<td>125</td>
<td>214.3</td>
<td>3.8</td>
<td>270.4</td>
</tr>
<tr>
<td>0 µm</td>
<td>122.8</td>
<td>204.8</td>
<td>4.5</td>
<td>269.6</td>
</tr>
<tr>
<td>5 µm</td>
<td>123.3</td>
<td>204.6</td>
<td>2.2</td>
<td>270.3</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>120.5</td>
<td>178.5</td>
<td>21.9</td>
<td>269.8</td>
</tr>
<tr>
<td>10 µm</td>
<td>120.6</td>
<td>179.2</td>
<td>20.0</td>
<td>270.1</td>
</tr>
<tr>
<td>90/10 PEN/LCP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 µm</td>
<td>122.2</td>
<td>172.4</td>
<td>21.4</td>
<td>269.3</td>
</tr>
<tr>
<td>5 µm</td>
<td>121.7</td>
<td>176.4</td>
<td>20.9</td>
<td>268.9</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>123.0</td>
<td>174.8</td>
<td>17.5</td>
<td>268.7</td>
</tr>
<tr>
<td>10 µm</td>
<td>119.7</td>
<td>165.5</td>
<td>35.4</td>
<td>269.5</td>
</tr>
<tr>
<td>80/20 PEN/LCP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 µm</td>
<td>122.8</td>
<td>177.4</td>
<td>16.2</td>
<td>268.7</td>
</tr>
<tr>
<td>5 µm</td>
<td>121.9</td>
<td>175.3</td>
<td>20.6</td>
<td>269.1</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>121.2</td>
<td>172.2</td>
<td>22.0</td>
<td>268.7</td>
</tr>
<tr>
<td>10 µm</td>
<td>120.0</td>
<td>170.9</td>
<td>28.1</td>
<td>269.1</td>
</tr>
</tbody>
</table>

The cold crystallization temperatures shown in Table 5.2 indicate the peak temperature in the crystallization exotherm. As shorter polymer chains crystallize faster, due to increased chain mobility and easier alignment, reduction in cold crystallization temperature indicates reduced molecular weight. This was also observed in PET/LCP1 blends when PET phase was degraded (section 4.8).
Figure 5.4. Heat flow vs. temperature curves during second heating in DSC for PEN without and with ultrasonic treatment.

Figure 5.4 shows heat flow as a function of temperature during DSC second heating for PEN without and with ultrasonic treatment. The crystallinity of virgin PEN was much lower than the PET that passed through the extruder. Shorter polymer chains crystallize faster due to greater chain mobility at lower molecular weights and the faster alignment of polymer chains for crystallization [318]. The cold crystallization temperature of PEN decreased with processing. An increase in its crystallinity can be observed from Table 5.2. This was a result of its molecular weight reduction, indicated by the viscosity measurements shown in section 5.3. With ultrasonic treatment at an amplitudes of 7.5 µm and 10 µm, the cold crystallinity peak of PEN shifted to even lower temperature and increased in intensity. This signified greater degradation of PEN with ultrasonic treatment at these amplitudes.
Figure 5.5. Heat flow vs. temperature curves during second heating in DSC for 90/10 PEN/LCP1 without and with ultrasonic treatment.

Figure 5.5 shows heat flow as a function of temperature during DSC second heating for 90/10 PEN/LCP1 blends without and with ultrasonic treatment. The cold crystallization peak of untreated 90/10 PEN/LCP1 blend shifted to slightly higher temperature with ultrasonic treatment at amplitudes of 5 and 7.5 µm. It was also observed to shift to a lower temperature and decreased in intensity with ultrasonic treatment at an amplitude of 10 µm. The latter indicated that PEN in the blend treated at 10 µm was crystallized to a greater extent during cooling. This suggested degradation of PEN in the blend at an amplitude of 10 µm. The slight increase in $T_{cc}$ of 90/10 PEN/LCP1 treated at an amplitude of 7.5 µm was in contrast to the significant decrease in that of pure PEN treated at the same amplitude. This difference in the effect of ultrasound on pure PEN and
the blend indicated some interaction of PEN with LCP1 upon ultrasonic treatment in the blend.

Figure 5.6 shows heat flow as a function of temperature during DSC second heating for 80/20 PEN/LCP1 blends without and with ultrasonic treatment. The cold crystallization peak of untreated 80/20 PEN/LCP1 blend shifted to slightly lower temperatures at increasing amplitudes of ultrasonic treatment. The crystallinity of blend treated at an amplitude of 10 µm was greater than that of the untreated blend, indicating PEN degradation at this condition.

Figure 5.6 shows heat flow as a function of temperature during DSC second heating for 80/20 PEN/LCP1 blends without and with ultrasonic treatment. The cold crystallization peak of untreated 80/20 PEN/LCP1 blend shifted to slightly lower temperatures at increasing amplitudes of ultrasonic treatment. The crystallinity of blend treated at an amplitude of 10 µm was greater than that of the untreated blend, indicating PEN degradation at this condition.
blends was lower than those of both untreated and treated PEN, indicating that LCP1 acted as a nucleating agent in PEN crystallization [230]. Crystallization of PEN was accelerated in the presence of LCP1. The cold crystallization temperature of both 90/10 and 80/20 PEN/LCP1 blends was observed to decrease substantially with ultrasonic treatment at an amplitude of 10 µm. These increases in crystallinity also indicated degradation with ultrasonic treatment at the specified amplitudes. No changes in the melting point of PEN and PEN/LCP1 blends were observed from the DSC measurements.

Figure 5.7. Heat flow vs. temperature curves during second heating in DSC for PEN, 90/10 PEN/LCP1 and 80/20 PEN/LCP1 without and with ultrasonic treatment at an amplitude of 10 µm.
5.5. Dynamic Mechanical Analysis

Figure 5.8a and b show the temperature dependence of storage and loss moduli, respectively, of PEN/LCP1 blends without and with ultrasonic treatment.

Figure 5.8. Moduli vs. temperature for PEN/LCP1 without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm: (a) storage, and (b) loss modulus.
The storage modulus of untreated PEN increased with LCP1 concentration in the blends. Pure LCP1 had the greatest storage modulus. Storage modulus of LCP1 was not affected by ultrasonic treatment, while that of PET/LCP1 blends was reduced with treatment at 10 µm, and that of PEN was reduced with treatment at both 7.5 and 10 µm. As no change was observed in the storage and loss modulus of PEN and blends at 5 µm, data at this amplitude was not included in Figure 5.8.

As can be observed from Figure 5.8b, the loss modulus of untreated 80/20 PEN/LCP1 blends was greater than that of 90/10 PEN/LCP1 blends, which was greater than that of PEN. The loss modulus of LCP1 was highest at temperature below the range of PEN second order phase transition. Similar to the storage modulus shown in Figure 5.8a, the loss modulus of PEN/LCP1 blends also was altered with treatment at an amplitude of 10 µm, and at both 7.5 and 10 µm for pure PEN. Ultrasonic treatment at these amplitudes led to reductions in the loss modulus and shift of inflection point along the E” vs. temperature curves to lower temperatures, due to the second order phase transition of PEN. No change in loss modulus was observed with treatment of LCP1. These results indicated degradation of PEN at the specified amplitudes.

Figure 5.9 shows the effect of ultrasonic amplitude on the glass transition temperature corresponding to tan δ peaks from DMTA. Loss tangent behavior also supported conclusion on degradation of PEN at amplitudes of 7.5 and 10 µm, and in 90/10 and 80/20 PEN/LCP1 blends at amplitude of 10 µm. At these conditions, the tan δ peak value was also observed to increase, indicating loss of elasticity with ultrasonic treatment at the specified amplitudes. The decrease in Tg signifies a substantial decrease in molecular weight of pure PEN at amplitudes of 7.5 and 10 µm and in PEN/LCP1
blends at 10 µm. The glass transition temperatures of PEN/LCP1 blends corresponding to the tan δ peaks were summarized in Table 5.3. \( T_g \) determined from DMA is higher than that determined by DSC, as expected [285].

Figure 5.9. Loss tangent vs. temperature for PEN/LCP1 without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm.

Table 5.3. Glass transition temperature of PEN/LCP1 blends without and with ultrasonic treatment, as determined from tan δ peaks in DMA.

<table>
<thead>
<tr>
<th>( T_g ) (°C)</th>
<th>PEN</th>
<th>90/10 PEN/LCP1</th>
<th>80/20 PEN/LCP1</th>
<th>LCP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>130</td>
<td>-</td>
<td>-</td>
<td>107</td>
</tr>
<tr>
<td>0 µm</td>
<td>131</td>
<td>126</td>
<td>130</td>
<td>107</td>
</tr>
<tr>
<td>5 µm</td>
<td>130</td>
<td>127</td>
<td>130</td>
<td>106</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>129</td>
<td>128</td>
<td>129</td>
<td>106</td>
</tr>
<tr>
<td>10 µm</td>
<td>126</td>
<td>122</td>
<td>124</td>
<td>106</td>
</tr>
</tbody>
</table>
It can be observed from Table 5.3 that there was more variation in the distribution of \( T_g \) determined by DMA than there was in results obtained from DSC. It can be observed that the glass transition temperatures obtained by DMA were also higher than those obtained by DSC, as expected [285].

5.6. FTIR spectroscopy

FT-IR spectra of PEN, and its blends with LCP1 were captured without and with ultrasonic treatment, in an effort to identify possible chemical changes occurring in the blends. However, similar to observation on FT-IR spectroscopy on PET/LCP1 blends discussed in section 4.5, no changes in the spectra of PEN or the blends were observed with ultrasonic treatment. The position of peaks in the ATR FT-IR spectra of PEN was the same without and with ultrasonic treatment. 90/10 and 80/20 PEN/LCP1 blends had virtually the same spectra, and also with and without ultrasonic treatment. Representative spectra of PEN, LCP1 and the blend are shown is Figure 5.10.

The spectra of PEN/LCP1 blend shown Figure 5.10 was a combination of the spectra of pure LCP1 and PEN. The expected structure of PEN/LCP1 copolymer that could be formed by transesterification of PEN and LCP1 is shown in Figure 5.11. PET/LCP1 copolymerization is indicated by MALDI-TOF MS analysis in the next section (5.7).
Figure 5.10. ATR FT-IR spectra of PEN, 80/20 PEN/LCP1, and LCP1, representative all processing conditions, each spectra was virtually the same without and with ultrasonic treatment.

It can be observed from Figure 5.11 that the structure of linkage in the copolymer is very similar to those already existing in PEN and LCP1. This renders the detection of copolymers by FT-IR very difficult. It is most probable that the ester groups of the LCP1 and its copolymer with PEN overlapped. Additionally, the amount of copolymer could have been too small to be detected by ATR FT-IR.
5.7. Mass spectroscopy

Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectroscopy of PEN, LCP1, and their 90/10 blend was performed in order to investigate structural changes and the presence of copolymer with ultrasonic treatment.

Structural changes in PEN with ultrasonic treatment at amplitudes of 7.5 and 10 \( \mu m \) were identified in section 6.6. The formation of new end groups and changes in the relative intensities of peaks from different species were also identified in that section. MALDI-TOF spectra of LCP1 without and with treatment at amplitudes of 7.5 and 10 \( \mu m \) in SONIC1 at a flow rate of 1 kg/hr are shown in Figure 4.15 and Figure 4.16.

In this section, mass spectra of 90/10 PEN/LCP1 blend in SONIC1 without treatment and with treatment at an amplitudes of 7.5 \( \mu m \) and 10 \( \mu m \) are shown. Figure 5.12 shows the mass spectra of these blends in the m/z range from 2870-3300. Increase in intensity of some peaks that were also present without treatment, and the formation of new peaks were observed with treatment at an amplitude of 10 \( \mu m \). The new peaks
formed with ultrasonic treatment at an amplitude of 10 µm appeared at 2884.0, 2896.0, 2943.1, 2954.1, 2972.1, 3139.1, and 3196.0 Daltons. These peaks were not present in the blend without treatment and indicated the formation of PET/LCP1 copolymer. The particular copolymer species corresponding to each peak could not be identified due to the complexity of the possible combinations of PET, HBA, and HNA, and their cyclics or end groups.

Figure 5.12. MALDI-TOF spectra of 90/10 PEN/LCP1 blends without and with treatment at ultrasonic amplitudes of 7.5 and 10 µm in the m/z range of 2870-3300.
As can be seen from Figure 5.13, mass spectra of both untreated and ultrasonically treated 90/10 PEN/LCP1 indicated new peaks that were not present in the spectra of LCP1 and PET in the m/z range of 1630-1730. This indicated the presence of PEN/LCP1 copolymer in the blends. The intensity of labeled peaks at m/z of 1682 and 1686 was higher in the blend ultrasonically treated at an amplitude of 10 µm. Hence, the extent of copolymerization was higher with ultrasonic treatment at this amplitude.
Mass spectra of both untreated and ultrasonically treated 90/10 PEN/LCP1 indicated new peaks that were not present in the spectra of LCP1 and PET. This indicated the presence of PEN/LCP1 copolymer in the blends. The intensity of labeled peaks at m/z of 1682 and 1686 was higher in the blend ultrasonically treated at an amplitude of 10 µm. Hence, the extent of copolymerization was higher with ultrasonic treatment at this amplitude.

Figure 5.14. MALDI-TOF spectra of (a) LCP1, (b) untreated 90/10 PEN/LCP1 blend, (c) 90/10 PEN/LCP1 blend treated at an ultrasonic amplitude of 7.5 µm, (d) untreated PEN, (e) PEN treated at an amplitude of 10 µm, in the m/z range of 1870-1970.
As shown in Figure 5.14a-e, the presence of new PEN/LCP1 copolymer peaks were also observed in the m/z range of 1870-1970. The intensity of peaks in 90/10 PEN/LCP1 treated at an amplitude of 10 µm was greater around an m/z value of 1924, also indicating greater copolymerization with ultrasonic treatment. The peaks attributed to PEN/LCP1 copolymer species were sharper and their distribution was different with ultrasonic treatment.

5.8. Mechanical Properties

Figure 5.15a and b show the effect of ultrasonic amplitude on the tensile strength and Young’s modulus of PEN/LCP1 blends, respectively. These properties for the untreated blends are higher in comparison with prior studies [238], probably owing to higher orientation and greater skin layer in molded mini-tensile bars as compared to larger injection molded tensile specimens [65]. In this section, virgin PET and LCP1 were injection molded into specimens for testing without any other processing for comparison of mechanical properties with materials that were extruded before injection molding. While the Young’s modulus and tensile strength of PEN and PEN/LCP1 blends are not affected at ultrasonic amplitudes of 5 and 7.5 µm, they decreased with treatment at 10 µm. The improvements in properties of pure LCP1 following ultrasonic treatment seen in Figure 5.15 were discussed in section 4.9.
Figure 5.15. Mechanical properties of PEN/LCP1 blends versus LCP1 concentration: (a) tensile strength, and (b) Young’s modulus, without and with treatment at different ultrasonic amplitudes. Lines connecting 20% LCP1 concentration to pure LCP1 are drawn for convenience.

Figure 5.16a and b show the effect of ultrasonic amplitude on the elongation at break and unnotched Izod impact strength, respectively, of PEN/LCP1 blends. It should be noted that PEN shows yielding at all processing conditions except with treatment at an amplitude of 10 µm. 90/10 PEN/LCP1 treated at an amplitude of 7.5 µm also exhibited yielding. However, the elongation at break of these samples had a large variation. This could be due to defects introduced on dumbbells by the extensometer during their necking. Therefore, only elongation at yield was reported for these samples in Figure 5.16a. The blends become increasingly brittle with incorporation of LCP1. The elongation at break decreased significantly with treatment at an amplitude of 10 µm for PEN and the blends, indicating their degradation. The elongation at break of 90/10 PEN/LCP1 blends increased with ultrasonic treatment at amplitudes of 5 and 7.5 µm.
Figure 5.16. Mechanical properties of PEN/LCP1 blends versus LCP1 concentration: (a) elongation at break, and (b) average unnotched Izod impact strength, without and with ultrasonic treatment. Elongation at yield is reported for PET and 90/10 PEN/LCP1 blends treated at 7.5 μm. Lines connecting 20% LCP1 concentration to pure LCP1 are drawn for convenience.

The impact strength of injection molded rectangular flex bars were determined by testing them in two parts: the dead end (DE) and gate end (GE). The results of impact properties of samples from these two locations were very close, and the averages of results from DE and GE samples were shown in Figure 5.16b. As seen in this figure, the impact strength of pure PEN decreases significantly at an amplitude of 7.5 μm. While there is no change in 80/20 PEN/LCP1 until an amplitude of 10 μm, 90/10 PEN/LCP1 exhibits 21% greater impact strength with treatment at an amplitude of 7.5 μm. This increase in impact strength could be an indication of improved compatibility in this blend. Moreover, the different impact behavior of pure PEN and the blends indicates that the ultrasonic energy applied affected PEN differently in the presence of LCP1. The ultrasonic energy applied to PEN/LCP1 blends could have triggered recombination reactions following chain scission in PEN at an amplitude of 7.5 μm.
Figure 5.17. Unnotched Izod impact strength of DE (solid symbols and lines) and GE (open symbols and dashed lines) of PEN and PEN/LCP1 blends vs. LCP1 concentration (values shifted along abscissa for clarity).

Figure 5.17 presents the unnotched Izod impact strength of the dead end (DE) and gate end (GE) of moldings of PEN and PEN/LCP1 blends as functions of LCP1 concentration, with the error ranges indicating 95% confidence intervals. As can be seen from the error bars, the results from DE and GE samples were very similar. At an amplitude of 10 µm, which caused degradation and loss in impact strength for PEN and blends, there was no difference between tests using DE and GE samples. The reproducibility of impact data was better in blends than in PEN. In the blends, the impact strength of DE samples was generally observed to lie higher than GE samples. Impact strength in LCP1 and their blends depends on orientation and morphology of LCP1 domains. Fibrillation of the LCP1 phase occurs during molding of thermoplastic/LCP1 blends [169]. In the injection molding of PEN/LCP1 blends, high injection speed and low mold temperature were used, as discussed in section 3.2.2. This would be expected to facilitate faster freezing and greater frozen-in orientation in DE of the sample, which is
injected first and is further away from the warmer GE. The impact strength is positively correlated with orientation of LCP1 fibrils. While there was little separation between the data, results indicated greater impact strength in DE samples of blends.

Impact strength of PEN had a greater scatter in both DE and GE samples than the blends, as indicated in Figure 5.17. In pure PEN, little change in orientation would not be expected to have as strong an influence on impact strength as in blends with LCP1, and the distribution of impact strength of DE and GE samples appeared to be random.

Dependence of impact strength of blends on sample position in moldings (DE and GE) was not substantial in view of a large error. Thus, Figure 5.17 was presented and discussed here for completeness and to show the error in impact testing of moldings. As this was not the focus of this project, further studies were not conducted on this behavior. Values of impact strength calculated by averaging GE and DE samples (Figure 5.16b) presented sufficient accuracy and were used for discussions on the effect of ultrasound on the impact properties of PEN/LCP1 blends.

5.9. Morphology

PEN/LCP1 blends had spherical droplets in the core, and highly elongated fibers of various diameters in the skin region. The skin region formed a substantial portion of the injection molded mini-tensile bars as a result of their small cross sectional area.

Figure 5.18 a-f show the effect of ultrasonic treatment on the skin and core regions of molding of 90/10 PEN/LCP1 blends. Small LCP1 droplets in the core, (Figure 5.18) and LCP1 fibrils of 100 nm diameter in the skin (Figure 5.18b) were observed in the untreated blend. While any change in LCP1 particle size in moldings was not obvious
with treatment at an amplitude of 7.5 µm (Figure 5.18c-d), ultrasonic treatment at an amplitude of 10 µm clearly led to generation of larger droplets in the core (Figure 5.18e), and thick fibrils in the skin (Figure 5.18f). The larger LCP1 particles observed with treatment at an amplitude of 10 µm were due to the reduced viscosity ratio of PEN1 to LCP1, as seen in Figure 5.3a-b.

Figure 5.18. SEM micrographs of 90/10 PEN/LCP1 blends, (a) untreated core region, (b) untreated skin region, (c) core region treated at 7.5 µm, (d) skin region treated at 7.5 µm, (e) core region treated at 10 µm, (f) skin region treated at 10 µm.
Figure 5.19 a-f show the effect of ultrasonic treatment on the skin and core regions of molding of 80/20 PEN/LCP1 blends. LCP1 domain sizes in the 80/20 PEN/LCP1 without and with ultrasonic treatment were observed to be greater than in 90/10 PEN/LCP1 blends (Figure 5.18 a-f).
In order to observe the PEN/LCP1 interface in the blends, micrographs were captured at 10,000 times magnification, and are presented in Figure 5.20a-l. It should be noted that the resolution at this very high magnification was not as good as in Figure 5.18 and Figure 5.19. Moreover, the small area observed at this length scale was not as representative of the whole sample as images at lower magnification of 2,000x.

Comparing Figure 5.20a-c reveal differences in 90/10 PEN/LCP1 core region morphology. In untreated blend (Figure 5.20a), voids are visible around LCP1 droplets. These indicated exclusion of LCP1 phase from the PEN matrix. LCP1 droplet surfaces were also very smooth, indicating poor adhesion between the phases. With treatment at an amplitude of 7.5 µm (Figure 5.20b), voids were still present around droplets in the core, however surface of droplets were not as smooth, indicating somewhat greater interaction between PEN and LCP1. At an amplitude of 10 µm (Figure 5.20c), much larger LCP1 droplets were observed alongside small LCP1 droplets. The presence of LCP1 agglomerates at this amplitude indicated poor deformation of LCP1 phase by the lower viscosity PEN matrix.

Figure 5.20d-f provided a comparison between the skin region morphology of untreated and ultrasonically treated 90/10 PEN/LCP1 blends. In the untreated blend (Figure 5.20d), LCP1 fibrils were uniform in size but showed poor attachment to the PEN matrix. With treatment at an amplitude of 7.5 µm (Figure 5.20e), the PEN matrix and LCP1 domains appeared to be tightly bound together. The sample topography was also rougher, indicating greater interaction between the two components of the blend. With treatment at an amplitude of 10 µm (Figure 5.20f), large droplets and fibers were observed along with small fibers. Presence of LCP1 agglomerates also in the skin
affirmed that poor LCP1 fibrillation was responsible for the poor mechanical properties at this condition.

Figure 5.20. SEM micrographs of core and skin regions of untreated and ultrasonically treated PEN/LCP1 blends at a magnification of 10,000x, (a) 90/10 core 0 μm, (b) 90/10 core 7.5 μm, (c) 90/10 core 10 μm, (d) 90/10 skin 0 μm, (e) 90/10 skin 7.5 μm, (f) 90/10 skin 10 μm, (g) 80/20 core 0 μm, (h) 80/20 core 7.5 μm, (i) 80/20 core 10 μm, (j) 80/20 skin 0 μm, (k) 80/20 skin 7.5 μm, (l) 80/20 skin 10 μm.
Figure 5.20g-i show the core region morphology of 80/20 PEN/LCP1 blends. Without treatment (Figure 5.20g), uniformly distributed droplets were observed. These LCP1 domains appeared to be largely excluded from the PEN matrix. The size of these LCP1 domains were larger than those in the core region of untreated 90/10 PEN/LCP1 (Figure 5.20a). This was attributed to the higher volume fraction of LCP1 in 80/20 blends. With treatment at an amplitude of 7.5 µm (Figure 5.20h), the morphology was similar to that of the core region of untreated 80/20 PEN/LCP1 blends (Figure 5.20g). With treatment at an amplitude of 10 µm, the size of droplets was larger. These droplets were also hairy, indicating improved adhesion of LCP1 phase to the PEN matrix. Moreover, voids were not observed between the LCP1 and PEN phases and appeared to be replaced by a broader interface, at an amplitude of 10 µm.

Figure 5.20j-l were used to compare the morphology of the skin region of 80/20 PEN/LCP1 blends. Without treatment (j), LCP1 fibers were pulled out from matrix, leaving large voids behind. With treatment at an amplitude of 7.5 µm, LCP1 fibers were embedded stronger in the PEN phase and appeared to be deformed together, indicating better interfacial adhesion. However, fibers were not as numerous and were possibly embedded in the PEN phase. With treatment at an amplitude of 10 µm (l), large LCP1 droplets were observed in the skin along with small broken fibrils. The poor dispersion of LCP1 phase and lack of its uniform fibrillation resulted in the reduced mechanical properties in this condition, as shown in section 5.8.
5.10. Conclusions

PEN/LCP1 blends were prepared in SONIC1 at a flow rate of 1 kg/hr. Ultrasonic treatment led to reduced pressure during extrusion, and also reduced the viscosity of the PEN melt. In 90/10 and 80/20 PEN/LCP1 blends, the viscosity and mechanical properties did not decrease except with treatment at an ultrasonic amplitude of 10 µm. The glass transition temperature of pure PEN and PEN in the blends was reduced with treatment at an amplitude of 10 µm.

MALDI-TOF mass spectroscopy was performed on PEN, 90/10 PEN/LCP1 and LCP1 without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm. The formation of new species in blends was observed without and with ultrasonic treatment. Ultrasonic treatment of 90/10 PEN/LCP1 blends was shown to induce the formation of new species and increase the intensity of peaks that were present without treatment, possibly indicating greater copolymer formation with ultrasonic treatment.

LCP1 acted as a nucleating agent in PEN/LCP1 blends. Crystallinity of pure PEN increased with ultrasonic treatment at amplitudes of 7.5 and 10 µm. In the PEN/LCP1 blends, crystallinity only increased with ultrasonic treatment at an amplitude of 10 µm. The value of tan δ determined from DMA increased and its peak shifted to lower temperatures with ultrasonic treatment at amplitudes of 7.5 and 10 µm for PEN, and only at an amplitude of 10 µm for PEN/LCP1 blends. The latter results indicated the stabilizing effect of LCP1 against PEN degradation under ultrasonic treatment, due to enhanced recombination reactions as shown by MALDI-TOF.
SEM micrographs showed presence of LCP1 droplets in the core region, and fibers in the skin region of moldings. Size of LCP1 fibrils was in the order of 100 nm in the skin region of 90/10 PEN/LCP1 blends without and with ultrasonic treatment at amplitude of 7.5 \( \mu \text{m} \). The LCP1 domain size in 80/20 PEN/LCP1 blends was observed to be slightly larger than 90/10 PEN/LCP1 blends, due to agglomeration of LCP1 domains at the higher concentration. 90/10 PEN/LCP1 blends treated at an amplitude of 7.5 \( \mu \text{m} \) indicated improved attachment of LCP1 phase to PEN. Ultrasonic treatment at an amplitude of 10 \( \mu \text{m} \) led to grossly undeformed LCP1 domains in the core and skin regions of 90/10 and 80/20 PEN/LCP1 blends. This suggested that any beneficial effects of exchange reactions were masked by reduced viscosity ratio of PEN to LCP1 at an amplitude of 10 \( \mu \text{m} \).

Ultrasonic treatment of 90/10 PEN/LCP1 at an amplitude of 7.5 \( \mu \text{m} \) improved its impact strength and elongation at yield. Elongation at yield of this blend was also slightly improved at an amplitude of 5 \( \mu \text{m} \). These improvements in 90/10 PEN/LCP1 blend were due to in-situ interfacial compatibilization with ultrasonic treatment.
CHAPTER VI
PET/PEN BLENDS

PET, PEN, and their 50/50 blend were processed by ultrasonically-aided extrusion at various amplitudes. Rheological, thermal, mechanical, morphological and spectroscopic characterizations were carried out to demonstrate enhanced transesterification in polyester blends with ultrasonic treatment.

6.1. Introduction

PET/PEN blends offer advantages over PET in their mechanical, thermal and barrier properties. These blends are immiscible [100], but may undergo interchange reactions, which create a copolymer that act as a compatibilizer. Copolymerization in PET/PEN blends is necessary to attain optically clear blends with desirable properties [119].

Transesterification reactions occur in polyesters having chains terminated by hydroxyl or carboxyl groups. At the start of transesterification, block copolymers with large segment lengths are formed. At higher extents of transesterification, sequence lengths of PET and PEN decrease, leading to random copolymers [111].

In order to achieve optically clear PET/PEN blends, multiple passes through a single screw extruder are commonly required. Twin screw extrusion can provide more uniform thermal distribution and good mixing and lead to good clarity after the first pass
A comprehensive review of PET/PEN literature was presented in section 2.3. Ultrasonic treatment in the melt can induce copolymerization reactions in polymer blends. In PET/PEN blends, ultrasonic extrusion is expected to enhance transesterification reactions. Ultrasonic oscillations lead to chemical reactions through the scission of polymeric chains and their recombination. Chemical structure and amplitude of ultrasonic oscillations dictate the effects of ultrasound on materials [9]. The effects of ultrasonic treatment during extrusion of 50/50 PET/PEN blends were studied in this chapter.

6.2. Process Characteristics

SONIC1 was used for processing of PET, PEN and their blends. The flow rate was set at 1 kg/hr for all materials. In processing of PET, SONIC1 had a screw with an additional MSM mixing section after the sonication zone, as shown in Figure 3.2. In processing of PEN and 50/50 PET/PEN blends, this mixing zone was replaced with screw flights; the screw used is shown in Figure 3.3.

The barrel temperature in the ultrasonic treatment zone ($T_{\text{ultra}}$), the melt temperature at the connection of the original extruder barrel to the ultrasonic attachment ($T_{\text{melt}}$), and extruder torque were recorded. The results are shown in Table 6.1. The standard deviation on the recorded temperatures was 2°C, and the percent standard deviation (standard deviation/average) in torque readings was 10%.

Pure PEN was processed at a barrel temperature of 300°C, while PET and the blends were processed at 285°C. Pressure fluctuations in the treatment of PEN at lower temperatures due to its incomplete melting prompted its extrusion at 300°C. On the other
hand, pressure was stable during processing of 50/50 PEN/PET blend, and it was extruded at the same temperature as PET, 285°C, in order to limit thermal degradation. Fluctuations in barrel temperature at the ultrasonic treatment zone were negligible in each case.

Table 6.1. Temperature at ultrasonic treatment zone, melt temperature, and extruder torque measured during processing of PET/PEN blends.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Amplitude (µm)</th>
<th>T_{ultrasound}(°C)</th>
<th>T_{melt}(°C)</th>
<th>Torque (amp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0</td>
<td>284</td>
<td>289</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>284</td>
<td>290</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>285</td>
<td>289</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>286</td>
<td>292</td>
<td>1.6</td>
</tr>
<tr>
<td>50/50 PET/PEN</td>
<td>0</td>
<td>284</td>
<td>279</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>285</td>
<td>282</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>285</td>
<td>282</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>285</td>
<td>284</td>
<td>3.2</td>
</tr>
<tr>
<td>PEN</td>
<td>0</td>
<td>299</td>
<td>287</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>289</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>289</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>300</td>
<td>292</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The melt temperatures during processing of PET/PEN blends, shown in Table 6.1, were observed to increase with amplitude of ultrasonic treatment. Treatment at an amplitude of 10 µm resulted in the highest increase in melt temperature (3°C for PET, and 5°C for PEN and the blend). The torque for 50/50 PEN/PET blend also decreased with ultrasonic treatment.

Comparing extruder torque shown in Table 6.1 for untreated materials, it was seen that torque was highest during processing of PEN, and was lowest for PET. With that for the untreated blend lying in between. With ultrasonic treatment, torque for PET was
unaffected at 5 µm, increased at 7.5 µm and decreased at 10 µm, in comparison with the untreated material. The largest reductions in torque with ultrasonic treatment were recorded for PEN among all materials. Torque for PEN was observed to decrease most substantially at amplitudes of 7.5 and 10 µm.

Figure 6.1 shows ultrasonic power consumption and pressure before the ultrasonic treatment zone for PET, PEN and their blend. The reported power consumption was the average net power consumption of the two ultrasonic horns after the subtraction of zero power consumption, determined with the horn in air. Overall, ultrasonic power consumption increased, and pressure decreased with amplitude of ultrasonic treatment.

![Graph showing ultrasonic power consumption and pressure](image)

Figure 6.1. Ultrasonic power consumption and extrusion pressure for PEN, PET and their 50/50 blend.

The ultrasonic power consumption was higher for PEN and the blend, than it was for PET. The pressure for PEN was lower than that for PET and the blends because the processing temperature for PEN was selected higher, at 300°C, to ensure its complete
melting, while those for PET and the blends were set at 285°C. Even though the melt temperature at the connection of extruder to ultrasonic attachment was similar for PET and PEN, pressure was recorded right before the ultrasonic horn (as described in section 3.2.1.1) and the temperature at and after this zone could have been higher than that set for PEN. As extrusion pressure is related to viscosity, and as viscosity follows an Arrhenius type dependence with temperature, variations in temperature along the ultrasonic attachment would influence pressure readings greatly. Moreover, the blends had higher pressure than PET at a set temperature of 285°C, inferring that PEN would be expected to exhibit the highest pressure in processing at a set temperature of 285°C.

Pressure was observed to decrease with ultrasonic amplitude in all three materials. This was due to the thixotropic and permanent changes in viscosity with ultrasonic treatment, as well as the possible slip of polymer melt along the surface of the horns [7]. Pressure during extrusion does not indicate the final effect on polymers since its value depends on complicated thixotropic behavior of materials. Nevertheless, reduction in pressure with treatment was the least in the blend, indicating that the pressure reduction in the blend with increasing ultrasonic amplitude were due not only to permanent viscosity change caused by degradation in pure PET and PEN, but also to other reactions occurring in the blend.

6.3. Rheology

Complex viscosities of PET, PEN and their 50/50 blend were determined in a parallel plate rheometer at 280°C. A temperature of 280°C was chosen primarily to limit polymer degradation during viscosity measurements. Dynamic viscosity measurements in
rotational rheometer were performed faster than they could be performed in a capillary rheometer. This was due to faster pressure equilibration and shorter packing and melting times in the rotational rheometer, which was performed under a nitrogen atmosphere. Dynamic viscosity measurements were chosen as they minimized PET degradation and further transesterification during testing. Figure 6.2 illustrates the frequency dependence of complex viscosity for untreated and ultrasonically treated PET, PEN and blends. In this section, virgin PET and PEN were compression molded into discs and tested without any other processing for comparison of rheology with the extruded materials.

![Graph](image)

Figure 6.2. Complex viscosity at 280°C vs. ultrasonic amplitude for PET, PEN and their blend at angular frequencies of (a) 1 rad/s, and (b) 100 rad/s, with and without treatment.
From Figure 6.2a and b, it was observed that viscosity of untreated PEN is greater than viscosity of untreated 50/50 PEN/PET blend. Viscosity of the blend is higher than the viscosity of untreated PET. The viscosity of PEN decreased at all amplitudes of ultrasonic treatment. Ultrasonic treatment at an amplitude of 7.5 µm led to increased viscosity of PET. The viscosity of 50/50 PET/PEN blends did not change with ultrasonic treatment up to an amplitude of 10 µm, at which it increased slightly. While PET and the blends showed Newtonian behavior without and with ultrasonic treatment, PEN became more shear thinning with treatment at ultrasonic amplitudes of 7.5 and 10 µm, indicating extensive structural changes.

![Figure 6.3. Loss tangent vs. angular frequency at 280°C for PEN (solid symbols), 50/50 PEN/PET (grey symbols), and PET (open symbols) without and with ultrasonic treatment.](image)

Figure 6.3 shows the loss tangent vs. frequency behavior of PEN, PET, and 50/50 PEN/PET, without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm. Tan δ of PEN increased substantially with ultrasonic treatment, indicating reduction in
elasticity. Tan δ of PET was higher than the untreated PET at an amplitude of 10 µm and lower at an amplitude of 7.5 µm. The latter signified its increased elasticity with treatment at an amplitude of 7.5 µm. There was no change in the tan δ behavior of the 50/50 PET/PEN blends with ultrasonic treatment. These results signified that ultrasound affected the pure polymers and their blend very differently.

Figure 6.4. Cole-Cole plots at 280°C for PEN, 50/50 PEN/PET blend and PET without and with ultrasonic treatment at an amplitude of 10 µm.

Figure 6.4 shows the Cole Cole plots (G’ vs. G”) of PEN, PET, and their blend without and with ultrasonic treatment at an amplitude of 10 µm. Comparing the untreated materials, it was observed that G’ and G” functions of PET lied above that of the blend, which lied above that of PEN. The curves for components approached each other at high values of G” and G”. G’ vs. G” curves of PET and the 50/50 PET/PEN blend treated at an amplitude of 10 µm lied on the same curve as the untreated blend. The G’ vs. G” curve of PEN treated at an amplitude of 10 µm lied above the untreated PEN curve. This
difference in storage versus loss modulus between treated and untreated PEN indicated that significant structural changes had occurred at an amplitude of 10 μm.

For both PEN and PET, there is some degradation associated with passing through the extruder, as observed by comparing viscosities of virgin and untreated PET and PEN in Figure 6.2a and b. Comparison of untreated samples shows that PEN, PET and their blend show the highest, lowest, and intermediate viscosities, respectively. In contrast to the homopolymerization of PET with ultrasonic treatment at an amplitude of 7.5 μm, as shown by the increase in its viscosity (section 4.3), only degradation of PEN is observed with treatment, as shown by the reduction in its viscosity (section 5.3). Moreover, PEN exhibits shear thinning with ultrasonic treatment at amplitudes of 7.5 and 10 μm. In case of the blends, there is considerably less change in viscosity with ultrasonic treatment; however, an increase in the viscosity of the blend was recorded with treatment at an amplitude of 10 μm. The lack of degradation and some increase in viscosity in the case of the blend indicate that homo- and copolymerization reactions could be taking place with ultrasonic treatment. As the change in viscosity of the blend can be due to the competing interchange and degradation reactions, it is difficult to isolate these effects from viscosity data, as suggested by Tharmapuram and Jabarin [129].

6.4. FT-IR Spectroscopy

ATR FT-IR spectroscopy of untreated and ultrasonically treated PET, PEN and their blends were performed. The spectra of virgin PET and PEN, and untreated and ultrasonically treated 50/50 PET/PEN blends are shown in Figure 6.5.
It was previously stated that the FT-IR spectra of PET and PEN do not change with ultrasonic treatment and extrusion (sections 4.5 and 5.6, respectively). The spectra shown in Figure 6.5 indicated that no significant changes in FT-IR spectrum of 50/50 PET/PEN occurred with ultrasonic treatment as well. The positions of peaks in the blend were similar to a combination of peaks from PET and PEN.

![Figure 6.5. ATR FT-IR spectra of 50/50 PET/PEN without and with treatment compared to virgin PEN and PET.](image)

It was concluded from the FT-IR spectroscopy of PET/PEN blends that this technique is unable to detect structural differences and reactions in the polyester blends studied. This is primarily due to overlap in functional groups of polyesters and similarity of chemical chains in the copolymer to a physical mixture of the two polymers.
spectroscopy provides greater resolution and allows quantification of extent of copolymerization, as shown in section 6.5

6.5. $^1$H NMR Spectroscopy

$^1$H NMR spectroscopy was performed on untreated and ultrasonically treated PET/PEN blends to determine the extent of copolymerization. The expected product of PET/PEN ester exchange reactions is shown in Figure 6.6.

![Figure 6.6. Expected structure of copolymer of PEN and PET by transesterification.](image)

Figure 6.6 shows the NMR spectra of PET/PEN blends without and with treatment at an ultrasonic amplitude of 10 µm. In this figure, the ethylenes from PEN (NEN) and PET (TET) are seen at 4.88 ppm and 4.78 ppm, respectively. The presence of copolymer is detected from the ethylenic protons in the PEN/PET copolymer located at 4.83 ppm (NET), as expected [111].
Figure 6.7. $^1$H NMR relative intensity in 5-4.70 ppm range for 50/50 PEN/PET blend without and with ultrasonic treatment at an amplitude of 10 µm, based on normalized intensity of –NEN- ethylenes peak of untreated blend.

The areas under the ethylene peaks were measured for untreated and ultrasonically treated blends. $A_{\text{tet}}$, area under the ethylenes peak of PET, $A_{\text{nen}}$, area under the ethylenes peak of PEN, and $A_{\text{net}}$, area under the ethylenes peak of PET/PEN copolymer were measured after normalizing with respect to $A_{\text{nen}}$ for all conditions. These areas under NMR peaks and parameters calculated based on the equations 6.1-6.5, are shown in Table 6.2. Percent standard deviation (standard deviation/average*100) on the determined degree of randomness (B) was 0.2%.

Table 6.2. Areas of ethylene glycol groups of PEN, PET, and PEN/PET copolymer under $^1$H NMR peaks, and calculated parameters including degree of randomness (B) and average sequence lengths (L) of PET and PEN chains of untreated and ultrasonically treated PEN/PET blends.

<table>
<thead>
<tr>
<th>Amp.</th>
<th>$A_{\text{tet}}$</th>
<th>$A_{\text{net}}$</th>
<th>$A_{\text{nen}}$</th>
<th>$A_{\text{total}}$</th>
<th>$P_{\text{net}}$</th>
<th>$P_{\text{nen}}$</th>
<th>$P_n$</th>
<th>B (%)</th>
<th>L(N)</th>
<th>L(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm</td>
<td>2.38</td>
<td>0.62</td>
<td>2</td>
<td>4.97</td>
<td>0.125</td>
<td>0.402</td>
<td>0.465</td>
<td>25.1%</td>
<td>7.45</td>
<td>8.66</td>
</tr>
<tr>
<td>5 µm</td>
<td>2.74</td>
<td>0.7</td>
<td>2</td>
<td>5.44</td>
<td>0.129</td>
<td>0.368</td>
<td>0.432</td>
<td>26.2%</td>
<td>6.71</td>
<td>8.83</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>2.6</td>
<td>0.76</td>
<td>2</td>
<td>5.36</td>
<td>0.142</td>
<td>0.373</td>
<td>0.444</td>
<td>28.7%</td>
<td>6.26</td>
<td>7.84</td>
</tr>
<tr>
<td>10 µm</td>
<td>2.41</td>
<td>0.86</td>
<td>2</td>
<td>5.27</td>
<td>0.163</td>
<td>0.380</td>
<td>0.461</td>
<td>32.8%</td>
<td>5.65</td>
<td>6.60</td>
</tr>
</tbody>
</table>
Degree of randomness (% transesterification) was calculated based on the work by Stewart et al. [111]. The total area under the ethylene glycol peaks ($A_{\text{total}}$) was defined as:

$$A_{\text{total}} = A_{\text{tet}} + A_{\text{net}} + A_{\text{nen}}$$  \hspace{1cm} (6.1)

The mole fraction of ethylene glycols from PET ($P_{\text{tet}}$), copolymer ($P_{\text{net}}$), and PEN ($P_{\text{nen}}$) were:

$$P_{\text{tet}} = \frac{A_{\text{tet}}}{A_{\text{total}}}$$  \hspace{1cm} (6.2)

$$P_{\text{net}} = \frac{A_{\text{net}}}{A_{\text{total}}}$$  \hspace{1cm} (6.3)

$$P_{\text{nen}} = \frac{A_{\text{nen}}}{A_{\text{total}}}$$  \hspace{1cm} (6.4)

As equal amounts of ethylene glycols from PET and PEN were taken to be present in the copolymer, mole fractions of terephthalate ($P_{t}$) and naphthalate ($P_{n}$) units were obtained from

$$P_{t} = \frac{P_{\text{net}}}{2} + P_{\text{tet}}$$  \hspace{1cm} (6.5)

$$P_{n} = \frac{P_{\text{net}}}{2} + P_{\text{nen}}$$  \hspace{1cm} (6.6)

In a PEN/PET copolymer chain, the probability of finding an N unit next to a T unit ($P_{m}$) is

$$P_{m} = \frac{P_{\text{net}}}{2 \cdot P_{t}}$$  \hspace{1cm} (6.7)

Similarly, probability of finding a T unit next to an N unit in a PEN/PET copolymer chain ($P_{nt}$) is
\[ P_{nt} = \frac{P_{net}}{2 \times P_n} \]  \hspace{1cm} (6.8)

The degree of randomness (B) is defined as:

\[ B = P_{nt} + P_{in} = \frac{P_{net}}{2P_t} + \frac{P_{net}}{2P_n} \]  \hspace{1cm} (6.9)

From probability theory,

\[ P_t = 1 - P_n \]  \hspace{1cm} (6.10)

Therefore,

\[ B = \frac{P_{net}}{2 \times P_n \times (1 - P_n)} \]  \hspace{1cm} (6.11)

Defining the following

\[ (Net)_{exp} = P_{net} \]  \hspace{1cm} (6.12)

\[ (Net)_{cal} = 2P_n \times (1 - P_n) \]  \hspace{1cm} (6.13)

where (Net)_{exp} and (Net)_{cal} are the experimentally and statistically calculated ethylene glycol moieties from PEN/PET copolymer. Hence, degree of randomness (B), which is also defined as the extent of transesterification, is given by:

\[ B = \frac{(Net)_{exp}}{(Net)_{cal}} \]  \hspace{1cm} (6.14)

According to this definition, the value of B describes extent of copolymerization and its nature, as follows:

1. When B=1, N and T units are distributed randomly within the copolymer, such that a random copolymer following Bernoulli statistics is formed.
2. When B<1, N and T units form blocks of different length, leading to block copolymers.
3. When B=0, no copolymers are present and there is a mixture of homopolymers.

4. When B>1, sequence lengths decrease, leading to formation of alternating copolymers.

5. When B=2, a copolymer of alternating N and T units is formed.

The number average sequence lengths of N and T units are given by [310]:

\[
L(N) = \frac{2P_n}{P_{net}} = \frac{1}{P_{nt}} \\
L(T) = \frac{2P_t}{P_{net}} = \frac{1}{P_{tn}}
\]  

(6.15)  

(6.16)

The fraction of the area of copolymer peak to the total area of the three peaks was observed to increase from 12 to 16% with ultrasonic treatment at an amplitude of 10 μm. The extent of transesterification (B) in untreated and ultrasonically treated PEN/PET was calculated following Stewart et al. [111] based on the calculations presented above. The extent of transesterification was plotted against the amplitude of ultrasonic treatment in Figure 6.8. The extent of transesterification in PEN/PET blends after single screw extrusion without sonication was 25.0%. The extent of transesterification increased with amplitude of ultrasonic treatment, and was highest (32.8%) with treatment at an amplitude of 10 μm. The mean residence time in the extruder was 4.8 minutes. The long residence time, coupled with presence of shear intensive UCM and melt star mixing sections in the screw led to the high extent of transesterification just by extrusion. However, only 7 s ultrasonic treatment (mean residence time under ultrasonic horns in SONIC1 at 1 kg/hr) of the blend led to a 31% increase in extent of transesterification with treatment at an amplitude of 10 μm.
Figure 6.8. Extent of transesterification vs. ultrasonic amplitude for 50/50 PEN/PET blends.

The average sequence lengths of PET and PEN in the copolymer were calculated from Equations 6.15 and 6.16. These values are plotted in Figure 6.9.

Figure 6.9. Average sequence length L(N) of PEN, and L(T) of PET units in PEN/PET copolymer vs. amplitude of ultrasonic treatment.

As seen from Figure 6.9, the average sequence length of PET was higher in the copolymer. This was expected as the PET used in this study had a higher MW than PEN, as indicated by their intrinsic viscosities being 0.74 dl/g and 0.64 dl/g respectively. The
average sequence length of PEN blocks in the copolymer monotonously decreased with ultrasonic amplitude. The average sequence length of PET block in the copolymer was not affected with treatment at an amplitude of 5 µm, but decreased faster than for PEN at amplitudes of 7.5 and 10 µm. This could indicate that with treatment at 5 µm, chain scission of PEN phase occurred more readily and these shorter chains copolymerized with longer PET blocks. No conclusion could be drawn as to the rate of chain scission in PET and PEN components in the blend at amplitudes of 7.5 and 10 µm ultrasonic treatment based on Figure 6.9. However, as PEN is more viscous, its rate of diffusion is expected to be less than that of PET. It is therefore likely that PET blocks reacted in greater frequency than the PEN blocks with sonication at amplitudes of 7.5 and 10 µm, leading to larger decrease in average segment length of PET block than of the PEN block [111].

6.6. Mass Spectroscopy

   Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) spectroscopy was performed on PET, PEN, and their blends without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm. The aim of this study was to identify structural changes with ultrasonic treatment of pure PET, PEN and their 50/50 blend.

   Due to limited ionization of PET and PEN, the intensity at lower mass to charge (m/z) ratio range was higher, leading to higher signal to noise ratio in studying oligomers. Therefore, m/z of up to about 4000 was studied for comparison of structure of untreated and ultrasonically treated materials.
MALDI-TOF mass spectroscopy of PET was studied in literature [311, 312, 313]. The possible end groups suggested by Samperi et al. were used as a basis for the identification of PET species in MALDI-TOF mass spectra (MS) [312, 313]. Identification of end groups is of particular interest, as they influence interchange reactions [313]. In case of ultrasonically treated PET, this can provide insight into the homopolymerization and degradation reactions occurring with treatment.

Table 6.3 shows the chemical structure of the probable PET species and the legend for assignment of peaks in MALDI-TOF MS. This was based on the work of Samperi et al. [312, 313], and includes some additional species observed in the current study. The mass numbers are given with respect to species A, which is cyclic PET and their number of repeat units are identifies as (N). The mass spectra of untreated and ultrasonically treated PET are analyzed and compared with reference to this table. As can be seen from this table, different end groups of PET are probable. A single sodium ion can be bonded to each species due to use of sodium salt in sample preparation. Considering the presence of more than one chemically bound sodium ion is not required as this would change the m/z ratio and would not be easily observed in PET spectra as high molecular weight chains are not as easily ionized.

Mass spectra of PET in m/z range of (a) 2280-2470 and (b) 3050-3230 are shown in Figure 6.10 a and b. In these spectra, labels X_n refer to Table 6.3, with X being the chemical structure present and n being the number of repeat units.
<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical structure</th>
<th>M + Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Chemical structure A" /></td>
<td>(N) 0</td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Chemical structure B" /></td>
<td>(N-1) -26</td>
</tr>
<tr>
<td>B’</td>
<td><img src="image" alt="Chemical structure B’" /></td>
<td>(N-1) -4</td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Chemical structure C" /></td>
<td>(N) +18</td>
</tr>
<tr>
<td>C’</td>
<td><img src="image" alt="Chemical structure C’" /></td>
<td>(N) +40</td>
</tr>
<tr>
<td>D</td>
<td><img src="image" alt="Chemical structure D" /></td>
<td>(N) +44</td>
</tr>
<tr>
<td>E</td>
<td><img src="image" alt="Chemical structure E" /></td>
<td>(N) +62</td>
</tr>
<tr>
<td>F</td>
<td><img src="image" alt="Chemical structure F" /></td>
<td>(N) +84</td>
</tr>
<tr>
<td>G</td>
<td><img src="image" alt="Chemical structure G" /></td>
<td>(N) +88</td>
</tr>
<tr>
<td>H</td>
<td><img src="image" alt="Chemical structure H" /></td>
<td>(N) +132</td>
</tr>
<tr>
<td>I</td>
<td><img src="image" alt="Chemical structure I" /></td>
<td>(N) +148</td>
</tr>
<tr>
<td>J</td>
<td><img src="image" alt="Chemical structure J" /></td>
<td>(N-1) +122</td>
</tr>
<tr>
<td>K</td>
<td><img src="image" alt="Chemical structure K" /></td>
<td>(N-2) +78</td>
</tr>
</tbody>
</table>
Figure 6.10. Mass spectra of untreated and ultrasonically treated PET in m/z range of (a) 2280-2470 and (b) 3050-3230.
It can be seen from Figure 6.10 a and b that greater amounts of some species were present with treatment at an amplitude of 10 µm. These were the B, C, C’ and F groups. With reference to Table 6.3, the presence of these species indicated greater amount of hydroxyl and carboxyl end group terminated PET species after treatment at an amplitude of 10 µm. This could be due to greater extent of chain scission reactions at this amplitude. In fact, the presence of greater amount of F species in PET treated at 10 µm also indicated greater fractionation. The presence of a greater number of these end groups would promote interchange reactions, such as transesterification [103]. This explains why a greater amount of copolymer was observed by $^1$H NMR spectroscopy in 50/50 PET/PEN blends treated at an amplitude of 10 µm, as shown in section 6.5. Table 6.4 shows the chemical structure of the probable PEN species and legend for assignment of peaks in MALDI spectra. It should be noted that the species shown in this are very similar to those for PET shown in Table 6.3, with the presence of the naphthalene unit instead of the benzene ring. This was based on the provided for PET, which was developed with reference to the work of Samperi et al. [312, 313]. The mass numbers are given with respect to species A, which is cyclic PEN, and their number of repeat units is identified as (N). The mass spectra of untreated and ultrasonically treated PEN are analyzed and compared with reference to this table.

The mass spectra of PEN without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm in m/z range of (a) 3860-4030 and (b) 2880-3080 are shown in Figure 6.11a and b. In these spectra, labels $X_n$ refer to Table 6.4, with X being the species present and n the number of repeat units. Increase and decrease in relative intensities of spectral peaks are identified by (+) and (-), respectively.
Table 6.4. Probable PEN species and legend for peak assignment in MALDI spectra.

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical structure</th>
<th>M + Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Chemical structure of A" /></td>
<td>(N) 0</td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Chemical structure of B" /></td>
<td>(N-1) -26</td>
</tr>
<tr>
<td>B’</td>
<td><img src="image" alt="Chemical structure of B’" /></td>
<td>(N-1) -4</td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Chemical structure of C" /></td>
<td>(N) +18</td>
</tr>
<tr>
<td>C’</td>
<td><img src="image" alt="Chemical structure of C’" /></td>
<td>(N) +40</td>
</tr>
<tr>
<td>D</td>
<td><img src="image" alt="Chemical structure of D" /></td>
<td>(N) +44</td>
</tr>
<tr>
<td>E</td>
<td><img src="image" alt="Chemical structure of E" /></td>
<td>(N) +62</td>
</tr>
<tr>
<td>F</td>
<td><img src="image" alt="Chemical structure of F" /></td>
<td>(N) +84</td>
</tr>
<tr>
<td>G</td>
<td><img src="image" alt="Chemical structure of G" /></td>
<td>(N) +88</td>
</tr>
<tr>
<td>I</td>
<td><img src="image" alt="Chemical structure of I" /></td>
<td>(N) +1  +198</td>
</tr>
</tbody>
</table>
Figure 6.11. Mass spectra of untreated and ultrasonically treated PEN in m/z range of (a) 3860-4030 and (b) 2880-3080.
It is observed from Figure 6.11a and b that changes occur in the relative intensities of B, B’, C, D, E, G species. Greater amount of B, B’, C, and D species signified the presence of a larger number of hydroxyl and carboxyl terminated PEN species. Similar to observation on PET ultrasonically treated at an amplitude of 10 µm, the presence of greater number of hydroxyl and carboxyl end groups indicated greater potential for interchange reactions.

The increase in the amount of D, E and G species present in spectra of PEN with ultrasonic treatment at amplitudes of 7.5 and 10 µm indicated greater fractionation of PEN with treatment. This indicated more degradation of PEN with ultrasonic treatment. It should be noted that species D and G were also cyclic. The increased amount of these species with ultrasonic treatment indicated greater interchange reactions, in this case intrachain recombination to create cyclic PEN.

Mass spectra of the 50/50 PET/PEN blend were analyzed in order to observe the copolymer units present and their structure. Cyclic PET/PEN copolymer, $A_{x,y}$, is expected to have the following structure:

![Cyclic PET/PEN copolymer structure](image)

where $x$ and $y$ are the number of PET and PEN repeat units in the copolymer with a total of $N$ repeat units. Molecular weight of PET repeat unit is 192.17 g/mol, while that of PEN is 242.23 g/mol. Molecular weight of sodium (Na) is 22.99 g/mol. Based on these values, the molecular weights of possible copolymers of PET/PEN blends containing Na$^+$...
was calculated. The results for copolymers with molar mass of up to 3000 g/mol molecular are shown in Table 6.5.

Table 6.5. Molecular weights of Na$^+$ containing cyclic oligomers of PET (x), PEN (y), and cyclic PET/PEN (x,y) copolymers with molecular weights up to 3000 g/mol.

| x,y Polyethylene terephthalate (PET), x | Polyethylene naphthalate (PEN), y |
|----------------------------------------|
| 0 1 2 3 4 5 6 7 8 9 10 11 12          | 265 507 749 991 1233 1475 1717 1959 2202 2444 2686 2928 |
| 1 215 457 699 941 1183 1425 1667 1909 2151 2394 2636 2878 |
| 2 407 649 891 1133 1375 1617 1859 2101 2344 2586 2828 |
| 3 599 841 1083 1325 1567 1809 2051 2294 2536 2778 |
| 4 791 1033 1275 1517 1759 2001 2244 2486 2728 2970 |
| 5 983 1225 1467 1709 1951 2193 2436 2678 2920 |
| 6 1175 1417 1659 1901 2143 2386 2628 2870 |
| 7 1367 1609 1851 2093 2336 2578 2820 |
| 8 1559 1801 2043 2286 2528 2770 |
| 9 1751 1993 2235 2478 2720 2962 |
| 10 1943 2185 2428 2670 2912 |
| 11 2135 2378 2620 2862 |
| 12 2327 2570 2812 |
| 13 2520 2762 |
| 14 2712 2954 |
| 15 2904 |

The spectra of untreated PET, PEN and 50/50 PET/PEN blend were compared in order to identify the presence of copolymer. A comparison of spectra in the m/z range of 1980 to 2940 is presented in Figure 6.12a-c. In this figure, copolymer species were identified as $A_{x,y}$. A referred to the cyclic PET/PEN copolymer species, and x, y referred to the number of PET and PEN segments in the copolymer. It should be noted that the copolymers present were not necessarily diblock or random; their block structure could not be identified from mass spectra. However, average block length of PET and PEN in the untreated and ultrasonically treated 50/50 blend was determined by $^1$H NMR, as explained in section 6.5.
Effect of ultrasonic treatment on the presence of copolymers in 50/50 PET/PEN blends was also studied. Mass spectra of untreated and ultrasonically treated 50/50 PET/PEN blends in the m/z range of (a) 1970-1480 and (b) 2320-2800 are shown in Figure 6.13. In these spectra \( H_{6,0} \) identified with reference to Table 6.3 is the cyclic PET species without an alkyl group. The cyclic copolymers were identified by \( A_{x,y} \). (+) and (-) following \( A_{x,y} \) was used to denote increases and reductions, respectively, in intensity of copolymer peaks. It can be observed that the amount of copolymer increases over that present without treatment following ultrasonic treatment at an amplitude of 7.5 \( \mu \text{m} \), and further increases with treatment at an amplitude of 10 \( \mu \text{m} \).
Figure 6.13. Mass spectra of ultrasonically treated and untreated 50/50 PET/PEN blends with copolymers indicated in the m/z range of (a) 1970-1480 and (b) 2320-2800.
6.7. Thermal analysis

Thermal characterization of PET, PEN and their 50/50 blend was performed by differential scanning calorimetry (DSC). The results from the second heating run were used for comparison to eliminate the effect of different thermal histories. The DSC endotherms of PET, PEN and 50/50 PET/PEN blend without and with ultrasonic treatment at an amplitude of 10 µm are shown in Figure 6.14a and b, respectively.

Figure 6.14. Heat flow vs. temperature during DSC second heating for (a) PEN, PET, and 50/50 PEN/PET without treatment, and (b) with ultrasonic treatment at an ultrasonic amplitude of 10 µm.
The glass transition ($T_g$), cold crystallization ($T_{cc}$) and melting temperatures ($T_m$), and crystallinity ($X_c$) of PET and PEN are reported in Table 6.6. It should be noted that the 50/50 PEN/PET blends showed no crystallization exotherms or melting endotherms, without and with ultrasonic treatment.

Table 6.6. DSC results for PEN and PET.

<table>
<thead>
<tr>
<th>DSC 2nd heating</th>
<th>PET</th>
<th></th>
<th>PEN</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Virgin</td>
<td>77.3</td>
<td>165.1</td>
<td>0.4</td>
</tr>
<tr>
<td>0 μm</td>
<td>76.5</td>
<td>130.5</td>
<td>20.9</td>
<td>251.4</td>
</tr>
<tr>
<td>5 μm</td>
<td>76.4</td>
<td>129.8</td>
<td>22.3</td>
<td>251.4</td>
</tr>
<tr>
<td>7.5 μm</td>
<td>77.0</td>
<td>132.5</td>
<td>21.6</td>
<td>252.2</td>
</tr>
<tr>
<td>10 μm</td>
<td>75.4</td>
<td>121.9</td>
<td>26.4</td>
<td>252.7</td>
</tr>
<tr>
<td>Virgin</td>
<td>125.0</td>
<td>214.3</td>
<td>3.8</td>
<td>270.4</td>
</tr>
<tr>
<td>0 μm</td>
<td>122.8</td>
<td>204.8</td>
<td>4.5</td>
<td>269.6</td>
</tr>
<tr>
<td>5 μm</td>
<td>123.3</td>
<td>204.6</td>
<td>2.2</td>
<td>270.3</td>
</tr>
<tr>
<td>7.5 μm</td>
<td>120.5</td>
<td>178.5</td>
<td>21.9</td>
<td>269.8</td>
</tr>
<tr>
<td>10 μm</td>
<td>120.6</td>
<td>179.2</td>
<td>20.0</td>
<td>270.1</td>
</tr>
</tbody>
</table>

From Table 6.6, it is seen that PET crystallinity in second heating run is much higher after extrusion. Moreover, crystallinity of extruded PEN treated at an amplitude of 10 μm is 20% in comparison with 4.5% for untreated (0 μm) PEN. These changes indicate reduction in MW of PET and PEN with treatment at the respective ultrasonic amplitudes. In contrast, the second heating run for the 50/50 PEN/PET blend does not show any crystallization or melting. Lower or no crystallinity is expected with transesterification in the blend [110, 113, 123] due to reduction in sequence length of PET and PEN blocks.
Figure 6.15 shows the heat flow versus temperature curves in the glass transition range for PET, PEN and 50/50 PET/PEN. The shape of the glass transition curve is different with ultrasonic treatment of PET and PEN. In 50/50 PET/PEN blends, a shift of glass transition temperature to higher temperature range is observed.

The glass transition temperatures of 50/50 PET/PEN blends that were experimentally determined by DSC second heating runs and theoretically calculated by employing Fox, and Gibbs-DiMarzio relations are shown in Table 6.7. It should be noted that the Fox equation does not account for the different densities of the crystalline and amorphous phases in semicrystalline polymers. While Fox equation cannot provide an
accurate representation of the current system involving semicrystalline polymers, results obtained by this relation were provided for reference.

Table 6.7. Glass transition temperatures of 50/50 PET/PEN blends that were determined in DSC second heating runs and calculated by Fox, and Gibbs-DiMarzio relations.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$T_g$-exp (°C)</th>
<th>$T_g$-Fox eq. (°C)</th>
<th>$T_g$-Gibbs-DiMarzio (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>-</td>
<td>95.5</td>
<td>98.4</td>
</tr>
<tr>
<td>0 µm</td>
<td>95.1</td>
<td>94.3</td>
<td>97.0</td>
</tr>
<tr>
<td>5 µm</td>
<td>98.2</td>
<td>94.3</td>
<td>97.1</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>97.3</td>
<td>94.0</td>
<td>96.2</td>
</tr>
<tr>
<td>10 µm</td>
<td>98.0</td>
<td>92.8</td>
<td>95.4</td>
</tr>
</tbody>
</table>

Referring to Table 6.6, only a slight reduction in $T_g$ of PET is observed with ultrasonic treatment at an amplitude of 10 µm, while there is a pronounced decrease in $T_g$ for PEN at amplitudes of 7.5 and 10 µm, indicating its degradation. There is an increase in $T_g$ for the blend with ultrasonic treatment. $T_g$ of 50/50 PET/PEN blend is shown in Table 6.7. The experimentally determined $T_g$ of the untreated and ultrasonically treated blends was compared with theoretical predictions of $T_g$ from Fox equation (Eq. 2.6) and Gibbs-DiMarzio equation (Eq. 2.7).

Using the Fox equation (Eq. 2.6) for miscible blends [84] based on the $T_g$’s of virgin PEN and PET gives a value of 95.5°C for 50/50 PEN/PET. Using $T_g$’s of untreated (0 µm) PEN and PET, on the other hand, gives a value of 94.3°C for the blend. The experimentally determined $T_g$ of untreated blend was 95.1°C and lied in between the two predicted values, but was closer to theoretical value obtained using $T_g$’s of virgin materials. This indicated miscibility of the untreated PET/PEN blend, and suggested reduced degradation of PET and PEN with extrusion in the blend as compared to the
extrusion of pure materials. The latter could be due to recombination reactions that limit degradation in the blend.

The Gibbs-DiMarzio equation (Eq. 2.7) is used for random copolymers, rather than miscible polymer blends [85, 86]. Using this equation based on the $T_g$ of PEN and PET at 0 $\mu$m gives a value of 97.2 for 50/50 PEN/PET. This value is closer to $T_g$ of blend after ultrasonic treatment at different amplitudes. As also suggested by Shi and Jabarin, this indicated random copolymer behavior in PET/PEN blend [87, 314], signifying greater randomization and changes in chemical structure with ultrasonic treatment.

6.8. Dynamic Mechanical Analysis

Figure 6.16 shows the temperature dependence of loss tangent of PEN, PET and their blend as determined by DMA. It is observed that the value of tan $\delta$ peak of PEN increases and its position shifts to lower temperature with ultrasonic treatment, indicating its degradation at all amplitudes. Tan $\delta$ peak for 50/50 PEN/PET lies in between the respective peaks of PEN and PET. Its intensity was not affected by ultrasound. A slight shift to higher temperature was observed at an amplitude of 10 $\mu$m for 50/50 PEN/PET blends.
Figure 6.16. Loss tangent vs. temperature for PEN, PET and their blend with and without ultrasonic treatment.

6.9. Mechanical Properties

The changes in Young’s modulus, tensile strength, elongation at yield and impact strength of untreated and ultrasonically treated PET, PEN and 50/50 PET/PET blends were studied. In this section, virgin PET and PEN were injection molded into specimens for testing without any other processing for comparison of mechanical properties with materials that were extruded before injection molding.

The Young’s modulus (Figure 6.17) of PEN shows the highest values, followed by 50/50 PEN/PET, and PET. The 95% confidence intervals were shown in these figures. The changes in the Young’s modulus with ultrasonic treatment had relatively large confidence intervals. The Young’s modulus of PEN decreased with extrusion, and further
decreased with increasing amplitude of ultrasonic treatment. This indicated degradation of PEN with ultrasonic treatment. The Young’s modulus of PET was not affected by extrusion without and with ultrasonic treatment at amplitudes of 5 and 7.5 µm. The Young’s modulus of PET indicated a slight increase with treatment at an amplitude of 10 µm. 50/50 PET/PEN indicated an increase in the Young’s modulus with treatment at an amplitude 7.5 µm.

Figure 6.17. Young's modulus vs. ultrasonic amplitude for PEN, PET and their 50/50 blend (values shifted along abscissa for clarity).
Figure 6.18. Strength vs. ultrasonic amplitude for PEN, PET and their 50/50 blend (values shifted along abscissa for clarity).

Figure 6.18 shows the strength of PET, PEN and 50/50 PET/PEN versus amplitude of ultrasonic treatment. Untreated PEN shows the highest value of strength, followed by untreated 50/50 PEN/PET, and PET. Extrusion without treatment (0 µm) led to a decrease in the strength of PEN and an increase in that of PET. The strength of PEN was significantly reduced with ultrasonic treatment at an amplitude of 10 µm, indicating its degradation.
Elongation at yield (Figure 6.19) is highest in PET, followed by PEN and 50/50 PET/PEN. There is a slight decrease in elongation at yield for PEN and PET after extrusion and a further decrease for PEN with ultrasonic treatment at an amplitude of 10 µm. Elongation at yield of PET increased over untreated PET (0 µm) with ultrasonic treatment at amplitudes of 7.5 and 10 µm.
Figure 6.20. Impact strength vs. ultrasonic amplitude for PEN, PET and their 50/50 blend (values shifted along abscissa for clarity).

Impact strength of PEN, PET and 50/50 PET/PEN is shown in Figure 6.20. The indicated values were averages of dead end (DE) and gate end (GE) impact bars, which were found to be statistically indifferent. Impact strength of both virgin PET and PEN decreased with extrusion without treatment. Among the untreated materials (0 µm) the 50/50 blend had the greatest impact strength, followed by PET and PEN. This could be due to reduced degradation of the blend during extrusion due to exchange reactions in the extruder. The impact strength of 50/50 blend indicated a slight increase with treatment at amplitudes of 7.5 and 10 µm. On the other hand, impact strength of PEN dropped with treatment at 7.5 and 10 µm, while that of PET decreased only with treatment at an amplitude of 10 µm. PET also showed an increase in impact strength at an amplitude of
7.5 μm. Overall, it was concluded that the mechanical properties of the blend are retained with ultrasonic treatment, indicating that copolymerization dominates over degradation.

6.10. Oxygen Permeability

Oxygen permeability of PET, PEN and 50/50 PET/PEN blends were determined from compression molded films. The average thickness ± standard deviation for each prepared film is shown in Table 6.8. It should be noted that the sample of PEN treated at an amplitude of 10 μm was too brittle. Film for permeability testing of this material breaks down by removal from the mold. Therefore, it was not tested.

Table 6.8. Thickness of films (μm) of PET, PEN and their blend in μm, without and with ultrasonic treatment at amplitudes of 7.5 and 10 μm.

<table>
<thead>
<tr>
<th></th>
<th>0 μm</th>
<th>7.5 μm</th>
<th>10 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>216 ± 8</td>
<td>231 ± 12</td>
<td>218 ± 7</td>
</tr>
<tr>
<td>50/50 PET/PEN</td>
<td>227 ± 11</td>
<td>231 ± 15</td>
<td>250 ± 14</td>
</tr>
<tr>
<td>PEN</td>
<td>223 ± 8</td>
<td>219 ± 10</td>
<td>231 ± 16</td>
</tr>
</tbody>
</table>

Figure 6.21. Oxygen transmission rate vs. time curves for PET, PEN and their 50/50 blend without and with ultrasonic treatment.
Figure 6.21 shows the oxygen transmission rate vs. time plots of PET, PEN and their blend without and with ultrasonic treatment. These plots indicated good equilibration and validated the dependability of results. The $O_2$ permeability coefficient was obtained by multiplication of oxygen transmission rate obtained from testing by film thickness and its division by $O_2$ pressure. This yielded a normalized value to compare permeability of materials. Figure 6.22 shows $O_2$ permeability coefficient vs. ultrasonic amplitude for PET, PEN and 50/50 blend. No changes in $O_2$ permeability coefficient of PET, PEN, and their 50/50 blend were observed with ultrasonic treatment.

Figure 6.22. Oxygen permeability of PET, PEN and their blend without and with ultrasonic treatment at different amplitudes.

The most common range of values for $O_2$ permeation coefficient of unoriented PET indicated in literature at a testing temperature of 25°C are between 0.118-0.237 cm$^3$/m$^2$*h*0.1MPa (1.2-2.4 cm$^3$* mm/(m$^2$*day*atm) [315]). The untreated PET was determined to have an $O_2$ permeation coefficient of 0.148 cm$^3$/m$^2$*h*0.1MPa in this
study. Results are therefore within the range reported in literature. For unoriented PEN in literature, $O_2$ permeation coefficient values are between 0.052-0.148 cm$^3$/(m$^2$*24h*0.1MPa) (0.525-1.5 cm$^3$*mm/(m$^2$*day*atm) [315]). This value was 0.044 cm$^3$/(m$^2$*24h*0.1MPa) for untreated PEN in this study. Variations between results of different research groups could be explained by differences in crystallinity, molecular weight, and additives used in materials. Nevertheless, the permeation coefficient results are highly reproducible with a standard deviation of 3%.

Gas permeability of polymer blends depends on the permeabilities of pure components, and their miscibility. Robeson defined limits of gas permeability, $P$, based on miscibility and immiscibility of a given system [316]. For miscible blends indicating presence of copolymers, it value is given by:

$$\ln P = \phi_a \ln P_a + \phi_b \ln P_b$$  \hspace{1cm} (6.19)

For immiscible blends, the upper bound model for $P$ given by parallel combination holds, when the more permeable component is the continuous phase:

$$P = \phi_1 P_1 + \phi_2 P_2$$  \hspace{1cm} (6.20)

The lower bound model for $P$ given by series combination holds, when less permeable component is the continuous phase:

$$P = \frac{P_1 + P_2}{\phi_1 P_1 + \phi_2 P_2}$$  \hspace{1cm} (6.21)
Figure 6.23. Oxygen permeability of PET/PEN blend in comparison to theoretical predictions based on blend miscibility.

The oxygen permeability of untreated PET, PEN and 50/50 blend were plotted against theoretical predictions of permeability of immiscible and miscible polymers in Figure 6.23. The permeability coefficient for 50/50 PET/PEN blends lied closest to the miscible system, although did not follow it exactly.

6.11. Optical transmittance of the molded films

Optical clarity of polymers is important in many applications. Especially in packaging industry, for which PET and PEN are commonly used, optically good clarity is generally a requirement.
Figure 6.24. Transmittance in wavelength range of 800-200 nm for untreated and ultrasonically treated (a) PET, (b) PEN, (c) 50/50 PET/PEN blends.
As previously described, PET/PEN films with only 10% variation in thickness were molded under the same conditions, including the fast cooling of the films. All films appeared visually clear and differences in transparency of PET, PEN and 50/50 PEN/PET films without and with ultrasound could not be identified visually. Transmittance of these films to UV-visible-near infrared (wavelengths of 800-200 nm) was determined. The % transmittance vs. wavenumber curves for PET, PEN, and their 50/50 blend, corrected for thickness with respect to an average film thickness of 230 µm (as indicated by Table 6.8) using Beer-Lambert law as explained in section 3.3.13, are shown in Figure 6.24a-c.

It can be observed from Figure 6.24a-c that transmittance of PEN and 50/50 PET/PEN to the UV region drops at a wavelength of 380 nm. On the other hand, PET starts blocking UV light at a wavelength of about 320 nm. The lower transmittance of PEN and the blends to UV light can be employed in UV barrier applications [301]. The transparency to visible light was around 90% in all conditions. The average transmittance to visible light, calculated in the wavelength range of 750-450 nm, is shown in Table 6.9. It should be noted that the tabulated results were already corrected for differences in sample thickness, and are the average transmittance values for 230 µm thick films.

As seen from Table 6.9, the average optical transparency of PET and 50/50 PET/PEN indicated little change with ultrasonic treatment. On the other hand, the

<table>
<thead>
<tr>
<th>Amplitude (µm)</th>
<th>PET</th>
<th>PEN</th>
<th>50/50 PET/PEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.7</td>
<td>90.2</td>
<td>90.0</td>
</tr>
<tr>
<td>7.5</td>
<td>90.0</td>
<td>87.2</td>
<td>89.1</td>
</tr>
<tr>
<td>10</td>
<td>88.2</td>
<td>85.3</td>
<td>89.7</td>
</tr>
</tbody>
</table>

Table 6.9. Average transmittance (%) of PET, PEN and 50/50 PET/PEN to visible light in the wavelength range of 750-450 nm.
transmittance of PEN was observed to decrease with amplitude of ultrasonic treatment. The reduction in transmittance of PEN could be due to ultrasonically created microcavities in PEN, which could not be totally removed during compression molding of films. The lack of significant change in transmittance of 50/50 PET/PEN blend with amplitude of ultrasonic treatment indicated that the extended transesterification due to ultrasonic treatment had no influence on its transparency.

Total random copolymer formation in PET/PEN blends is not required to obtain optically clear blends. Approximately 10% transesterification is sufficient to obtain total clear blends. Above this critical level, additional transesterification is not expected to affect transparency [111]. The extent of transesterification of PET/PEN blends in this work is 25.0% without treatment, which is above the critical value required for optical clarity.

Multiple passes through a single screw extruder or shear intensive twin screw extrusion are commonly required in order to obtain optically clear blends [121]. However, in the study of ultrasonic extrusion of PET/PEN blends, very low screw speed (13 rpm) was used. This led to an average residence time of 4.8 minutes in the extruder, as calculated from the free volume in the extruder and the volumetric flow rate. Therefore, an already high level of transesterification was obtained after passing through the extruder once without treatment. The residence time in the ultrasonic treatment zone, in extruder was 7s for a flow rate of 1 kg/hr. The ultrasonic extrusion process can be scaled up to larger extruders. Comparable residence times and effects of ultrasonic treatment can therefore be obtained at higher flow rates. Hence, ultrasonic treatment could provide a level of transesterification to significantly affect optical properties when
the extent of transesterification in extruded blends is below the critical level (5 mol% [119]) required for clarity after extrusion without treatment. This would translate to faster processing with extrusion at higher rpms, use of less shear intensive section and reduced number of passes through the extruder with sonication. Each additional processing operation causes degradation of polymer melt, which can adversely affect mechanical properties and cause yellowing of the sample [115]. Degradation was not observed with ultrasonic treatment of PET/PEN blends based on the rheological, thermal and mechanical properties studied in this chapter. Hence, it could be expected that in order to obtain blends with good clarity, less polymer degradation could be obtained in ultrasonic extrusion of PET/PEN blends than with multiple-step, high-shear processing or high temperature processing [121, 122].

6.12. Conclusions

PEN, PET and their 50/50 blend were ultrasonically extruded. The effects of ultrasonic treatment on the 50/50 PET/PEN blend, the amount and structure of PET/PEN copolymers were studied.

Fast homopolymerization during extrusion of PET was found to occur at an ultrasonic amplitude of 7.5 μm. In contrast, degradation of PEN was observed with ultrasonic treatment. MALDI-TOF spectra of PET treated at an amplitude of 10 μm and of PEN treated at amplitudes of 7.5 and 10 μm showed increased amounts of hydroxyl and carboxyl terminated chain. This indicated greater reactivity of PET and PEN with ultrasonic treatment. Ultrasonic treatment at short residence time led to the enhancement
of transesterification reaction in the PEN/PET blend, indicating that more copolymerization occurred during ultrasonic treatment.

The untreated PET/PEN blends were miscible, as indicated by their $T_g$. The extent of transesterification of untreated blend was determined to be 25.0% by $^1$H NMR. The ultrasonic treatment of 50/50 PEN/PET increased the extent of transesterification to 32.9% at an amplitude of 10 $\mu$m. The block length of PET and PEN domains decreased with increasing amplitude of ultrasonic treatment. MALDI-TOF mass spectroscopy of the blends indicated the formation of greater amount of copolymer species with ultrasonic treatment, which were mostly cyclic in the range of 2000-3000 Daltons.

While PET and PEN exhibited cold crystallization exotherms and melting endotherms upon second heating, these phase transitions were absent in 50/50 PET/PEN blends, both without and with ultrasonic treatment. This indicated that the degree of randomness in the PET/PEN copolymer formed by blending was too high to permit crystallization of PET and PEN blocks under the studied conditions. This also showed that co-crystallization was absent in PET/PEN blends under the testing conditions.

The glass transition temperatures of ultrasonically treated blends determined by DSC were higher and correlated with those obtained for the blend by the Gibbs-DiMarzio equation using $T_g$’s of untreated and as-received PET and PEN. This also indicated increased chemical reactions and copolymer of greater degree of randomness with ultrasonic treatment. Viscosity of the blend was highest at an amplitude of 10 $\mu$m. Mechanical properties of the blend were not affected by ultrasonic treatment.

The oxygen permeability of 50/50 PET/PEN blends lied in between PET and PEN, close to theoretical prediction of permeability of miscible polymers. The
permeabilities of PET, PEN and 50/50 PET/PEN were not affected by ultrasonic treatment.

The average optical transmittance of compression molded films prepared from PET, PEN and their 50/50 blend were around 90% without ultrasonic treatment. Transmittance of PEN was observed to decrease with amplitude of ultrasonic treatment. There were no significant changes in transmittance of PET and the blend with ultrasonic treatment. The lack of change in clarity of blends with sonication was attributed to the already high extent of transesterification after extrusion without treatment.
CHAPTER VII
BLEND OF LCP1/LCP2

LCP1 based on hydroxybenzoic and hydroxynaphthoic acid, and LCP2 based on terephthalic and isophthalic acid, and dioxydiphenyl, and their blends were studied in this section. Rheological, thermo-mechanical, mechanical, and morphological characterizations were carried out to investigate effect of ultrasonic treatment in this system.

7.1. Introduction

Liquid crystalline polymers have many advantages over thermoplastics in a variety of application. The major attraction of LCPs is the in-situ formation of highly oriented fibrillar structures under elongational flows during processing. LCP1 domains are readily oriented during processing, leading to reduced viscosity and pressure which can be cost saving features [1]. Many commercial LCPs are highly aromatic, and possess good thermal properties, chemical resistance and superior mechanical properties in fibers and moldings.

Blending of two LCPs provides different effects than blending of semicrystalline polymers as they are processed in the liquid crystalline state. Due to the presence of mesogenic backbone or side chain groups, LCPs form semiflexible rods during processing, which can chemically interact with one another.
Kenig et al. studied orientation in blends of LCP1 with 60/20/20 HNA/TA/acetoxy-acid aniline, enhanced orientation was observed in the blends due to synergistic fibrillation, which was attributed to miscibility [249]. Enhanced fibrillation of LCP1 (HBA/HNA copolymer)/LCP2 (terephthalic acid, isophthalic acid, dioxydiphenyl copolymer) blends in injection moldings was observed by Akhtar and Isayev [12]. Blending at equal ratios was observed to lead to enhanced molecular orientation due to better deformation of the LCPs and resulted in synergistic improvements in the secant modulus at 1% strain, tensile strength, and impact strength, above that of either component. A more detailed literature survey on blends of LCPs was presented in section 2.6.4. In summary, it was found that the morphology and mechanical properties of blends were governed by the block structure of the LCPs, composition, viscosities and miscibility [157, 158].

The effects ultrasonic treatment on LCP1 and the improved mechanical properties observed with its ultrasonic treatment were discussed in CHAPTER IV. Pure LCP1 was not processed again for this study, and results from the previous chapters were used for comparison. It was of interest to investigate the effect of ultrasonic treatment on another wholly aromatic liquid crystalline copolyester.

Blends of liquid crystalline polymers are not expected to follow the rule of mixtures. A synergic fibrillation effect can occur during the processing of LCP blends. As LCP1/LCP2 blends were reported to be immiscible and exhibit synergic fibrillation in moldings [12], it was of interest to study if compatibilization could be introduced in this blend by ultrasonic treatment.
7.2. Process Characteristics

LCP2 and LCP1/LCP2 blends were processed in SONIC1 at a temperature of 300°C. The screw used had two mixing sections and with screw flights after the ultrasonic treatment zone. LCP1 was first extruded at 285°C in the earlier study presented in CHAPTER IV. In order to compare process characteristics of LCP1 with LCP2 and the blends at 300°C, LCP1 had been extruded again at 300°C without the collection of material. The results for LCP1 process characteristics presented in this section are those of LCP1 extruded at 300°C, presented in section 5.2. All other data reported for LCP1 in this chapter are based on results obtained with extrusion at a temperature of 285°C in SONIC1 with the additional mixing section at the end of the screw, and are the same as those for LCP1 presented in CHAPTER IV. For processing of LCP2 and LCP1/LCP2 blends, the temperature control system of the ultrasonic horns was modified. Instead of being cooled with constant flow rate tap water, they were regulated at a temperature of 80°C by temperature controller recirculating water.

The barrel temperature at the ultrasonic treatment zone ($T_{\text{ultra}}$), the melt temperature at the connection of the original extruder barrel to the ultrasonic attachment ($T_{\text{melt}}$), and the extruder torque were recorded. The results are listed in Table 7.1. The torque was rather low at 1.5 Amps and was the same for all conditions with a standard deviation of 0.2 Amps.

As can be observed from Table 7.1, the barrel temperatures in the ultrasonic treatment zone ($T_{\text{ultra}}$) were similar during extrusion of different samples. LCP1 barrel temperature without treatment, and its melt temperature both without and with treatment were lower. These lower than set temperatures during extrusion were also observed in the
processing of PEN/LCP1 blends (section 5.2). These lower than set melt temperature could be due to reduced efficiency of a heater at the connection of the ultrasonic attachment to the original extruder at the time when pure LCP1 was processed at a set temperature of 300°C for comparison of process characteristics.

Table 7.1. Temperature at the ultrasonic treatment zone ($T_{\text{ultra}}$), melt temperature ($T_{\text{melt}}$), and extruder torque measured during processing of LCP1/LCP2 blends.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Amplitude (µm)</th>
<th>$T_{\text{ultra}}$ (°C)</th>
<th>$T_{\text{melt}}$ (°C)</th>
<th>Torque (Amp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCP1</td>
<td>0</td>
<td>293</td>
<td>286</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>286</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>287</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>286</td>
<td></td>
</tr>
<tr>
<td>75/25 LCP1/LCP2</td>
<td>0</td>
<td>299</td>
<td>299</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>50/50 LCP1/LCP2</td>
<td>0</td>
<td>299</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>301</td>
<td>304</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>299</td>
<td></td>
</tr>
<tr>
<td>25/75 LCP1/LCP2</td>
<td>0</td>
<td>299</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>297</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>297</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>299</td>
<td></td>
</tr>
<tr>
<td>LCP2</td>
<td>0</td>
<td>299</td>
<td>308</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>300</td>
<td>303</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>301</td>
<td>303</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>296</td>
<td></td>
</tr>
</tbody>
</table>

There was some variation in the melt temperatures. Use of high power ultrasound is expected to increase temperature of the process due to dissipation of some of the sonic energy as heat. The temperature of the horns was regulated at 80°C in LCP2 and LCP1/LCP2, as opposed to cooling with constant temperature tap water. The changes in
melt temperatures in this system did not appear to follow any particular pattern and has a larger standard deviation than in the processing of the other blends. As the only difference was the use of a water temperature controller for the blends, the changes in melt temperatures, measured in close proximity to the ultrasonic horns controlled by the newly installed temperature controller, could account for the variations in temperature. Nevertheless, the control of temperature of water passing through ultrasonic horns was expected to improve the process characteristics as compared to cooling of the horns with tap water at constant flow rate.

![Graph showing ultrasonic power consumption vs. LCP1 concentration](image)

**Figure 7.1.** Average ultrasonic power consumption vs. LCP1 concentration in untreated and ultrasonically treated LCP1/LCP2 blends.

The average ultrasonic power consumption of the horns is shown in Figure 7.1, along with standard deviations. It was observed that LCP1 had slightly higher power consumption than LCP2 and the blends, which had similar power consumption. In 75/25
LCP1/LCP2 blends, the variation in power consumption was higher than in the other blends. This could be due to the higher power consumption of LCP1.

![Figure 7.2. Pressure vs. LCP1 concentration in untreated and ultrasonically treated LCP1/LCP2 blends.](image)

The pressure before the ultrasonic treatment zone is shown in Figure 7.2, along with standard deviations. Untreated LCP1 had the highest pressure, probably due to the lower melt temperature at this condition. Pressure was observed to decrease with ultrasonic treatment. The change in pressure is a result of thixotropic and permanent changes with ultrasonic treatment. The decrease in pressure was largest for LCP1. This could be due to lower melt temperature and higher pressure without treatment for LCP1, which could have resulted in a greater thixotropic reduction with ultrasonic treatment. The pressure was lowest for the ultrasonically treated LCP2, indicating greater thixotropic or permanent effects of ultrasonic treatment on its viscosity. It should also be noted that the pressures for both untreated and treated 25/75 LCP1/LCP2 blends were
higher than that for the untreated and treated LCP2 and 50/50 LCP1/LCP2 blends. This indicated greater viscosity in 25/75 LCP1/LCP2 blends than that of LCP2 and 50/50 LCP1/LCP2.

7.3. Rheology

The viscosity of LCP1, LCP2 and their blends was determined by a capillary rheometer at a temperature of 300°C. The same apparent viscosity vs. concentration at low and high shear rates are shown in Figure 7.3a and b, respectively. The same apparent shear rates were used for comparison of viscosity of samples obtained at the different amplitudes.

Figure 7.3a indicates a reduction in the viscosity of LCP2 at a shear rate of 105 s\(^{-1}\) compared to virgin LCP2, first upon passing through the extruder without treatment, and a further reduction with ultrasonic treatment at an amplitude of 10 µm. The viscosity of 25/75 LCP1, LCP2 blend and LCP1 were also observed to decrease with ultrasonic treatment at an amplitude of 10 µm at an apparent shear rate of 105 s\(^{-1}\). 25/75 LCP1/LCP2 blends had higher viscosity than extruded LCP2, and the other blends, except with treatment at an amplitude of 10 µm. The increased viscosity for this blend could be due to the reduced degradation of LCP2 with extrusion in the presence of LCP1. The lowest viscosity was observed for 50/50 LCP1/LCP2 blends. The viscosity of these blends was lower than that of the pure components, indicating synergistic effect by mixing at equal weight ratios. This could be due to the enhanced deformation of LCP1 and LCP2 domains at this concentration. 75/25 LCP1/LCP2 blend had a significantly lower viscosity than that of LCP1, indicating that the presence of only 25% by weight
LCP2 acted as a processing aid. This further confirmed that a synergistic viscosity reduction occurred in LCP1/LCP2 blends. The viscosity of 50/50 and 75/25 LCP1/LCP2 blends was not affected by ultrasonic treatment, indicating that the effect of ultrasound differed by composition.

Figure 7.3. Apparent viscosity at apparent shear rates of (a) 105 s\(^{-1}\) and (b) 957 s\(^{-1}\) for LCP1/LCP2 blends at a temperature of 300°C.

Figure 7.3b shows the change in viscosity of LCP1/LCP2 blends without and with ultrasonic treatment at an apparent shear rate of 957 s\(^{-1}\). By comparing Figure 7.3a and b,
it is seen that all studied materials are highly shear thinning, as characteristic of LCPs. The viscosity reduction with ultrasonic treatment of LCP1, 25/75 LCP1/LCP2, and LCP2 at an amplitude of 10 µm observed in Figure 7.3a cannot be seen in Figure 7.3b. This is due to the domain orientation and the highly shear thinning nature of LCPs [38, 39]. The viscosity differences are masked at high shear rates due to readily aligned fibrillar structures in the nematic state.

Figure 7.4 compares the apparent viscosity versus shear rate behavior of LCP1/LCP2 blends. Shear rate was calculated with the correction for Figure 7.4, and was observed induced some shift in the plots. However, the corrected shear rate values were not too distant from the apparent shear rate, and the qualitative comparison provided in Figure 7.3a and b was not affected by the Rabinowitsch correction. LCP1 exhibited greater shear thinning behavior than LCP2 and the blends.

![Graph showing apparent viscosity vs. shear rate for untreated LCP1/LCP2 blends.](image)

Figure 7.4. Apparent viscosity vs. shear rate for untreated LCP1/LCP2 blends.
7.4. Dynamic Mechanical Analysis

Thermo-mechanical analysis of untreated and ultrasonically treated LCP1, LCP2 and their blends was performed to study changes in the storage and loss moduli, and glass transition temperature with blend composition and amplitude of treatment. Largest changes in these properties of LCP1/LCP2 blends occurred at an amplitude of 10 µm, which was therefore chosen to be included in the following figures for comparison.

![Graphs showing storage and loss modulus vs. temperature for LCP1, LCP2, and their blends with and without ultrasonic treatment.]

Figure 7.5 Moduli vs. temperature for LCP1, LCP2, and their blends: (a) storage, and (b) loss modulus, without and with ultrasonic treatment at an amplitude of 10 µm.
Figure 7.5a and b show the storage and loss moduli, respectively, of LCP1/LCP2 blends, without and with treatment at an ultrasonic amplitude of 10 \( \mu \text{m} \). The storage moduli of the blends were larger than the pure components below a temperature of approximately 125\(^\circ\)C, indicating enhanced rigidity of the molded blends. This indicated greater orientation in the blends. The storage modulus of LCP1 decreased at a slightly larger slope below, rather than above, its glass transition temperature (107\(^\circ\)C). On the other hand, the storage modulus of LCP2 exhibited a sharp decrease above its glass transition temperature (140\(^\circ\)C). The reduction in the storage modulus of the blends was less as compared to LCP2, indicating better retention of stiffness at high temperature.

Value of the storage modulus of LCP1 was higher than that of LCP2 below 125-130\(^\circ\)C. The storage modulus curve of LCP1 treated at an amplitude of 10 \( \mu \text{m} \) lied higher than that of untreated LCP1. This indicated increased elasticity of LCP1 with ultrasonic treatment at an amplitude of 10 \( \mu \text{m} \). On the other hand, the storage modulus curve of LCP2 lied lower and shifted to lower temperature with ultrasonic treatment at 10 \( \mu \text{m} \). The latter indicated its degradation with treatment at 10 \( \mu \text{m} \). Changes in the loss tangent will also be discussed and are generally more conclusive as they incorporate viscous behavior obtained from the loss modulus as well. The storage modulus of blends appeared to be very similar without and with treatment at the low temperature range and showed larger variations at the high temperature range in Figure 7.5a. While the storage modulus of 50/50 LCP1/LCP2 and 75/25 LCP1/LCP2 blends indicated little change with treatment, 25/75 LCP1/LCP2 blends showed an increase in the storage modulus with ultrasonic treatment. The latter indicated increased elasticity of 25/75 LCP1/LCP2 blends at the higher temperature range with ultrasonic treatment.
The loss modulus of LCP1/LCP2 blends is shown in Figure 7.5b. While LCP1 showed a shoulder, LCP2 had a peak around the glass transition temperature. The loss modulus of LCP2 was lower than that of LCP1 at the lower temperatures, but higher roughly above the glass transition temperature of LCP1. The blends exhibited a greater loss modulus than the pure components. The loss modulus of 25/75 LCP1/LCP2 was larger than that of 50/50 LCP1/LCP2, which in turn was larger than 75/25 LCP1/LCP2 blends. Hence, the addition of LCP1 to the blends reduced viscous dissipation, especially at the high temperature range.

The loss modulus of both untreated and ultrasonically treated LCP1 was higher at the low temperature range and that of LCP2. The loss tangent curves for LCP1 and LCP2 were observed to crossover at 105-110°C, above which the loss tangent of LCP2 was greater than that of LCP1. The loss modulus of LCP1/LCP2 blends also indicated differences with ultrasonic treatment. The loss modulus of 25/75 LCP1/LCP2 blend increased with ultrasonic treatment at an amplitude of 10 µm. The loss modulus of 50/50 LCP1/LC2 and 75/25 LCP1/LCP2 blends lied higher with treatment at an amplitude of 10 µm at temperatures corresponding to those below the loss tangent peaks of the respective untreated blends. The increased loss modulus of LCP1/LCP2 blends observed approximately below the glass transition temperatures indicated greater viscous dissipation with ultrasonic treatment at an amplitude of 10 µm.

Figure 7.6 shows the temperature dependence of the loss tangent for LCP1/LCP2 blends without and with treatment at an ultrasonic amplitude of 10 µm. LCP1 had the lowest loss tangent, LCP2 had the highest, and those of the blends lied in between. The tan δ peak, which lied at the highest temperature for LCP2, was observed to move to
lower temperatures with increasing LCP1 concentration, indicating partial miscibility. However, the temperature corresponding to tan δ peak of all the blends lied closer to that of LCP2.

The value of tan δ decreased for LCP1 with ultrasonic treatment at an amplitude of 10 µm. Value of tan δ was observed to increase for LCP2, and shifted to a lower temperature, indicating the existence of some degradation of LCP2 with treatment at 10 µm. In the blends, the temperature corresponding to tan delta peak was observed to shift to lower temperatures with ultrasonic treatment at an amplitude of 10 µm, possibly indicating improved miscibility with ultrasonic treatment.

The values of tan δ at temperatures above the corresponding peaks in tan δ were compared for LCP1, LCP2 and their blends without and with ultrasonic treatment at an amplitude of 10 µm. While tan δ curve shifted to lower temperature with ultrasonication at 10 µm, its value above 140°C was similar without and with treatment. The value of tan δ at temperatures above its peak value were lower for ultrasonically treated LCP1 and 25/75, 50/50 LCP1/LCP2 blends, indicating their enhanced elasticity with ultrasonic treatment. The value of tan δ for 75/25 LCP1/LCP2 blend lied higher with ultrasonic treatment, indicating greater viscous dissipation with ultrasonic treatment for this blend. These variations in ratio of the storage to the loss modulus with ultrasonic treatment indicate structural changes in LCP1, LCP2 and their blends at an amplitude of 10 µm. Additionally, the change in this behavior with the changes in glass transition temperature indicate a permanent effect of ultrasonic treatment on the mobility of both LCPs. Hence, ultrasound not only affected the pure components, but also affected the blends such that
the molecular mobility of either LCP has an effect on the dynamic mechanical properties of the blends.

Figure 7.6. Loss tangent vs. temperature for LCP1, LCP2, and their blends without and with ultrasonic treatment at an amplitude of 10 µm.

Figure 7.7. Temperature corresponding to tan δ peak vs. LCP1 concentration in LCP1/LCP2 blends without and with ultrasonic treatment at 10 µm, and its comparison to prediction from Fox equation.
Figure 7.7 shows the change in $T_g$ of LCP1/LCP2 blends with LCP1 concentration and with ultrasonic treatment at an amplitude of 10 $\mu$m, along with comparison of $T_g$ obtained from Fox equation (eq. 2.6). It should be noted that Fox equation is used for amorphous polymer blends and cannot be correctly applied in the presence of a semi-crystalline phase due to differences in density. The data from Fox equation is presented with the intent of providing a comparison to theoretical predictions by neglecting crystallinity of the LCPs. The $T_g$’s of LCP2 and LCP1/LCP2 blends were observed to decrease with ultrasonic treatment at an amplitude of 10 $\mu$m. While no change in the $T_g$ of LCP1 was observed, it should be noted that greater error was expected in the determination of $T_g$ due to the broad tan $\delta$ peak in contrast to the well defined tan $\delta$ peak observed for LCP2 and blends.

The reduced $T_g$ of LCP2 indicated its degradation with ultrasonic treatment. As the $T_g$ of blends decreased at all concentrations, this decrease cannot be attributed completely to degradation of LCP2. Rather, it also indicated enhanced miscibility in LCP1/LCP2 blends due to the continued reduction in $T_g$ following ultrasonic treatment with increasing content of LCP1. The reduced $T_g$ in the ultrasonically treated blends indicated greater interaction between the components, and the $T_g$ of treated blends were observed to slightly move toward $T_g$ predicted by Fox equation. However, as LCP1 exhibited a wider tan $\delta$ peak than that of LCP2. It is possible that the less pronounced tan $\delta$ transition of LCP1 at the glass transition temperature contributed less to the tan $\delta$ peak of the blends. This could have influenced the observed $T_g$’s to move slightly toward $T_g$ predicted by the Fox equation, indicating partial miscibility of LCP1 and LCP2. 75/25 LCP1/LCP2 without and with treatment and 50/50 LCP1/LCP2 with treatment at an
amplitude of 10 µm showed greater shift of the temperature corresponding to the tan δ peak toward T_g predicted by the Fox equation.

7.5. Mechanical properties

The Young’s modulus, secant modulus at 1% elongation, strength, elongation at break, and impact strength of LCP1/LCP2 blends were studied.

The Young’s modulus of LCP1/LCP2 blends is shown in Figure 7.8, with the error bars indicating 95% confidence intervals. In this section, virgin LCP1 and LCP2 were injection molded into specimens for testing without any other processing for comparison of mechanical properties with materials that were extruded before injection molding.

LCP1 and LCP2 had similar moduli, while those of the blends were significantly higher. The Young’s modulus of 25/75 LCP1/LCP2 blends was more than twice that of the pure components, while that of 50/50 and 75/25 LCP1/LCP2 blends was more than 2.5 times that of the pure components. Modulus is a function of sample orientation. Liquid crystalline polymers form highly oriented fibrillar structures under elongational flow fields [60]. Greater modulus of the blends indicates mutually improved orientation of the LCPs. The Young’s modulus was higher in 75/25 LCP1/LCP2 blends than in 25/75 LCP1/LCP2 blends. This indicated that the orientation in LCP1/LCP2 blends was greater when LCP1 was the major component. In an effort to reduce standard deviation in modulus results, secant modulus at 1% elongation was calculated, and is shown in Figure 7.9 along with error bars indicating 95% confidence intervals. From Figure 7.9, it was observed that the modulus of 50/50 LCP1/LCP2 blends was indeed higher than the other
blends, indicating greatest synergistic increase in orientation of moldings at equal weight ratios of LCP1 and LCP2 in the blends. A similar effect was also observed by Akhtar and Isayev in injection moldings of LCP1/LCP2 blends [12].

Both the Young’s modulus (Figure 7.8) and secant modulus (Figure 7.9) indicated no change in LCP2, and 50/50 LCP1/LCP2, and 75/25 LCP1/LCP2 blends with ultrasonic treatment. The modulus of LCP1 was improved over the virgin material with extrusion without treatment. Also, both the Young’s and secant moduli of ultrasonically treated 25/75 LCP1/LCP2 blend indicated slight improvements over that of the untreated samples.

![Figure 7.8. Young's modulus of LCP1/LCP2 blends without and with ultrasonic treatment at different amplitudes. Values shifted along abscissa for clarity.](image-url)
Figure 7.9. Secant modulus at 1% elongation vs. LCP1 concentration in LCP1/LCP2 blends with and without ultrasonic treatment.

Figure 7.10 shows the strength of LCP1/LCP2 blends, with the error bars indicating 95% confidence intervals. The strength of untreated and ultrasonically treated blends was higher than the pure components. The highest strength was achieved for 50/50 LCP1/LCP2 blends, followed by 75/25, and 25/75 LCP1/LCP2 blends. The strength of LCP1 increased with processing and with ultrasonic treatment at an amplitude of 10 µm. On the other hand, strength of LCP2 decreased at an amplitude of 10 µm. The latter indicated the degradation LCP2. While strength of 25/75 LCP1/LCP2 blends was not as significantly affected by ultrasonic treatment, the strength of 50/50 and 75/25 LCP1/LCP2 blends were observed to decrease with ultrasonic amplitude.
Figure 7.10. Strength of LCP1/LCP2 blends without and with ultrasonic treatment at different amplitudes. Values shifted along abscissa for clarity.

Figure 7.11 shows the elongation at break of LCP1/LCP2 blends, with the error bars indicating 95% confidence intervals. The elongation at break of LCP1 was higher than that of LCP2, while that of the blends was lower. As blends had greater stiffness and indicated higher orientation as shown from the modulus results, reduced elongation was expected. The elongation at break of LCP1 decreased with ultrasonic treatment at an amplitude of 10 µm. The elongation at break of the blends also decreased with ultrasonic treatment. Elongation at break of LCP1 decreased with extrusion as compared to the virgin material, but did not change with ultrasonic treatment.
Figure 7.11. Elongation at break of LCP1/LCP2 blends without and with ultrasonic treatment at different amplitudes. Values shifted along abscissa for clarity.

Figure 7.12 showed the toughness of LCP1/LCP2 blends, with the error bars indicating 95% confidence intervals. The toughness of LCP1 was the highest. Toughness of untreated LCP2, and blends were the same, within 95% confidence intervals. The toughness of LCP2 decreased with treatment at 10 μm. The toughness of blends decreased with ultrasonic treatment, with the highest reduction occurring at an amplitude of 10 μm. Toughness is a function of strength and elongation at break. Reduced toughness of LCP2 could indicate its degradation with ultrasonic treatment at an amplitude of 10 μm. Reduction in the toughness of the blends with treatment could be explained by reduced fibrillation, which would adversely affect mechanical properties due to poor deformation of the LCPs with LCP2 degradation. If compatibilization of LCP1/LCP2 blends occurred with ultrasonic treatment, it could also lead to some loss of fibrillation due to improved miscibility and reduced phase separation. While such an
effect could not be discerned by mechanical properties alone, ultrasonic treatment apparently was not beneficiary for the mechanical properties of the LCP1/LCP2 blends.

![Toughness of LCP1/LCP2 blends without and with ultrasonic treatment at different amplitudes](image)

Figure 7.12. Toughness of LCP1/LCP2 blends without and with ultrasonic treatment at different amplitudes. Values shifted along abscissa for clarity.

The impact strength of LCP1/LCP2 blends was determined both without and with notching. Injection molded flex bars were cut in two equal pieces; dead end (DE) and gate end (GE) samples were tested and their impact strengths were reported separately. Unnotched impact strength of DE (Figure 7.13a) and GE (Figure 7.13b) of untreated and treated LCP1/LCP2 blends were compared. It should be noted that DE and GE samples were averaged and reported together for LCP1 in both Figure 7.13a and Figure 7.13b, as they were originally tested with PET/LCP1 blends for which there had appeared to be no statistically significant difference in the two sections of moldings. While this observation was made for PET and PET/LCP1 blends, it probably was not the case for LCP1, as indicated by the comparison of DE and GE moldings of LCP2 and LCP1/LCP2 blends. This could account for the greater error in impact strength of LCP1.
The impact strength of the DE was observed to be greater than GE in LCP2 and the blends. Izod impact strength is a function of the energy absorbed by the polymer when a hammer that strikes the sample perpendicular to the machine direction, along its shortest side. In LCPs and their blends, a highly fibrillar, wood-like structure, is present [60]. This fibrillar structure imparts high impact strength to moldings as each individual
fibril must be “chopped” by the striking hammer. These highly aligned fibrils in moldings containing LCPs are crushed by a hammer, rather than being cut by a sharp object. The failure mechanism resembles chopping down a tree with an axe, in that a highly oriented fibrillar structure must be crushed perpendicular to the orientation direction. Accordingly, greater orientation will impart greater impact strength to moldings of LCPs. High orientation of LCPs is due to their processing in the nematic state, and is more easily manipulated by processing conditions than in thermoplastics [66], resulting in more pronounced differences in impact strength with orientation in LCPs.

Injection molding of LCP flex bars used for impact testing was carried out at high injection speed and low mold temperature. This would lead to high orientation in moldings. As the material injected earlier into the cavity experiences the greatest shear at the mold wall and freezes the fastest, it is expected to have greater orientation than the material that is injected later and stays warm for longer. As injected material dwells longer at the melt temperature, it has greater time to relax and lose orientation. Therefore, the material injected first, which forms the DE of the impact bar, has greater frozen in orientation than the GE. It should be noted that the position along the flex bar where the hammer strikes is not exactly at the end or gate of the molding. The impact point on DE samples is located at three fourths of the length of the flex bar away from the gate, while that on GE sample is at a location one fourths of the length of the flex bar from the gate. Hence, effect of reduced orientation of melt due to diverging flow at the GE, and due to filling at the end of cavity would not influence the impact strength of LCP2 and LCP1/LCP2 blends. Similar position dependence of the impact strength was observed by Ding and Isayev on notched injection molded bars of LCP1/Ultrax 4003 blends [247].
They reported greatest and lowest impact strength for DE and GE, respectively, with the middle section having intermediate values.

As shown in Figure 7.13a and b, the impact strength of LCP2 was higher than that of LCP1. Untreated 50/50 LCP1/LCP2 blends had higher impact strength than the pure components. The greatest impact strength was observed in untreated 75/25 LCP1/LCP2 blends, indicating a synergistic increase in orientation with blending. The higher impact strength of 75/25 than 50/50 LCP1/LCP2 blends was more pronounced in the DE samples. This could be due to the higher effect of orientation in LCP blends (observed from modulus measurements) due to synergistic fibrillation. The reason for the impact strength to peak at this concentration rather than at equal composition of LCP1 and LCP2 in the blends could be due to the higher impact strength of LCP1 than LCP2. Impact strength of LCP1 was improved with ultrasonic treatment at an amplitude of 7.5 $\mu$m. Impact strength of LCP2 and the blends were lower with ultrasonic treatment, with the greatest loss in impact properties occurring with treatment at an amplitude of 10 $\mu$m. This indicated degradation of LCP2 and reduced orientation in LCP blends with ultrasonic treatment.

Figure 7.14a and b show the notched Izod impact strength of DE and GE of LCP1/LCP2 blends, respectively. While the values of impact strength were lower than those obtained without notching, impact strength followed a similar trend as discussed for Figure 7.13a and b. Additionally, reduced impact strength of LCP2 with extrusion was observed from these figures. This indicated its degradation with extrusion.
Figure 7.14. Notched Izod impact strength of (a) dead end, and (b) gate end moldings of LCP1/LCP2 blends with and without ultrasonic treatment.

7.6. Morphology

The SEM micrographs of core region of injection moldings were taken at a location close to the gate, as shown in Figure 3.14. The micrographs showed orientation of LCP fibrils parallel to the fracture surface. The orientation of SEM images was random with respect to one another, as samples were not aligned in the same way before
taking images. However, the orientation of fibrils was in the machine direction for all injection molded samples, as shown by arrows in Figure 7.15 and Figure 7.16.

Figure 7.15. SEM micrographs at 2,000x magnification for LCP1/LCP2 blends without treatment at concentrations of (a) 75/25, (b) 50/50, (c) 25/75, with treatment at an amplitude of 7.5 µm at concentrations of (d) 75/25, (e) 50/50, (f) 25/75, with treatment at an amplitude of 10 µm at concentrations of (g) 75/25, (h) 50/50, (i) 25/75. Axis of machine direction is indicated by arrows in figures.

Figure 7.15a-i showed the SEM micrographs of LCP1/LCP2 blends without treatment, and with ultrasonic treatment at amplitudes of 7.5 and 10 µm, at a magnification of 2000x. Hierarchical fibrillar structures composed of large and small LCP fibrils were identified. LCP1 and LCP2 domains could not separately identified in the micrographs, as they were dominated by a uniform fibrillar structure. Extraction of
one of the phases was not possible to observe differences in fibrils of LCP1 and LCP2, as both only dissolve in highly fluorinated aromatic solvents and at very low concentrations [26].

Figure 7.16. SEM micrographs at 10,000x magnification for LCP1/LCP2 blends without treatment at concentrations of (a) 75/25, (b) 50/50, (c) 25/75, with treatment at an amplitude of 7.5 µm at concentrations of (d) 75/25, (e) 50/50, (f) 25/75, with treatment at an amplitude of 10 µm at concentrations of (g) 75/25, (h) 50/50, (i) 25/75. Axes of machine direction are indicated by arrows in figures.

Figure 7.16a-i show high magnification SEM micrographs of LCP1/LCP2 blends without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm. The micrographs showed intertwined fibrils of diameter in the order of 100 nm. 50/50 and 75/25
LCP1/LCP2 blends (Figure 7.16d,g) indicated greater fibrillation than 25/75 LCP1/LCP2 (Figure 7.16a) blend.

25/75 LCP1/LCP2 blends indicated a reduced number of fibrils with ultrasonic treatment (Figure 7.16b-c) as compared to the untreated 25/75 LCP1/LCP2 blend (Figure 7.16a). 50/50 and 75/25 LCP1/LCP2 blends also indicated reduced number of fibrils with treatment at an amplitude of 10 µm (Figure 7.16f,i). Deformation of LCP domains is affected by viscosity ratio of the phases [1, 158]. Evidently, reduced viscosity of LCP2 matrix with treatment at an amplitude of 10 µm reduced the amount of LCP1 fibrils.

A smooth fracture surface was observed in LCP1/LCP2 blends treated at an amplitude of 10 µm (Figure 7.16c,f,i), indicating not only reduced fibrillation, but also lack of good interfacial adhesion at this amplitude. This was due to the severe degradation of LCP2 with treatment at an amplitude of 10 µm. In contrast, a rougher surface created by intertwined fibrils that deformed together, was observed with treatment at an amplitude of 7.5 µm in 50/50 LCP1/LCP2 (Figure 7.16e) and 75/25 LCP1/LCP2 (Figure 7.16h). The latter indicated improved interfacial adhesion with ultrasonic treatment at these conditions. As the extent of LCP2 degradation would greatly influence fibrillation in LCP1/LCP2 blends, interfacial adhesion was not the decisive factor in determining the useful properties of the blend, primarily the mechanical properties.

7.7. Conclusions

Effects of ultrasonic extrusion on blends containing two wholly aromatic liquid crystalline polymers based on 6-oxy-2-napththoyl and p-oxybenzoyl moieties (LCP1),
and p-oxybenzoyl, terephthaloyl and hydroquinone moieties (LCP2) were studied. Rheological, thermal, mechanical and morphological studies were carried out. The viscosity ratio of LCP1 to LCP2 ranged from about 2.5 to about 6 at shear rates of about 20 to 1000 s\(^{-1}\), respectively. The glass transition temperature (\(T_g\)) of the blends, determined by the tan \(\delta\) peak of LCP2, was observed to decrease with concentration of LCP1, however lied away from the Fox relation for miscibility.

A synergistic reinforcement effect was observed in the blends, with the strength and Young’s modulus of the blends lying significantly higher than those of both LCPs. The synergistic improvement of the mechanical properties of blends was due to the LCPs enhancing each other’s orientation and creating an intertwined microfibrillar morphology. Reduced fibrillation and smooth fracture surfaces were observed with treatment at an amplitude of 10 \(\mu\)m in the blends, indicating reduced deformation and poor interfacial adhesion. With treatment at an amplitude of 7.5 \(\mu\)m, 50/50 and 75/25 LCP1/LCP2 blends indicated improved interfacial adhesion, observed in the form of rougher fracture surfaces with intertwined LCP fibrils.

Ultrasonic treatment led to a decrease in pressure during extrusion of the LCPs and their blends. While treatment of LCP1 at certain ultrasonic amplitudes led to improvements in some of its mechanical properties, treatment of LCP2 at an amplitude of 10 \(\mu\)m resulted in reduced impact strength, tensile strength, elongation at break and toughness. \(T_g\) of LCP2 and the blends decreased with ultrasonic treatment at an amplitude of 10 \(\mu\)m, possibly improving their miscibility. While the Young’s and secant moduli of the blends were not affected by ultrasonic treatment, a decrease was observed in the strength, elongation at break, and toughness of the blends with treatment at an ultrasonic
amplitude of 10 µm. The reductions in mechanical properties with ultrasonic treatment were attributed to degradation of LCP2, and changes in the self-reinforcing fibrillation mechanism of the blends.
CHAPTER VIII
EFFECT OF CATALYSTS ON ULTRASONIC EXTRUSION

The effect of adding transesterification catalysts without and with ultrasonic treatment to 80/20 PEN/LCP1 blend was studied through rheological, thermal, mechanical, spectroscopic and morphological characterization.

8.1. Introduction

In situ ultrasonic treatment was primarily studied to investigate the changes occurring in structure and properties of blends of flexible chain polyester and wholly aromatic liquid crystalline copolyester blends. In situ ultrasonic reactions were shown to result in enhanced compatibilization in some blend compositions and certain amplitudes of treatment. However, ultrasonic treatment alone did not have a positive effect on the morphology and mechanical properties of blends at all studied blend compositions. While the primary focus of this study was not to investigate the effect of catalyst on the studied blends, use of these catalyst previously studied in literature with successful improvement of compatibility for polyester/LCP blends, in combination with ultrasonic treatment had potential for enhanced effects in these blends.

Two different catalysts mentioned in literature with positive effects in blends of thermoplastic polyester/LCPs were chosen. These catalysts were tetrabutyl orthotitanate (TBOT) and antimony trioxide (Sb$_2$O$_3$). 80/20 PEN/LCP1 blends had indicated no
improvement in interfacial adhesion or mechanical properties with ultrasonic treatment. This blend was chosen for catalyst studies to observe whether the addition of catalyst in a combination of ultrasonic treatment could lead to improved compatibilization.

Catalysts can increase the rate of reaction by decreasing the activation energy required. A literature survey of transesterification reaction catalysis was provided in section 2.4.2. In the case of in-situ compatibilization of polyester blends, this reaction is transesterification to create block copolymers [101]. Ultrasonic treatment at certain conditions was shown to induce changes in the studied polymers. While homopolymerization or degradation of the blend components occurred under certain conditions, this did not always translate into recombination between the created active sites and formation of copolymer. In this regard, it was of interest to observe whether the use catalyst could promote enhanced copolymerization reactions.

TBOT is a tetrafunctional catalyst. It has been employed to promote transesterification reactions in the melt processing of polycarbonate/polyester [277], flexible chain polyester/LCP [157], and LCP/LCP [158] blends. Antimony trioxide (Sb$_2$O$_3$) is a catalyst mainly used in polycondensation reaction of polyesters. It is commonly used in production of polyethyleneterephthalate in the polycondensation step where glycolic esters combine to form polymers [109]. As a transesterification catalyst it has been used in the melt mixing of PET/poly(ethylene sebacate) blends [110] and blends of PET with different LCPs (HBA/HNA copolymer and PET/HBA copolymer) [156]

In this chapter, the effect of adding transesterification catalysts TBOT and Sb$_2$O$_3$ on pure PEN, and on both untreated and ultrasonically treated 80/20 PEN/LCP1 blend is studied.
8.2. Process characteristics

The conditions used for the ultrasonic extrusion of 80/20 PEN/LCP1 blends described in section 5.2 were utilized for processing with added catalyst. However, there were some differences in the preparation of compounds with Sb$_2$O$_3$ and TBOT. Sb$_2$O$_3$ was available in powder form and was added directly to the prepared 80/20 PEN/LCP1 pellet mixture, at a concentration of 0.5 wt%. On the other hand, TBOT was a viscous liquid and had to be dozed into the extruder during feeding. This was achieved by preparation of a masterbatch in a twin screw extruder.

As flood feeding was used for all ultrasonic extrusion, and only one feeding hole was available in the single screw extruder, therefore TBOT could not be added directly to 80/20 PEN/LCP1 blends during processing in SONIC1 while keeping other processing conditions the same. As starve feeding could change the effect of ultrasound in this system, and mixing fluid with solids was not directly possible, a twin screw extruder was used to compound masterbatches containing TBOT.

In the preparation of masterbatch containing TBOT, there were three options: 1) add TBOT to LCP1, 2) add TBOT to PEN, 3) add TBOT to PEN/LCP1 blend. As the aim of the catalyst study was to investigate the effect of catalyst addition with ultrasonic treatment, the third option was not applicable. The aim was to aid TBOT with no or little chemical change to the polymers and to ensure that it stays in the extruded masterbatch. First, addition of PEN to TBOT was studied, as it could be diluted further in SONIC1. On the other hand, as LCP1 was the minor fraction in the blend, all LCP1 that would be compounded with PEN was to be prepared as a masterbatch with TBOT, to obtain blends with good uniformity.
During the preparation of PEN and LCP1 masterbatches containing 2% and 1.5% TBOT, respectively, a generation of fumes occurred at the feed section of the twin screw extruder. In order to limit TBOT lost to the atmosphere and reduce associated health risks, the cooling rate in the feed throat of the twin screw extruder was kept high for the size of the extruder, using water flow rate of 1900 cm³/min.

Color change was observed with the addition of catalysts. PEN extrudate, which was transparent without addition of catalysts, had a slight greenish tint with the addition of Sb₂O₃. 80/20 PEN/LCP1 blends, which were white in color, also took on a greenish tint. During compounding in the twin screw extruder, addition of TBOT to PEN led to a reddish brown color and a very brittle extrudate. A similar color change was observed a transesterification of PC/copolyester blends in the presence of TBOT [277]. Addition of TBOT to LCP1 led to a slightly brownish cream color, as opposed to the light cream color of LCP1 extruded without catalyst. The LCP1 extrudate was not observed to become brittle with TBOT catalyst. Vapor venting was observed at the die in twin screw extrusion with TBOT catalyst. However, the melt was extruded directly into a cold water bath to limit the evaporation of TBOT catalyst after exiting from the die. As excessive degradation of PEN occurred during compounding of the masterbatch, this material was not used for preparation of 80/20/0.3 PEN/LCP1/TBOT blends. Following the twin screw extrusion of LCP1/TBOT, the extrudate strands were pelletized and bag mixed with PEN for extrusion in SONIC1. During compounding of the LCP1/1.5% TBOT masterbatch in the single screw extruder to produce 80/20/0.3 PEN/LCP1/TBOT blends, the brownish color of the LCP1 masterbatch was observed in the extruded blends. These color changes indicated chemical changes in the blend, most likely some degradation of the polymers.
Venting of TBOT fumes at the exit of the single screw extruder suggested that most of the TBOT made its way into the blend compounded in SONIC1. While some amount of TBOT could have been lost to evaporation in preparation of masterbatch, and the exact concentration of TBOT in the extruded 80/20 PEN/LCP1 blends could not be determined.

Table 8.1. Torque and pressure during preparation of LCP1/TBOT and PEN/TBOT masterbatches in the twin screw extruder without and with TBOT catalyst.

<table>
<thead>
<tr>
<th>Material</th>
<th>TBOT concentration</th>
<th>Torque virgin</th>
<th>Torque with TBOT</th>
<th>Pressure virgin (bar)</th>
<th>Pressure with TBOT (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCP1</td>
<td>1.50%</td>
<td>40%</td>
<td>30%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PEN</td>
<td>2%</td>
<td>65%</td>
<td>12%</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

The extruder torque and die pressure with and without TBOT catalyst during the preparation of LCP1 and PEN masterbatches containing 1.5% and 2% TBOT, respectively, are shown in Table 8.1. The pressure with extrusion of LCP1 was too low to be recorded without and with TBOT. For PEN, pressure was observed to decrease 3-fold with the addition of TBOT. While torque was reduced by 25% with the addition of TBOT to LCP1, the reduction was more than 5-fold in PEN. This indicated that significant degradation of PEN took place during twin screw compounding with TBOT. The reduction in torque of LCP1, while less, also indicated its degradation in the presence of TBOT. However, there was no alternative method to the step process employed for the preparation of ultrasonically treated PEN/LCP1 blends containing TBOT. Hence, the LCP1 masterbatch, which indicated less change after compounding with TBOT, was chosen for preparation of 80/20 PEN/LCP1 blends containing 0.3% TBOT in SONIC1.
Table 8.2. Temperature at ultrasonic treatment zone, melt temperature, and extruder torque measured during processing of PEN and 80/20 PEN/LCP1 blends without and with catalyst in SONIC1.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Amplitude (µm)</th>
<th>$T_{\text{ultra}}$ (°C)</th>
<th>$T_{\text{melt}}$ (°C)</th>
<th>Torque (Amp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN</td>
<td>0</td>
<td>299</td>
<td>287</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>299</td>
<td>289</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>300</td>
<td>289</td>
<td>2.0</td>
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<tr>
<td></td>
<td>10</td>
<td>300</td>
<td>292</td>
<td>2.0</td>
</tr>
<tr>
<td>PEN/0.5% Sb$_2$O$_3$</td>
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<td>284</td>
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</tr>
<tr>
<td></td>
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<td>299</td>
<td>285</td>
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<td></td>
<td>7.5</td>
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<td></td>
<td>10</td>
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<td>6.0</td>
</tr>
<tr>
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<td>301</td>
<td>289</td>
<td>3.4</td>
</tr>
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<td>287</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>300</td>
<td>290</td>
<td>2.4</td>
</tr>
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<td></td>
<td>7.5</td>
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</tr>
<tr>
<td></td>
<td>10</td>
<td>301</td>
<td>291</td>
<td>1.9</td>
</tr>
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<td>80/20/1 PEN/LCP1/Sb$_2$O$_3$</td>
<td>10</td>
<td>302</td>
<td>290</td>
<td>1.9</td>
</tr>
<tr>
<td>80/20/0.3 TBOT</td>
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<td>297</td>
<td>302</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
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<td>0.3</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>301</td>
<td>302</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>304</td>
<td>303</td>
<td>0.3</td>
</tr>
</tbody>
</table>

PEN was extruded without and with Sb$_2$O$_3$ catalyst at a concentration of 0.5%, both without and with ultrasonic treatment. 80/20 PEN/LCP1 blends were prepared without and with 0.5% and 0.3% Sb$_2$O$_3$ and TBOT catalysts, respectively, both without and with ultrasonic treatment. Additionally, 1% Sb$_2$O$_3$ concentration at an ultrasonic amplitude of 10 µm was studied in 80/20 PEN/LCP1 blends in an attempt to increase its effect on the blend. The barrel temperature at the ultrasonic treatment zone ($T_{\text{ultra}}$), the
melt temperature at the connection of the original extruder barrel to the ultrasonic attachment ($T_{\text{melt}}$), and extruder torque were recorded during processing. These results are shown in Table 8.2.

The barrel and melt temperatures during the processing of all samples except the 80/20/0.3 PEN/LCP1/TBOT were very similar and indicated no significant changes with amplitude of ultrasonic treatment. The melt temperature recorded before the ultrasonic treatment zone during processing of 80/20 PEN/LCP1 with TBOT was higher. This could be due to its processing at a later time, and change in the heating efficiency of some heaters, after maintenance of the machine. As the barrel temperatures were closer between all compounds, the extrusion melt temperature at the die was probably closer between these conditions than that at the connection of the original extruder to ultrasonic barrel.

Change in torque with ultrasonic treatment provided insight into the permanent changes occurring with the addition of catalysts and with ultrasonic treatment. The torque during processing of PEN decreased with ultrasonic treatment, and was lowest at ultrasonic amplitudes of 7.5 and 10 µm. Extruder torque in processing of ultrasonically treated PEN was higher in the presence of Sb$_2$O$_3$ catalyst. No reduction in torque was observed with treatment at an amplitude of 10 µm. This indicated reduced degradation of PEN with ultrasonic treatment in the presence of Sb$_2$O$_3$. This effect could be due to recombination reactions with ultrasonic treatment in the presence of Sb$_2$O$_3$.

In the processing of 80/20 PEN/LCP1 blend, torque decreased with amplitude of ultrasonic treatment. The torque was lower in 80/20 PEN/LCP1 blend processed in the presence of Sb$_2$O$_3$ catalyst without and with ultrasonic treatment. The torque decreased
substantially with addition of TBOT catalyst to 80/20 PEN/LCP1 blends, indicating degradation of the blend. It was previously shown in Table 5.1 that processing of pure PEN consumed higher torque than LCP1 (1.5 Amps) in SONIC1. It could be concluded that compounding of LCP1/TBOT masterbatch with PEN to make 80/20/0.3 PEN/LCP1/TBOT blends led to further degradation of PEN during compounding. The extent of TBOT induced degradation in the blend was substantially higher with ultrasonic treatment, as suggested by the very low torque of 0.3 Amps.

8.3. Rheology

Capillary rheometry at a temperature of 300°C was used to determine the viscosity of untreated and ultrasonically treated 80/20 PEN/LCP1 blends without and with Sb$_2$O$_3$ and TBOT catalysts. The viscosity of these materials were plotted against true shear rate, calculated by the Rabinowitsch correction from apparent shear rates, and are shown in Figure 8.1. The viscosity of untreated 80/20 PEN/LCP1 blend was higher without any catalyst than that of the untreated blend containing 0.5% Sb$_2$O$_3$, which was higher than that of the untreated blend containing 0.3% TBOT. With ultrasonic treatment of 80/20 PEN/LCP1 blends without catalyst, the viscosity compared to the untreated blend was similar at an amplitude of 5 µm, slightly less at an amplitude of 7.5 µm and much lower at an amplitude of 10 µm. The substantial decrease in viscosity at 10 µm indicated degradation at this condition.
Ultrasonic treatment of 80/20 PEN/LCP1 blends containing 0.5% Sb$_2$O$_3$ led to reduced viscosity with increasing amplitude. The reduction in viscosity at an amplitude of 7.5 µm compared to that without treatment was more substantial in the presence of 0.5% Sb$_2$O$_3$ than without it. This indicated that presence of Sb$_2$O$_3$ catalyst amplified acoustic cavitation in 80/20 PEN/LCP1 blend and caused further degradation of the 80/20 PEN/LCP1 blend with ultrasonication. This was expected as effects of ultrasound may increase in the presence of fillers, due to greater number of structural imperfections [252]. With the addition of 1% Sb$_2$O$_3$ to the blend treated at an ultrasonic amplitude of 10 µm, the viscosity was lower than that in blends containing 0.5% Sb$_2$O$_3$ at the same condition. Therefore, the amount of Sb$_2$O$_3$ catalyst influenced the properties of 80/20 PEN/LCP1 blend, caused greater degradation at higher concentration.
Addition of TBOT catalyst was shown to degrade the 80/20 PEN/LCP1 blend in Figure 8.1. It was also observed that the viscosity of 80/20 PEN/LCP1 blend decreased rapidly with increasing ultrasonic amplitude in the presence of 0.3% TBOT. The degradation induced by TBOT with ultrasonic treatment was the most significant among all conditions, indicating greater interaction of TBOT with the blend upon ultrasonic treatment. This was expected as TBOT is a tetra-functional molecule, which readily reacts with hydroxyl groups of polyesters [317]. In 80/20 PEN/LCP1, degradation prevailed with the addition of TBOT.

8.4. Dynamic Mechanical Analysis

The storage and loss moduli and loss tangent were determined by DMA to analyze the effect of catalyst addition on untreated and ultrasonically treated 80/20 PEN/LCP1 blends.

The storage and loss moduli versus temperature behavior of 80/20 PEN/LCP1 blends without and with 0.5% Sb\textsubscript{2}O\textsubscript{3}, and 0.3% TBOT catalysts, without and with ultrasonic treatment at an amplitude of 10 µm are shown in Figure 8.2a and b, respectively.

The storage modulus (Figure 8.2a) of untreated 80/20 PEN/LCP1 was reduced substantially and started decreasing at lower temperatures with ultrasonic treatment at an amplitude of 10 µm. The storage modulus versus temperature behavior of 80/20 PEN/LCP1 blends in the presence of 0.5% Sb\textsubscript{2}O\textsubscript{3} was very similar to that of untreated blend without any catalyst. The storage modulus versus temperature behavior of 80/20 PEN/LCP1 blends in the presence of 0.3% TBOT were similar without and with
ultrasonic treatment, but lied slightly lower than the untreated blend without any catalyst. The latter indicated degradation of 80/20 PEN/LCP1 blends in the presence of TBOT. The storage modulus of 80/20 PEN/LCP1 blend containing Sb$_2$O$_3$ catalyst was reduced with ultrasonic treatment at an amplitude of 10 µm, also indicating degradation at this condition. The fact that the storage moduli of ultrasonically treated blends containing Sb$_2$O$_3$ and TBOT catalysts were higher at 10 µm than the blend without catalyst indicated the stabilizing effect of catalysts with ultrasonic treatment at 10 µm on the storage modulus of the blends.

The loss modulus (Figure 8.2b) of untreated 80/20 PEN/LCP1 was reduced substantially and the E’’ peak shifted to lower temperatures with ultrasonic treatment at an amplitude of 10 µm. The loss modulus versus temperature behavior of 80/20/0.5 PEN/LCP1 blends in the presence of 0.5% Sb$_2$O$_3$ were very similar to that of untreated blend without any catalyst. The loss modulus versus temperature behavior of 80/20/0.3 PEN/LCP1/TBOT was similar without and with ultrasonic treatment, and their E’’ peak had a lower value than that of the untreated blend without any catalyst. The latter indicated degradation of 80/20 PEN/LCP1 blends in the presence of TBOT. The loss modulus of 80/20 PEN/LCP1 blend containing 0.5% Sb$_2$O$_3$ catalyst was reduced with ultrasonic treatment at an amplitude of 10 µm, also indicating degradation at this condition. The fact that the loss moduli of ultrasonically treated blends containing Sb$_2$O$_3$ and TBOT catalysts were higher at 10 µm than the blend without catalyst indicated the stabilizing effect of catalysts with ultrasonic treatment at 10 µm on the loss modulus of the blends.
Figure 8.2. Effect of catalyst on the storage modulus (E’) (a), and loss modulus (E”) (b) vs. temperature behavior of 80/20 PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 10 µm.
The loss tangent versus temperature behavior of 80/20 PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 10 µm, and without and with 0.5% Sb$_2$O$_3$, and 0.3% TBOT catalysts is shown in Figure 8.3. Among 80/20 PEN/LCP1 blends, the value of tan δ in the range of 95 to 120°C was lowest in the untreated blend containing 0.5% Sb$_2$O$_3$. This indicated that the molecular weight distribution could be reduced with addition of Sb$_2$O$_3$ catalyst without treatment. The tan δ peak became broader and shifted to lower temperatures with treatment of blend without catalyst at an amplitude of 10 µm. The height of the tan δ peak also increased at this condition, indicating a loss in elasticity. The tan δ peak of 80/20 PEN blends containing 0.3% TBOT also exhibited broadening to the lower temperature side of the peak, indicating increased molecular weight distribution in the presence of this catalyst. A shift of tan δ
peak to lower temperature and increase in its intensity was observed with ultrasonic treatment at an amplitude of 10 µm in 80/20 PEN blends containing either 0.5% Sb$_2$O$_3$ or 0.3% TBOT catalyst. It should be noted that the shift in tan δ peak with ultrasonic treatment at 10 µm of 80/20 PEN/LCP1 blends containing either catalyst was less than that of the treated blend without catalyst, as compared to untreated blend without catalyst. The latter indicated stabilizing effect of catalyst on degradation of blend with ultrasonic treatment at an amplitude of 10 µm.

Figure 8.4 shows the effect of Sb$_2$O$_3$ catalyst on the storage (a) and loss moduli (b) of pure PEN without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm. The values of storage and loss moduli of virgin PEN, which was prepared by injection molding without any other processing, were higher than the PEN that underwent further processing without treatment and without catalyst. The storage and loss moduli of untreated PEN shifted to lower temperatures in the presence of 0.5% Sb$_2$O$_3$. With ultrasonic treatment at an amplitude of 7.5 µm, the storage and loss moduli of untreated PEN shifted to lower temperature both with and without Sb$_2$O$_3$. Ultrasonic treatment at an amplitude of 10 µm caused a further significant shift of storage and loss modulus curves to lower temperature without catalyst. On the other hand, the storage and loss moduli of PEN containing 0.5% Sb$_2$O$_3$ exhibited only a slight shift to lower temperature with treatment an amplitude of 10 µm from the curves obtained with treatment at an amplitude of 7.5 µm. The latter signified different effect of ultrasound on PEN in the presence of 0.5% Sb$_2$O$_3$ catalyst.
Figure 8.4. Effect of 0.5% Sb$_2$O$_3$ catalyst on the (a) storage and (b) loss modulus vs. temperature behavior of PEN without and with ultrasonic treatment.

Figure 8.5 shows the effect of adding 0.5% Sb$_2$O$_3$ catalyst on the loss tangent (tan $\delta$) versus temperature behavior of PEN without and with ultrasonic treatment at amplitudes of 7.5 and 10 $\mu$m. The value of tan $\delta$ increased with processing of virgin PEN without treatment. The presence of 0.5% Sb$_2$O$_3$, in addition to increasing tan $\delta$ peak,
caused its shift to lower temperature. The increases in the value of tan δ indicated degradation of PEN. Tan δ versus temperature behavior at an ultrasonic amplitude of 7.5 μm exhibited similar increase in value over that of untreated PEN both without and with catalyst. This signified degradation of PEN with treatment at 7.5 μm. Ultrasonic treatment at 10 μm caused a further shift in tan δ of PEN without catalyst to lower temperature. On the other hand, treatment at an amplitude of 10 μm for PEN containing 0.5% Sb₂O₃ did not affect its loss tangent, signifying reduced degradation of PEN at this amplitude in presence of the catalyst.

Figure 8.5. Effect of 0.5% Sb₂O₃ catalyst on the loss tangent vs. temperature behavior of PEN without and with ultrasonic treatment.

Effect of compounding 1.5% TBOT catalyst with virgin LCP1, which was prepared by injection molding without any other processing, on the storage and loss modulus is presented in Figure 8.6a and b, respectively. The storage modulus of virgin LCP1 was observed to decrease more than its loss modulus upon compounding with
TBOT. Consequently, its tan δ was increased. This indicated loss of elasticity in LCP1, and its degradation in the presence of TBOT.

Figure 8.6. Effect of adding 1.5% TBOT on the (a) storage, and (b) loss modulus vs. temperature behavior of LCP1.

Effect of compounding 1.5% TBOT catalyst with virgin LCP1 on its loss tangent is presented in Figure 8.7. Tan δ peak of virgin LCP1 shifted from 107.4°C to 105.8°C
with addition of 1.5% TBOT during twin screw compounding. This supported the conclusion on TBOT induced degradation in LCP1. The PEN/TBOT masterbatch prepared in the twin screw extruder appeared to be degraded to a very large extent and could be molded with great difficulty. Usually, the moldings fractured while removing from the mold of the piston driven small scale injection molding machine. The molded mini dumbbell samples consistently fractured while clamping into the sample holder of the DMA. Therefore, this data is not available for the PEN/TBOT masterbatch.

Figure 8.7. Effect of 1.5% TBOT on the loss tangent vs. temperature behavior of LCP1.

Temperatures corresponding to tan δ peak for untreated and ultrasonically treated PEN and 80/20 PEN/LCP1 without and with catalyst are shown in Table 8.3. Ultrasonic treatment of PEN without catalyst was observed to induce a 4°C reduction in its Tg at an amplitude of 10 µm, while treatment of PEN at the same ultrasonic amplitude in the presence of Sb2O3 was not observed to affect its Tg significantly. Tg of 80/20 PEN/LCP1
blend without catalyst was also significantly reduced (7°C) with ultrasonic treatment at an amplitude of 10 µm. On the other hand, the presence of either Sb₂O₃ or TBOT catalyst prevented this reduction in T_g with treatment at 10 µm. While the latter indicated that presence of either catalyst stabilized thermal degradation of the 80/20 PEN/LCP1 blends, the lack of shift in T_g indicates no improvement in miscibility of the blend with catalyst.

Table 8.3. Tan δ peak temperature for untreated and ultrasonically treated PEN and 80/20 PEN/LCP1 without and with catalyst.

<table>
<thead>
<tr>
<th>tan δ peak (°C)</th>
<th>PEN</th>
<th>PEN/0.5% Sb₂O₃</th>
<th>80/20 PEN/LCP1</th>
<th>80/20/0.5 PEN/LCP1/Sb₂O₃</th>
<th>80/20/0.3 PEN/LCP1/TBOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>130</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0um</td>
<td>131</td>
<td>129</td>
<td>132</td>
<td>131</td>
<td>130</td>
</tr>
<tr>
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<td>128</td>
<td>130</td>
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</tr>
<tr>
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<td>130</td>
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<tr>
<td>10um</td>
<td>126</td>
<td>128</td>
<td>125</td>
<td>131</td>
<td>130</td>
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</table>

8.5. Thermal analysis

Differential scanning calorimetry (DSC) of untreated and ultrasonically treated PEN and 80/20 PEN/LCP1 blends were analyzed without and with Sb₂O₃ and TBOT catalysts. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), percent crystallinity of PEN phase (X_c), and peak melting temperature (T_m) were determined.

DSC results for untreated and ultrasonically treated PEN without and with 0.5% Sb₂O₃, and PEN/TBOT masterbatch are summarized in Table 8.4. The PEN melting temperature in the 80/20 PEN/LCP1 blend was not affected by the addition of the catalysts studied, neither with nor without ultrasonic treatment. T_g determined by DSC is lower than that determined by DMA, as expected [285].
The $T_g$ of virgin PEN was observed to decrease with extrusion without catalyst or treatment. Ultrasonic treatment of PEN without catalyst at amplitudes of 7.5 and 10 µm reduced its $T_g$, indicating its degradation. In the presence of 0.5% Sb$_2$O$_3$, the $T_g$ of PEN was slightly reduced with treatment at an amplitude of 7.5 µm, albeit lower than that in PEN without catalyst. In the presence of catalyst, ultrasonic treatment of PEN at 10 µm was observed to increase $T_g$ of extruded PEN without treatment. The latter suggested recombination reactions of PEN in the presence of 0.5% Sb$_2$O$_3$. This was expected as antimony trioxide is used to catalyze polycondensation reactions [109] and promotes transesterification reactions [110, 156].

Table 8.4. DSC results for untreated and ultrasonically treated PEN and PEN with 0.5% Sb$_2$O$_3$, and PEN/TBOT masterbatch.

<table>
<thead>
<tr>
<th>DSC 2nd heating runs</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$X_c$ (%)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>125.0</td>
<td>214.3</td>
<td>3.8</td>
<td>270.4</td>
</tr>
<tr>
<td>0 µm</td>
<td>122.8</td>
<td>204.8</td>
<td>4.5</td>
<td>269.6</td>
</tr>
<tr>
<td>5 µm</td>
<td>123.3</td>
<td>204.6</td>
<td>2.2</td>
<td>270.3</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>120.5</td>
<td>178.5</td>
<td>21.9</td>
<td>269.8</td>
</tr>
<tr>
<td>10 µm</td>
<td>120.6</td>
<td>179.2</td>
<td>20.0</td>
<td>270.1</td>
</tr>
<tr>
<td>PEN/0.5% Sb$_2$O$_3$</td>
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<td>122.4</td>
<td>193.4</td>
<td>10.6</td>
</tr>
<tr>
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<td>122.4</td>
<td>190.8</td>
<td>13.8</td>
<td>269.9</td>
</tr>
<tr>
<td>7.5 µm</td>
<td>121.5</td>
<td>188.7</td>
<td>19.6</td>
<td>270.0</td>
</tr>
<tr>
<td>10 µm</td>
<td>124.7</td>
<td>192.9</td>
<td>9.8</td>
<td>270.4</td>
</tr>
<tr>
<td>PEN/2% TBOT</td>
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<td>N/A</td>
<td>33.8</td>
<td>264.63</td>
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</table>

Figure 8.8 shows the heat flow vs. temperature curves for pure PEN (a), and for PEN containing 0.5% Sb$_2$O$_3$ processed in SONIC1, and PEN masterbatch containing 2% TBOT prepared in a twin screw extruder (b), without and with ultrasonic treatment.
Figure 8.8. Heat flow vs. temperature during DSC second heating for (a) pure PEN, (b) PEN/0.5% Sb₂O₃ and PEN/2% TBOT masterbatch, without and with ultrasonic treatment.

From Figure 8.8a, it was observed that the cold crystallization exotherm of virgin PEN shifted further to lower temperature after passing through the extruder (0 µm). With
ultrasonic treatment at amplitudes of 7.5 and 10 µm, the cold crystallization exotherm shifted to lower temperatures and become narrower. The enhanced crystallization observed with treatment at the said conditions could be attributed to degradation of PEN, as lower molecular weight chains crystallize faster [318].

A shift in the cold crystallization peak to lower temperatures is observed from Figure 8.8b with ultrasonic treatment of Sb$_2$O$_3$ containing PEN at 5 and 7.5 µm. The cold crystallization exotherm was higher at 7.5 µm. Hence, PEN exhibited enhanced crystallization at this condition, possibly due to its degradation. Ultrasonic treatment of Sb$_2$O$_3$ containing PEN at an amplitude of 10 µm was observed to increase its cold crystallization temperature, indicating possibly higher molecular weight of PEN, due to slower crystallization of longer chains [318]. This suggested that combination of TBOT with ultrasound at an amplitude of 10 µm during processing could be counteracting PEN degradation through recombination reactions. This was also supported by the slightly higher $T_g$ observed in this compound. Melting temperature of PEN was not affected by the presence of Sb$_2$O$_3$ catalyst or by ultrasonic treatment.

Figure 8.8b shows that a significant reduction of cold crystallization temperature of PEN/2% TBOT masterbatch over that of virgin PEN. For the masterbatch, the onset of melting endotherm also shifted to lower temperature and a broader change in $\Delta H$ resembling the glass transition was observed around 100°C. While the latter could be due to possible residual water trapped in the sample after drying, the $\Delta H$ vs. temperature curve around 100°C was shaped more like a second order transition and indicated an inflection point, rather than a minimum as in endothermic first order transition. These
results indicated severe degradation and possible molecular weight broadening of PEN in the presence of 2% TBOT.

Table 8.5. DSC second heating results for untreated and ultrasonically treated 80/20 PEN/LCP1 with Sb$_2$O$_3$ and TBOT catalysts.

<table>
<thead>
<tr>
<th>DSC 2$^{nd}$ heating runs</th>
<th>80/20 PEN/LCP1</th>
<th>80/20/0.5 PEN/LCP1/Sb$_2$O$_3$</th>
<th>80/20/1 PEN/LCP1/Sb$_2$O$_3$</th>
<th>80/20/0.3 PEN/LCP1/TBOT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T$_g$ ($^\circ$C)</td>
<td>T$_cc$ ($^\circ$C)</td>
<td>X$_c$ (%)</td>
<td>T$_m$ ($^\circ$C)</td>
</tr>
<tr>
<td>0 $\mu$m</td>
<td>122.8</td>
<td>177.4</td>
<td>16.2</td>
<td>268.7</td>
</tr>
<tr>
<td>5 $\mu$m</td>
<td>121.9</td>
<td>175.3</td>
<td>20.6</td>
<td>268.1</td>
</tr>
<tr>
<td>7.5 $\mu$m</td>
<td>121.2</td>
<td>172.2</td>
<td>22.0</td>
<td>268.7</td>
</tr>
<tr>
<td>10 $\mu$m</td>
<td>120.0</td>
<td>164.0</td>
<td>28.1</td>
<td>269.1</td>
</tr>
<tr>
<td>0 $\mu$m</td>
<td>123.1</td>
<td>176.6</td>
<td>20.8</td>
<td>268.8</td>
</tr>
<tr>
<td>5 $\mu$m</td>
<td>122.7</td>
<td>178.2</td>
<td>19.8</td>
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</tr>
<tr>
<td>7.5 $\mu$m</td>
<td>123.1</td>
<td>177.5</td>
<td>21.7</td>
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<td>123.5</td>
<td>177.6</td>
<td>20.8</td>
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<td>169.5</td>
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</tr>
<tr>
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<td>119.0</td>
<td>170.6</td>
<td>28.4</td>
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</tr>
<tr>
<td>5 $\mu$m</td>
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<td>170.0</td>
<td>33.0</td>
<td>267.5</td>
</tr>
<tr>
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<td>118.9</td>
<td>170.9</td>
<td>26.1</td>
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</tr>
<tr>
<td>10 $\mu$m</td>
<td>120.5</td>
<td>174.5</td>
<td>22.9</td>
<td>267.8</td>
</tr>
</tbody>
</table>

Figure 8.9. Heat flow vs. temperature during DSC second heating for 80/20 PEN/LCP1 without and with ultrasonic treatment.
DSC results for untreated and ultrasonically treated 80/20 PEN/LCP1 with Sb$_2$O$_3$ and TBOT catalysts were shown in Table 8.5. In 80/20 PEN/LCP1 blends without catalyst, the cold crystallization temperature of PEN decreased and normalized PEN crystallinity increased with extrusion and increasing amplitude of ultrasonic treatment. These changes can also be observed from the DSC endotherms of 80/20 PEN/LCP1 blends without and with ultrasonic treatment shown in Figure 8.9.

![DSC endotherms of 80/20 PEN/LCP1 blends without and with ultrasonic treatment.](image)

Figure 8.10. Heat flow vs. temperature during DSC second heating for 80/20 PEN/LCP1 with Sb$_2$O$_3$ without and with ultrasonic treatment.

The crystallinity of 80/20 PEN/LCP1 blends containing 0.5% Sb$_2$O$_3$ was similar to the blend ultrasonically treated at an amplitude of 5 µm without catalyst. The crystallinity of the blend containing 0.5% Sb$_2$O$_3$ catalyst was not significantly affected by ultrasonic treatment. Increasing Sb$_2$O$_3$ catalyst to 1% with treatment at an ultrasonic amplitude of 10 µm led to a reduction in cold crystallization temperature, indicating
faster crystallization of this blend during heating, possibly due to its degradation. These changes can also be observed from the DSC endotherms of 80/20 PEN/LCP1 blends containing Sb$_2$O$_3$ without and with ultrasonic treatment shown in Figure 8.10.

![DSC endotherms for untreated and ultrasonically treated 80/20 PEN/LCP1 blends containing 0.3% TBOT catalyst are shown in Figure 8.11. Results indicated that the addition of 0.3% TBOT to 80/20 PEN/LCP1 blend caused reduction of $T_g$ except at an amplitude of 10 µm, indicating degradation. 80/20 PEN/LCP1 blends containing 0.3 TBOT% indicated higher $T_g$, high cold crystallization temperature, and lower crystallinity with ultrasonic treatment at an amplitude of 10 µm. This signified a reduction in extent of degradation with treatment at this amplitude. This was in contrast to 80/20 PEN/LCP1 blends without catalyst, for which ultrasonic treatment at an amplitude of 10 µm caused a further reduction in extent of degradation.](image-url)

Figure 8.11. Heat flow vs. temperature during DSC second heating for 80/20 PEN/LCP1 with 0.3% TBOT without and with ultrasonic treatment.
amplitude of 10 µm led to the highest degradation, based on its increased crystallinity and reduced T<sub>g</sub>. This signified different effect of ultrasound on 80/20 PEN/LCP1 blends without and with added catalysts. This could be due to recombination reactions in ultrasonically treated blend in the presence of TBOT catalyst.

8.6. FT-IR spectroscopy

FT-IR spectroscopy of untreated and ultrasonically treated 80/20 PEN/LCP1 blends were studied with and without the catalyst. No changes were observed in the FT-IR spectra neither with added catalysts or amplitude of ultrasonic treatment. A sample spectrum provided in Figure 8.12 indicates no changes with more than 1 cm<sup>-1</sup> shifts in peaks. The absence of new peaks would not rule out the possibility that reactions could have taken place in the melt. However, this indicated that new chemical groups which could have formed either overlapped with existing peaks or were too sparse to be detected by ATR FT-IR.

![FT-IR spectrum](image)

Figure 8.12. FT-IR spectrum of untreated and ultrasonically treated 80/20 PEN/LCP1 blends without and with added Sb<sub>2</sub>O<sub>3</sub> and TBOT catalyst; no changes were observed with catalyst or treatment.
8.7. Mechanical properties

Changes in mechanical properties of PEN and 80/20 PEN/LCP1 with addition of catalyst were determined. In this section, virgin PEN was injection molded into specimens for testing without any other processing for comparison with PEN that was extruded before injection molding. Young’s modulus, strength at yield, elongation at yield, and unnotched Izod impact strength of untreated and ultrasonically treated PEN without and with 0.5% Sb$_2$O$_3$ catalyst were compared. Young’s modulus, strength, elongation at break, and unnotched Izod impact strength of untreated and ultrasonically treated 80/20 PEN/LCP1 blends were studied without and with Sb$_2$O$_3$ and TBOT catalysts.

![Figure 8.13. Young's modulus vs. ultrasonic amplitude for PEN without and with Sb$_2$O$_3$ catalyst.](image)

Figure 8.13. Young's modulus vs. ultrasonic amplitude for PEN without and with Sb$_2$O$_3$ catalyst.

Young’s modulus versus ultrasonic amplitude for PEN without and with 0.5% Sb$_2$O$_3$ catalyst is shown in Figure 8.13. The Young’s modulus of untreated PEN was
higher without catalyst. Modulus of PEN without catalyst decreased with amplitude of ultrasonic treatment. On the other hand, the modulus of PEN with 0.5% Sb$_2$O$_3$ was not affected by amplitude of treatment.

![Figure 8.14. Yield stress vs. ultrasonic amplitude for PEN without and with 0.5% Sb$_2$O$_3$ catalyst.](image)

The yield stress versus ultrasonic amplitude for PEN without and with 0.5% Sb$_2$O$_3$ catalyst is shown in Figure 8.14. It should be noted that PEN did not exhibit yielding at an amplitude of 10 µm without, and at amplitudes of 7.5 and 10 µm with catalyst. Brittle fracture was observed at the said conditions. The strength of PEN without catalyst did not change with ultrasonic treatment except at an amplitude of 10 µm, at which it was reduced. On the other hand, the strength of PEN containing 0.5% Sb$_2$O$_3$ was observed to decrease with treatment at amplitudes of 7.5 and 10 µm. In PEN containing
Sb$_2$O$_3$ catalyst, the strength at an amplitude of 10 µm was higher than that at an amplitude of 7.5 µm.

The elongation at yield versus ultrasonic amplitude for PEN without and with 0.5% Sb$_2$O$_3$ catalyst is shown in Figure 8.15. The elongation of PEN without catalyst did not change with ultrasonic treatment except at an amplitude of 10 µm, at which it reduced. The elongation of PEN containing 0.5% Sb$_2$O$_3$ was observed to decrease with treatment at amplitudes of 7.5 and 10 µm. Samples treated at these amplitudes exhibited brittle fracture, i.e. did not yield. In PEN containing 0.5% Sb$_2$O$_3$ catalyst, the elongation at break at an amplitude of 10 µm was higher than that at an amplitude of 7.5 µm.

![Figure 8.15. Elongation at yield vs. ultrasonic amplitude for PEN without and with Sb$_2$O$_3$ catalyst.](image-url)
Figure 8.16. Effect of Sb$_2$O$_3$ on the unnotched Izod impact strength of PEN without and with ultrasonic treatment.

The impact strength of PEN without and with catalyst is presented in Figure 8.16 as an average of dead end (DE) and gate end (GE) impact bars, as there was no statistically significant difference between impact strengths at the two sample positions. Impact strength of PEN containing 0.5% Sb$_2$O$_3$ was lower than that of PEN without catalyst, and without and with treatment at amplitudes of 5 and 7.5 µm. Impact strength of PEN was not affected by presence of 0.5% Sb$_2$O$_3$ catalyst with treatment at an amplitude of 10 µm.
The Young’s modulus versus ultrasonic amplitude for 80/20 PEN/LCP1 blends without and with 0.5% Sb$_2$O$_3$ and 0.3% TBOT catalysts is shown in Figure 8.17. The Young’s modulus of 80/20 PEN/LCP1 blends was similarly higher in the presence of 0.5% Sb$_2$O$_3$ and 0.3% TBOT than that of the blend without catalyst. The higher Young’s modulus in presence of catalyst indicated greater orientation in these samples. While the Young’s modulus of 80/20 PEN/LCP1 without catalyst decreased substantially with treatment at an amplitude of 10 µm, it stayed the same in presence of either catalyst at this amplitude. This signified that the presence of catalyst during ultrasonic treatment affected the blends differently.
Figure 8.18. Strength vs. ultrasonic amplitude for 80/20 PEN/LCP1 blends with and without Sb$_2$O$_3$ and TBOT catalysts.

Strength vs. ultrasonic amplitude for 80/20 PEN/LCP1 blends without and with 0.5% Sb$_2$O$_3$ and 0.3% TBOT catalysts is shown in Figure 8.18. The strength of 80/20 PEN/LCP1 blends without and with 0.3% Sb$_2$O$_3$ catalyst was similar except with treatment at an amplitude of 10 µm. At this amplitude, the blend without catalyst lost more than half its strength, while only slight reduction in strength was observed in the presence of 0.5% Sb$_2$O$_3$. The 80/20 PEN/LCP1 blend containing 0.3% TBOT had lower strength than the blend without catalyst, except at an amplitude of 10 µm. The strength of 80/20 PEN/LCP1 blend containing 0.5% TBOT increased slightly with ultrasonic treatment at an amplitude of 10 µm. The strength of blend containing TBOT was less than that of blend containing Sb$_2$O$_3$ without and with treatment. This could be due to the degradation of LCP1 during compounding of masterbatch as previously discussed.
The elongation at break vs. ultrasonic amplitude for 80/20 PEN/LCP1 blends with and without 0.5% Sb$_2$O$_3$ and 0.3% TBOT catalysts is shown in Figure 8.19. The elongation at break of PEN/LCP1 with 0.5% Sb$_2$O$_3$ catalyst was higher than without catalyst for untreated and ultrasonically treated blends. In both the 80/20 PEN/LCP1 blend without and with Sb$_2$O$_3$ catalyst, the elongation at break was observed to decrease at an amplitude of 10 µm, indicating degradation with ultrasonic treatment at this amplitude. The elongation at break of blend containing TBOT was less than that of the blend without catalyst at all conditions, except with treatment at an amplitude of 10 µm. While a reduction in elongation at break was observed at an amplitude of 10 µm in PEN without catalyst, no appreciable decrease was observed in the blend with 0.5% TBOT at this amplitude.
Unnotched Izod impact strength of 80/20 PEN/LCP1 blends, determined separately in dead end (DE) and gate end (GE) impact bars, is shown in Figure 8.20 for untreated and ultrasonically treated blends with and without 0.5% Sb$_2$O$_3$ and 0.3% TBOT catalysts. The DE samples of 80/20 PEN/LCP1 without catalyst exhibited greater impact strength than the GE samples due to higher orientation in the DE samples at the employed injection molding conditions. There was no statistical difference in the impact strength of DE and GE moldings in 80/20 PEN/LCP1 blend with catalyst. This indicated a reduction in LCP1 fibrillation since the orientation of LCP1 fibers, as previously observed (section 7.5), introduced greater differences in impact properties of DE and GE samples. This could be due to the lower impact strength with catalyst. The impact strength of the blend without catalyst was observed to decrease substantially with ultrasonic treatment at an amplitude of 10 µm. This was lower than the impact strength of blends containing TBOT and Sb$_2$O$_3$ catalysts, which were also treated at an amplitude of
10 μm. The impact strength of untreated and ultrasonically treated 80/20 PEN/LCP1 blend containing 0.5% Sb₂O₃ was higher than that of the blend containing 0.3% TBOT. This could be due to weaker fibrils of LCP1 in blend with TBOT. The weakness of LCP1 phase in these blends was a result of LCP1 degradation during preparation of LCP1/1.5% TBOT masterbatch in twin screw extrusion.

8.8. Morphology

The morphology of 80/20 PEN/LCP1 blends containing 0.5% Sb₂O₃ and 0.3% TBOT were studied through SEM micrographs of the core and skin regions of injection moldings. The SEM micrographs of 80/20 PEN/LCP1 blends without catalyst, without and with treatment at ultrasonic amplitudes of 7.5 and 10 μm are shown in Figure 5.19a-f, and discussed in section 5.9.

Figure 8.21a-f show SEM micrographs of the core and skin regions of moldings of 80/20 PEN/LCP1 blends with 0.5% Sb₂O₃ catalyst, without and with ultrasonic treatment at amplitudes of 7.5 and 10 μm at a magnification of 2,000x. In the blend without ultrasonic treatment, no differences could be identified between the skin and core morphologies indicating LCP1 fibrillation throughout. This could be due to inhibition of PEN thermo-mechanical degradation by the presence of 0.5% Sb₂O₃. With increasing ultrasonic amplitude, the core and skin morphologies become distinctly different, with droplets and fibrils of LCPs appearing in the core and skin regions, respectively. LCP1 domain size was also increased with ultrasonic treatment. The LCP1 domain size in 80/20 PEN/LCP1 blend at an amplitude of 10 μm in the presence of 0.5% Sb₂O₃ (Figure 8.21e-f) was smaller than that without catalyst (Figure 5.19e-f).
Figure 8.21. SEM micrographs at 2,000x magnification for 80/20 PEN/LCP1 blends with 0.5% Sb$_2$O$_3$, (a) 0 μm core, (b) 0 μm skin, (c) 7.5 μm core, (d) 7.5 μm skin, (e) 10 μm core, (f) 10 μm skin.
Figure 8.22. SEM micrographs at 4,000x magnification for 80/20 PEN/LCP1 blends with 0.5% Sb$_2$O$_3$, (a) 0 µm core, (b) 0 µm skin, (c) 7.5 µm core, (d) 7.5 µm skin, (e) 10 µm core, (f) 10 µm skin.

Figure 8.22a-f show the at 4,000x magnification SEM micrographs of the core and skin regions of moldings of 80/20 PEN/LCP1 blends with 0.5% Sb$_2$O$_3$ catalyst,
without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm. No changes in LCP1/PEN interfaces were identified with addition of Sb$_2$O$_3$ catalyst. Voids around LCP1 droplets and fibrils could still be identified in the presence of catalyst, both without or with ultrasonic treatment.

Figure 8.23a-f show SEM micrographs of the core and skin regions of moldings of 80/20 PEN/LCP1 blends with 0.3% TBOT catalyst, without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm at a magnification of 2,000x. Figure 8.23a-b indicated large LCP1 droplets in the core, and fine fibrils in the skin region of moldings were accompanied by large chunks of undeformed LCP1 in the untreated blend with TBOT. There appeared to be poor adhesion in the core region. The size of LCP1 domains was larger than without catalyst (Figure 5.19a-b), indicating reduced LCP1 deformation due to reduced viscosity of matrix to LCP1. The deformation of LCP1 droplets in the core was improved with ultrasonic treatment at an amplitude of 7.5 µm (Figure 8.23c), while size of LCP1 fibrillar domains in the skin was increased (Figure 8.23d). With ultrasonic treatment at an amplitude of 10 µm, size of LCP1 droplets in the core (Figure 8.23e) was much larger, and the droplets appeared to be embedded in the PEN phase, indicating good interfacial adhesion. With treatment at 10 µm, fine fibrils were accompanied by large undeformed LCP1 domains in the skin (Figure 8.23f). In summary, the SEM micrographs of 80/20 PEN/LCP1 blends indicated improved interfacial adhesion with ultrasonic treatment. The presence of agglomerates at an amplitude of 10 µm indicated poor deformation of LCP1 phase and suggested a competition between degradation and in-situ compatibilization with ultrasonic treatment in the 80/20 PEN/LCP1 with 0.3% TBOT catalyst.
Figure 8.23. SEM micrographs of 80/20 PEN/LCP1 blends with 0.3% TBOT, (a) 0 μm core, (b) 0 μm skin, (c) 7.5 μm core, (d) 7.5 μm skin, (e) 10 μm core, (f) 10 μm skin.
8.9. Conclusions

Addition of 0.5% Sb$_2$O$_3$ catalyst to pure PEN resulted in reduced degradation of PEN with ultrasonic treatment. This suggested enhanced recombination reactions in the presence of Sb$_2$O$_3$. On the other hand, addition of 2% TBOT to PEN during catalyst masterbatch preparation led to complete degradation of PEN. Addition of 1.5% TBOT to LCP1 led to some degradation, but was a necessary step for incorporation into blends.

Addition of 0.5% Sb$_2$O$_3$ to PEN stabilized the increase in tan δ with ultrasonic treatment an amplitude of 10 µm. Addition of 1.5% TBOT to LCP1 for preparation of masterbatch increased value of tan δ and caused a 2°C drop in its peak value, indicating degradation of LCP1 in the presence of TBOT.

Addition of Sb$_2$O$_3$ to 80/20 PEN/LCP1 blend led to reduced viscosity as compared to blend without catalyst. Ultrasonic treatment of 80/20 PEN/LCP1 containing Sb$_2$O$_3$ was observed to reduce viscosity more than that of the blend without catalyst. Addition of 1% Sb$_2$O$_3$ increased extent of degradation compared to 0.5% Sb$_2$O$_3$ at an amplitude of 10 µm. The viscosity of 80/20 PEN/LCP1 blends containing 0.5% TBOT were lower with ultrasonic treatment than any of the other blends.

Tan δ peak of 80/20 PEN/LCP1 from DMA increased most with ultrasonic treatment without catalyst at an amplitude of 10 µm. Addition of TBOT broadened the tan δ peak of 80/20 PEN/LCP1 to lower temperatures. While tan δ peak of 80/20 PEN/LCP1 in presence of 0.5% Sb$_2$O$_3$ was lower in intensity than the untreated blend without catalyst, ultrasonic treatment increased this peak to the higher level in the presence of 0.3% TBOT. Results indicated a greater initial degradation with TBOT, but better retention of elasticity with ultrasonic treatment. In the presence of Sb$_2$O$_3$,
ultrasonic treatment stabilized the blend against the degradation observed in the blend without catalyst at 10 µm, indicating greater recombination reactions in the presence of catalyst at this amplitude. Ultrasonic treatment with catalyst did not lead to significant changes in T_g, while ultrasonic treatment of PEN at an amplitude of 10 µm led to a reduction in its T_g by 6-7°C, as determined by DMA.

Addition of TBOT to 80/20 PEN/LCP1 blend was shown to increase its crystallinity. Crystallinity increase in presence of Sb_2O_3 was only observed when it was present at a concentration of 1% in blend ultrasonically treated at an amplitude of 10 µm. The increase in crystallinity in the latter was 13% over that of 80/20 PEN/LCP1 blend containing 0.5% Sb_2O_3 with ultrasonic treatment at an amplitude of 10 µm.

Mechanical properties of PEN were observed to decrease with treatment at an amplitude of 10 µm without and with 0.5% Sb_2O_3 catalyst. Comparing untreated 80/20 PEN/LCP1 blends mechanical properties of 80/20 PEN/LCP1 with 0.3% TBOT were lower than those without catalyst and with 0.5% Sb_2O_3 catalyst content. While properties of blend without catalyst diminished with treatment at an amplitude of 10 µm, Young’s modulus and strength of 80/20 PEN/LCP1 blends containing either 0.3% TBOT or 0.5% Sb_2O_3 stayed the same with treatment at 10 µm. Impact strength of 80/20 PEN/LCP1 blends without catalyst decreased substantially with ultrasonic treatment at an amplitude of 10 µm. The impact properties of blends containing either catalyst, although were lower than untreated 80/20 PEN/LCP1 blends, did not deteriorate at an amplitude of 10 µm. Moreover, blends containing catalyst did not show any statistically significant difference
between impact strength of gate end and dead end samples observed for blends without catalyst. This suggested change in LCP1 fibrillation in the presence of catalysts.

The LCP1 domain size in 80/20 PEN/LCP1 at an amplitude of 10 µm in the presence of 0.5% Sb$_2$O$_3$ was finer than that in the blend treated at 10 µm without catalyst. SEM micrographs of blends containing Sb$_2$O$_3$ did not show improved interfacial adhesion, as indicated by the presence of voids around LCP1 domains. In blend containing 0.3% TBOT, ultrasonic treatment at an amplitude of 10 µm increased the size of LCP1 droplets in the core, which appeared to be better embedded in the PEN matrix. The latter indicated good interfacial adhesion in PEN/LCP1 blends ultrasonically treated at an amplitude of 10 µm in the presence of TBOT. Treatment at this amplitude in the presence of TBOT was accompanied by presence of larger agglomerates in the skin and core regions of the blends, which indicated poor deformation of LCP1 phase. This suggested a competition between degradation and in-situ compatibilization with ultrasonic treatment in 80/20 PEN/LCP1 containing 0.3% TBOT catalyst.
CHAPTER IX
FIBER SPINNING

The mechanical properties of fiber spun from PET, PEN, LCP1, LCP2 and their blends will be discussed in this section. Morphology of PEN/LCP1 fibers will also be analyzed to determine the effect of ultrasonic treatment on the interfacial tension between the components.

9.1. Introduction

Fiber spinning introduces greater elongational flow than injection molding, allowing greater orientation in the machine direction. Fiber spinning of polymers typically leads to greater stiffness and strength than in injection moldings due to the higher orientation [181]. LCP fibrils are highly continuous in fiber spinning whereas they resemble chopped fibrils in injection moldings [216].

In liquid crystalline polymers, which are processed in the nematic phase, greater orientation can be attained compared to thermoplastics, leading to much higher stiffness and strength of LCPs and blends containing LCPs. Orientation in liquid crystalline polymers results in highly aligned fibrillar structures [52, 56, 60]. Fibrillation is caused by elongational flow, rather than shear flow. Hence, primarily the draw down ratio, rather than shear stress experienced by the melt during extrusion through the die, is responsible for LCP1 fibrillation.
Fibers of PET, PEN, LCP1, LCP2, and PET/LCP1, PEN/LCP1, PET/PEN, and LCP1/LCP2 blends were prepared by extruding from a capillary rheometer at 300°C. The plunger speed was constant for all conditions, resulting in a shear rate of 301 s⁻¹. Fibers were collected with no take up (drawdown ratio (DDR) of 1), and with DDR of 45, 76.5, and 112.5. The processing temperature of 300°C resulted in obtaining fine fibers of as-received polymers. However, there were some process instabilities during the spinning of extruded PET, and PET/LCP1 blends. During spinning, up to a 30% decrease in pressure was recorded for PET, 90/10 and 80/20 PET/LCP1 blends, indicating degradation of PET during extrusion from the capillary die at 300°C. 70/30 and 60/40 PET/LCP1 blends indicated less degradation. However, the pressure measured at the entrance to the capillary die dropped by up to 15% during processing of these blends. Due to instabilities in fiber spinning of PET and its blends with LCP1, fibers could not be spun or collected at certain conditions. Moreover, degradation of PET led to lower properties for PET and PET/LCP1 fibers. There was no appreciable change in pressure during extrusion of LCP1, LCP2, PEN, and PET/PEN, PEN/LCP1 blends, and uniform fibers were drawn at all intended DDRs.

Young’s modulus was used to infer orientation with DDR in the studied systems [38, 64]. The strength and elongation at break were also measured. Morphology of fibers of PEN/LCP1 blends was studied to observe LCP1 fibrillation and LCP1 to thermoplastic phase interfacial adhesion in this system with composition and ultrasonic treatment.
9.2. Mechanical properties of spun fibers

The mechanical properties of fibers drawn from pure materials and blends were determined. These results are presented in this section.

9.2.1. Fibers spun from as-received and processed pure materials

Fibers of as-received, untreated and ultrasonically treated PET, PEN, LCP1, and LCP2 were spun at different DDRs. Mechanical properties of these fibers will be discussed in this section.

9.2.1.1. PET and PEN

The fiber spinning temperature (300°C) was higher than melt temperature during the injection molding of PET and PEN. The higher temperature was chosen to obtain uniform fibers in their blends with LCP1.

The Young’s modulus as a function of DDR for fibers spun from as-received and extruded PET and PEN is shown in Figure 9.1. The Young’s modulus of as-received and extruded PEN increased with DDR. Young’s modulus of PET increased up to a DDR of 45, but did not change with drawing at higher DDRs. Extruded PET had process instabilities while spinning. The PET spun after extrusion had a much lower viscosity than as-received PEN. It degraded further at the high processing temperature of the capillary rheometer. Extruded PET was observed to fall under its own weight and could not be spun except at the highest motor speed. The Young’s modulus of extruded PET at a DDR of 112.5 was also lower than that without take-up. It should be noted that DDR of
1 could not be achieved for PET, since it was drawn under its own weight before collection at a distance of 5 cm from the exit of the die.

Figure 9.1. Young's modulus vs. drawdown ratio (DDR) for PET and PEN, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).

The yield stress for fibers spun from as-received and extruded PET and PEN is shown in Figure 9.2. The strength at yield of as-received and extruded PEN was not affected by DDR. Even though the orientation of PEN increased with DDR, as evidenced from modulus results, fibers still showed yielding behavior. The yield stress of as-received PET did not change with DDR, while that of extruded PET was observed to decrease due to its degradation. It should be noted the fibers were spun from low DDR to high DDR. Hence, fibers spun at high DDVs resided for a longer time inside the capillary rheometer and could experience greater degradation. This affected extruded PET the most, due to its lower MW than as-received PET, as shown by its viscosity in Figure 6.2.
Moreover the set temperature for PET spinning appeared to be too high. It is known that mechanical properties of polycondensation polymers increase and approach an asymptotic behavior with increasing molecular weight [319]. Hence, large molecular weight reductions cause a pronounced deterioration in mechanical properties.

![Graph showing yield stress vs. DDR for PET and PEN](image)

**Figure 9.2.** Yield stress vs. DDR for PET and PEN, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).

Elongation at yield as a function of DDR for fibers spun from as-received and extruded PET and PEN is shown in Figure 9.3. The elongation at yield decreased for both as-received and extruded PEN, which indicated greater stiffness and orientation in PEN with increasing DDR. On the other hand, the elongation at yield of PET did not change with DDR, indicating less orientation as compared to PEN. The lower melting temperature of PET and its slower solidification during spinning led to its reduced orientation.
Figure 9.3. Elongation at yield vs. DDR for PET and PEN, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).

The elongation at break as a function of DDR for fibers spun from as-received and extruded PET and PEN is shown in Figure 9.4. The elongation at break of as-received PEN was not reported in this figure since these data were inconsistent. This could be due to process instabilities without take-up for as-received PEN. Similarly, the elongation at break of extruded PET was not reported with drawing. The elongation at break of as-received and extruded PEN were higher with take-up than without (DDR=1). Extruded PEN exhibited slightly higher elongation at break than as-received PEN. The elongation at break of extruded PEN did not change with DDR. On the other hand, the elongation at break of PET was highest at a DDR of 45. As PET was expected to have less orientation compared to PEN due to its lower melting point, the decrease in its elongation at break at higher DDRs can be explained by its degradation with greater
residence time in the capillary rheometer. As previously mentioned, this is due to the sequence of processing in the same batch, which started from the lower DDRs.

Figure 9.4. Elongation at break vs. DDR for PET and PEN, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).

The strength at break as a function of DDR for fibers spun from as-received and extruded PET and PEN is shown in Figure 9.5. Strength at break of PEN was observed to increase with DDR, indicating greater stress-induced crystallization during necking of fibers. This indicated greater orientation of PEN at higher DDRs, which promoted strain-induced crystallization during mechanical testing. Extruded PEN spun at a DDR of 45 did not indicate an increase in the strength at break. The strength at break of as-received and extruded PEN were greater than their strength at yield at DDRs of 45, 76.5, 112.5 and 76.5, 112.5, respectively. This was due to strain-induced crystallization of PEN during cold drawing, induced by mechanical testing. The strength at break of fibers spun from
extruded PEN was slightly higher than that of those spun from as-received PEN at DDRs of 76.5 and 112.5, possibly indicating its greater orientation. By comparison with PEN fibers, the strength at yield and at break of PET fibers were much lower. Poor mechanical properties at break of PET fibers were due to degradation during fiber spinning at 300°C.

Figure 9.5. Strength at break vs. DDR for PET and PEN, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).

9.2.1.2. LCP1 and LCP2

The Young’s modulus as a function of DDR for fibers spun from as-received and extruded LCP1 and LCP2 were shown in Figure 9.6. At a DDR of 1, the Young’s modulus of LCP2 was higher than LCP1. However, the Young’s modulus of LCP1 increased more with DDR than that of LCP2, indicating greater stiffness in oriented LCP1. The Young’s moduli of as-received and extruded LCP1 were not significantly
different. On the other hand, the modulus of LCP2 was lower after extrusion compared to as-received sample. The latter indicated the degradation of LCP2 with processing.

![Figure 9.6. Young's modulus vs. DDR for LCP1 and LCP2, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).](image)

The strength as a function of DDR for fibers spun from as-received and extruded LCP1 and LCP2 is shown in Figure 9.7. It should be noted that LCPs did not show yielding behavior. At a DDR of 1, the strength of LCP1 and LCP2 were similar. The strength of LCP1 increased more with DDR than that of LCP2. The strength of as-received and extruded LCP1 were not significantly different. On the other hand, the strength of LCP2 was lower after extrusion compared to as-received sample, also indicating degradation of LCP2 with processing.
Figure 9.7. Strength vs. DDR for LCP1 and LCP2, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).

Figure 9.8. Elongation at break vs. DDR for LCP1 and LCP2, as-received (solid symbols and lines) and after passing through extruder with no treatment (open symbols and dashed lines).
The elongation at break as a function of DDR for fibers spun from as-received and extruded LCP1 and LCP2 were shown in Figure 9.8. The elongation at break at a DDR if 1 was greater for LCP1 than LCP2. The elongation at break decreased more rapidly with DDR and was lower with spinning in LCP1 as compared to LCP2. This indicated greater orientation in LCP1 than that in LCP2 after spinning. While the elongation at break of as-received and extruded LCP2 were not significantly different, that of as extruded LCP1 was greater than as-received LCP1.

9.2.2. Fibers spun from blends

Mechanical properties of fibers spun from blends of PET/LCP1, PEN/LCP1, PET/PEN and LPC1/LCP2 are presented and discussed in this section.

9.2.2.1. PET/LCP1 blends

Fibers spun from blends ultrasonically treated at an amplitude of 7.5 µm were chosen for comparison with fibers spun from untreated blends. This was because ultrasonic treatment at an amplitude of 5 µm was shown to have little effect on properties of PET/LCP1 blends, and treatment at 10 µm had resulted in significant PET degradation, resulting in poor mechanical properties of the blends.

PET and 90/10 PET/LCP1 blends were collected without drawing and at a DDR of 112.5. These materials had low viscosity and extended under their own weight during extrusion and could not be collected at intermediate DDRs. These results indicated degradation of PET during processing at 300°C. 80/20 PET/LCP1 blends were too brittle
to spin fibers, and therefore were collected without take-up. The latter indicated its degradation during fiber spinning.

The Young’s modulus as a function of DDR of fibers spun from untreated and ultrasonically treated blends of PET/LCP1 blends is shown in Figure 9.9. It should be noted that a logarithmic scale was used in the y-axis. The Young’s modulus of blends increased with LCP1 concentration. There was some distribution in the actual DDR obtained without spinning in PET and PET/LCP1 blends due to their low viscosity at 300°C, which led to drawing under gravity based on viscosity. The Young’s modulus of drawn fibers of blends increased with DDR. It should be noted that no data was available for 80/20 PET/LCP1 as the melt was too brittle during spinning. The Young’s modulus of fibers spun from 90/10 PET/LCP1 did not change with DDR. The Young’s modulus of fibers of 70/30, 60/40 PET/LCP1 blends increased with DDR. Young’s modulus of PET/LCP1 blends did not indicate differences without and with treatment.

![Figure 9.9. Young's modulus vs. DDR for PET/LCP1 blends without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).](image-url)
The strength as a function of DDR for fibers spun from untreated and ultrasonically treated blends of PET/LCP1 blends is shown in Figure 9.10. Since only PET and 90/10 PET/LCP1 fibers exhibited yielding, their yield strength was plotted along with the strength at break of LCP1 and other blends for comparison purposes. The strength of 90/10 PET/LCP1 blend was close to that of pure PET, and did not change with ultrasonic treatment. Strength of these blends was determined by fibrillation of LCP1 phase and its orientation, which is governed by viscosity ratio of dispersed to matrix phase (K) as described in section 2.4.3.1 [169]. This was due to the poor deformation of the dispersed LCP1 phase by the lower viscosity PET matrix during fiber spinning at a temperature of 300°C. The strength of 70/30 and 60/40 PET/LCP1 fibers increased with DDR. This indicated improved deformation of LCP1 phase in PET at these LCP1 concentrations. This was possibly due to reduced degradation of the PET phase during processing of blends and the correspondingly higher viscosity ratio of PET to LCP1 in blends with higher LCP1 concentrations, as presence of LCP1 is expected to improve thermal stability of PET [93]. The strength obtained in fibers spun from PET/LCP1 blends was much less than that in moldings, which were prepared at a barrel temperature of 285°C. This was attributed to reduced fibrillation of LCP1 during fiber spinning at 300°C as the matrix to LCP1 viscosity ratio was lower at the higher processing temperature. The continued degradation of PET with increasing residence time during processing at this higher temperature led to dependence of mechanical properties of PET/LCP1 fibers on many variables including time, processing sequence and effect of LCP1 content on PET degradation to the parameters governing fibrillation in PET/LCP1 blends.
Figure 9.10. Strength vs. DDR for PET/LCP1 blends without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).

Figure 9.11. Elongation at yield vs. DDR for PET/LCP1 blends without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines). Elongation at break of 80/20, 70/30, 60/40 PET/LCP1 blends and LCP1 were reported as they did not exhibit yielding.
The elongation at yield as a function of DDR for fibers spun from untreated and ultrasonically treated blends of PET/LCP1 blends is shown in Figure 9.11. It should be noted that 80/20, 70/30, 60/40 PET/LCP1 blends and LCP1 did not exhibit yielding, and their elongation at break were plotted together with the elongation at yield of PET and 90/10 PET/LCP1 blend. Overall, the elongation was observed to decrease with DDR. The elongations at yield for PET and at break for LCP1 were similar. The elongation at break of 70/30 and 60/40 PET/LCP1 blends were lower with ultrasonic treatment at an amplitude of 7.5 µm, than without. This could be due to degradation of these blends with treatment.

9.2.2.2. PEN/LCP1 blends

The stress strain plots of 90/10 PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm are shown in Figure 9.12a and b, respectively. In untreated blend, the strength and elongation at break were lower at DDR of 76.5 and 125. Only undrawn 90/10 PEN/LCP1 blend exhibited yielding behavior, and all drawn fibers of this blend exhibited brittle fracture. Undrawn 90/10 PEN/LCP1 fiber treated at an amplitude of 7.5 µm showed yielding behavior, similar to the untreated blend. Treated blend drawn at DDRs of 45 and 76.5 exhibited ductile fracture, breaking at 200-300% strain. The ultrasonically treated fiber drawn at DDR 112.5 was brittle. The improved elongation at break of 90/10 PEN/LCP1 blends with ultrasonic treatment at an amplitude of 7.5 µm indicated enhanced compatibility of 90/10 PEN/LCP1 blends. Ultrasonic treatment of these blends was observed to generate copolymer in-situ, as shown by
MALDI-TOF mass spectroscopy in section 6.6. Presence of copolymer compatibilizes the blend and improves interfacial stress transfer [80, 83].

Figure 9.12. Stress vs. strain curves for 90/10 PEN/LCP1 fibers at different DDRs, (a) without ultrasonic treatment, (b) with ultrasonic treatment at an amplitude of 7.5 µm.

Figure 9.13 shows the low strain region (up to 4%) of 90/10 PEN/LCP1 blends ultrasonically treated at an amplitude of 7.5 µm. The brittle fracture at the high DDR of
112.5 for the treated blend could be due to movement of the in-situ formed copolymer away from the interface under greater elongation flow, as in-situ copolymer must reside at the interface to compatibilize immiscible blends [80, 83].

Figure 9.13. Stress vs. strain curves up to 4% strain for 90/10 PEN/LCP1 fibers at different DDRs with ultrasonic treatment at an amplitude of 7.5 µm.

The Young’s modulus as a function of DDR for fibers spun from PEN/LCP1 blends without and with treatment at an amplitude of 7.5 µm is shown in Figure 9.14. It should be noted that a logarithmic scale was used in the y-axis. The Young’s modulus of blends increased with LCP1 concentration and DDR. The Young’s modulus of 80/20 PEN/LCP1 was lower with ultrasonic treatment at an amplitude of 7.5 µm. This could be due to reduced LCP1 fibrillation at an amplitude of 7.5 µm due to the lower viscosity of PEN with ultrasonic treatment. The Young’s modulus of 90/10 PEN/LCP1 did not change with ultrasonic treatment. This could be due to the lower concentration of LCP1 in this system and reduced LCP1 fibrillation during processing at 300°C. The processing temperature in fiber spinning was higher as compared to injection molding melt temperature of 285°C. While the higher temperature in melt spinning led to more stable
spinning of LCP1 fibers, it could also reduce the viscosity of PEN, which influences LCP1 deformation. Reduced LCP1 fibrillation would translate to lower stiffness and strength of fibers spun from the blends.

Figure 9.14. Young's modulus vs. DDR for PEN/LCP1 blends without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).

Figure 9.15. Yield strength vs. DDR for PEN/LCP1 blends without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines). Strength at break is presented for untreated 90/10 PEN/LCP1, and both untreated and treated 80/20 PEN/LCP1 and LCP1, as these samples did not yield.
The yield strength as a function of DDR for fibers spun from PEN/LCP1 blends without and with treatment at an amplitude of 7.5 µm is shown in Figure 9.15. It should be noted that only untreated and ultrasonically treated PEN and 90/10 PEN/LCP1 treated at an amplitude of 7.5 µm exhibited yielding. Thus, the strength at break was reported for the other samples. A logarithmic scale was used in the y-axis. The strength of blends increased with LCP1 concentration. The strength of untreated 80/20 PEN/LCP1 blends was observed to increase with DDR. The strength of 80/20 PEN/LCP1 was lower with ultrasonic treatment at an amplitude of 7.5 µm. This could be due to PEN degradation which led to reduced LCP1 fibrillation. Moreover, the strength of treated 80/20 PEN/LCP1 blend at a DDR of 112.5 was not increased in comparison with a DDR of 76.5. This was possibly due to degradation at this concentration, which could be expected as the highest DDR fibers that were spun last, and dwelled for longer time in the capillary rheometer allowing for greater thermal degradation. The strength of 90/10 PEN/LCP1 did not change with ultrasonic treatment.

The elongation at yield as a function of DDR for fibers spun from PEN/LCP1 blends without and with treatment at an amplitude of 7.5 µm is shown in Figure 9.16. It should be noted that only untreated and ultrasonically treated PEN and 90/10 PEN/LCP1 treated at an amplitude of 7.5 µm exhibited yielding. Thus, the elongation at break was reported for the other samples. LCP1 had the highest elongation at yield without take up and the lowest with spinning. It should be noted that undrawn samples did not have a DDR of 1 in all cases, resulting in variations in results obtained without spinning. The variation in the elongation at break without spinning was most obvious between untreated and ultrasonically treated 80/20 PEN/LCP1 blends. At a DDR of 112.5 for 80/20
PEN/LCP1 blend with ultrasonic treatment, there was less orientation of the LCP1 phase in the blend, and the elongation at break behavior approached that of pure LCP1 without take-up. With spinning, the elongation at break of 80/20 PEN/LCP1 blend was lower, and lied close to LCP1. The stiffness of fibers spun from ultrasonically treated 80/20 PEN/LCP1 was shown to be lower than that of the untreated blend. Accordingly, the elongation at break of ultrasonically treated 80/20 PEN/LCP1 blends would be expected to be higher. The elongation at break of ultrasonically treated 80/20 PEN/LCP1 blend was lower than that of the untreated blend at a DDR of 125 due to greater degradation of PEN at this condition. The elongation at yield of 90/10 PEN/LCP1 blends treated at an amplitude of 7.5 µm was higher than the elongation at break of the untreated 90/10 blend. The fact that 90/10 PEN/LCP1 blends exhibited yielding only when treated with ultrasound at an amplitude of 7.5 µm suggested improved compatibility for the 90/10 PEN/LCP1 blend with treatment at this condition.

**Figure 9.16.** Elongation at yield vs. DDR for PEN/LCP1 blends without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines). Elongation at break is presented for untreated 90/10 PEN/LCP1, and both untreated and treated 80/20 PEN/LCP1 and LCP1, as these samples did not yield.
Figure 9.17. Elongation at break vs. DDR for PEN, PET and 50/50 PEN/PET blends without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).

The elongation at break as a function of DDR for fibers spun from PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm was shown in Figure 9.17. It should be noted that the y-axis is plotted in logarithmic scale. The observed differences between the different conditions and blends were statistically significant. In contrast to PEN and ultrasonically treated 90/10 PEN/LCP1 blend which exhibited yielding, untreated 90/10 PEN/LCP1 blend, and both untreated and ultrasonically treated 80/20 PEN/LCP1 blend and LCP1 exhibited brittle fracture. Improved ductility of 90/10 PEN/LCP1 blends at DDR of 45 and 76.5 suggested improved compatibilization with ultrasonic treatment at an amplitude of 7.5 µm. The brittle fracture observed for undrawn fibers of ultrasonically treated PEN and 90/10 PEN/LCP1 could be due to processing defects. On the other hand, spinning at high DDR could destroy the ultrasonically compatibilized PEN/LCP1 interface by LCP1 fibril
pullout under high elongation stresses attained at the higher DDR. This would again lead to brittle fracture of fibers.

9.2.2.3. PEN/PET blends

The Young’s modulus as a function of DDR for fibers spun from PEN, PET and 50/50 PEN/PET blend without and with treatment at an amplitude of 7.5 µm is shown in Figure 9.18.

![Figure 9.18. Young's modulus vs. DDR for PEN, PET and 50/50 PEN/PET without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).](image)

As seen from Figure 9.18, the Young’s modulus of PEN and 50/50 PEN/PET blend increased with DDR, while that of PET decreased. The decrease for PET was previously discussed and linked to its degradation during spinning at 300°C. As DDR was not equal to one in all undrawn fibers, strictly speaking, this condition could not be compared. In spun fibers, the Young’s modulus of PEN decreased with ultrasonic
treatment at a DDR of 45, which could be due to its degradation with ultrasonic treatment. However, this difference was masked at higher DDR. The Young’s moduli of untreated and ultrasonically treated PEN at DDR of 76.5 and 112.5, and treated and untreated spun fibers of 50/50 PET/PEN were similar.

The stress at yield as a function of DDR for fibers spun from PEN, PET and 50/50 PEN/PET blend without and with treatment at an amplitude of 7.5 µm was shown in Figure 9.19. The yield stress of PEN was greater than that of the blend, which was greater than that of PET. While DDR did not affect the yield stress of PEN and 5/50 blend, the strength of PET was reduced at a DDR of 112.5, as explained in section 9.2.1.1. While ultrasonic treatment reduced the yield stress of PEN at DDR of 1 and 45, it had no effect on that of the 50/50 PET/PEN blend.

![Figure 9.19. Yield stress vs. DDR for PEN, PET and 50/50 PEN/PET without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).](image-url)

Figure 9.19. Yield stress vs. DDR for PEN, PET and 50/50 PEN/PET without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).
The elongation at yield of fibers spun from PEN, PET and 50/50 PEN/PET without and with treatment at an amplitude of 7.5 µm is shown in Figure 9.20. The elongation at yield of untreated PEN was greater than 50/50 PEN/PEN blend, which was greater than that of PET. The elongation at yield of PEN was significantly lower with ultrasonic treatment, indicating its degradation with treatment at an amplitude of 7.5 µm. On the other hand, the elongation at yield of the 50/50 PET/PEN blend was not affected by ultrasonic treatment. While elongation at yield of untreated PEN decreased strongly with DDR, that of untreated PEN and PET were unaffected. 50/50 PET/PEN blend showed little decrease in elongation at yield with ultrasonic treatment, indicating that its stiffness increased slightly with DDR.

Figure 9.20. Elongation at yield vs. DDR for PEN, PET and 50/50 PEN/PET without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).
Elongation at break as a function of DDR for fibers spun from PEN, PET and 50/50 PEN/PET blend without and with treatment at an amplitude of 7.5 µm is shown in Figure 9.21. The elongation at break of untreated PEN was greater than that of 50/50 PEN/PET blend, which was greater than that of PET. The elongation at break of PEN was significantly lower with ultrasonic treatment, indicating its degradation with treatment at an amplitude of 7.5 µm. On the other hand, the elongation at break of the 50/50 PET/PEN blend was not affected by ultrasonic treatment. The elongation at break of undrawn fibers were significantly lower than that of the spun fibers, except for PET which degraded during fiber spinning and did not show consistent yielding at a DDR of 112.5, which is why it was not reported. The elongation at break of spun fibers of untreated PEN, and both treated and untreated PET/PEN blend were observed to decrease slightly with DDR, indicating improved orientation at these conditions.

Figure 9.21. Elongation at break vs. DDR for PEN, PET and 50/50 PEN/PET without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).
The strength at break as a function of DDR for fibers spun from PEN/PET blends without and with treatment at an amplitude of 7.5 µm is shown in Figure 9.22. The strength at break of untreated PEN was greater than that of 50/50 PEN/LCP1 blend, which was greater than that of PET. The strength at break of PEN was significantly reduced with ultrasonic treatment, confirming its degradation with treatment at an amplitude of 7.5 µm. On the other hand, the strength at break of PET/PEN blend was not affected by ultrasonic treatment. The strongest increase in the strength at break with DDR was recorded in untreated PEN. The strength at break of treated PEN was also observed to increase with DDR, while that of 50/50 PET/PEN blends was not significantly affected.

![Figure 9.22. Strength at break vs. DDR for PET, PEN, 50/50 PET/PEN, and 50/50 PEN/LCP1.](image_url)

Figure 9.22. Strength at break vs. DDR for PET, PEN, 50/50 PET/PEN, and 50/50 PEN/LCP1 without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (open symbols and dashed lines).
9.2.2.4. LCP1/LCP2 blends

The Young’s modulus vs. DDR behavior of LCP1, LCP2, and 50/50 LCP1/LCP2 blends, without and with treatment at ultrasonic amplitudes of 7.5 and 10 µm is shown in Figure 9.23. The elongation and modulus values of fibers were measured without an extensometer. Therefore, these valued not be compared with Young’s modulus of injection molding, which were tested with an extensometer. Nevertheless, it is known that fiber spinning introduces greater orientation than injection molding in LCPs, due to greater elongational flows in fiber spinning [66, 216]. Hence, the modulus of spun fibers would be expected to be higher than injection moldings, had they been tested in the same manner (without extensometer). The Young’s modulus of LCP1 was greater than that of 50/50 LCP1/LCP2 blend, which was greater than LCP2. It was further observed that Young’s modulus of LCP1 increased strongly with DDR, while that of 50/50 blend increased with DDR but saturated at a DDR of 125, and that of LCP2 increased little above a DDR of 45.

The synergistic fibrillation effect, discussed in section 7.5 for moldings of LCP1/LCP2 blends, was not observed in the spun fibers. The main factor governing the orientation of LCPs is elongational flow, which is greater in fiber spinning than injection molding [66, 216]. As the orientation, defining Young’s modulus, of 50/50 LCP1/LCP2 blend was already saturated at low DDR in comparison to LCP1 which kept increasing with DDR, the synergistic effect of improved fibrillation could not observed in fiber spinning of LCP blends. Similar saturation of LCP orientation with DDR was reported in literature [47, 196, 248]. The main difference between LCP1 and LCP2 was the maximum level of orientation attained and its dependence on DDR in fiber spinning. As
orientation of LCP2 saturated around a DDR of 50, that of the blend was not further improved by LCP2 orientation but rather by the orientation of LCP1 at higher DDRs. Hence, any synergistic effect of LCP fibrillation that would cause higher stiffness of blends than the components could only occur at lower DDRs, where orientation would be similar to that experienced during injection molding.

![Graph showing Young's modulus vs. DDR for LCP1, LCP2, and 50/50 LCP1/LCP2 blend without and with treatment at ultrasonic amplitudes of 7.5 µm and 10 µm.](image)

Figure 9.23. Young's modulus vs. DDR for LCP1, LCP2, and 50/50 LCP1/LCP2 blend without (black filled symbols and lines) and with treatment at ultrasonic amplitudes of 7.5 µm (gray filled symbols and dashed lines), and 10 µm (open symbols and dotted lines).

Ultrasonic treatment of LCP1 was not observed to have an effect on the Young’s moduli of its fibers. While this appears to be in contrast with the improvements observed in moldings, the difference in the effect of ultrasound between injection molding and spun fibers further supports that the mechanical properties are mainly governed by orientation in LCPs [66]. The saturation of orientation of LCP phase in spun fibers [47,
could have masked the incremental improvement in orientation with ultrasonic treatment of LCP1.

The Young’s modulus of spun LCP2 fibers was improved with ultrasonic treatment at an amplitude of 7.5 µm, indicating greater orientation [38, 64] at this condition. On the other hand, the Young’s modulus of LCP2 fibers diminished with treatment at an amplitude of 10 µm. This was due to LCP2 degradation at 10 µm. The Young’s modulus of 50/50 LCP1/LCP2 blends decreased with treatment at an amplitude of 7.5 and 10 µm. The reduction in the Young’s modulus at 10 µm was due to the degradation of LCP2 leading to a reduction in its deformation at this amplitude, and reduced capacity to deform the LCP1 phase in the blends. The decrease in the modulus of 50/50 LCP1/LCP2 blend at an amplitude of 7.5 µm signified a reduction in the orientation. It was previously shown in section 7.5 that the modulus and strength of moldings of LCP2 were not affected by ultrasonic treatment at an amplitude of 7.5 µm, while those of the moldings of LCP1/LCP2 blends were reduced at the same amplitude. Similarly, in the case of fibers, the effect of ultrasound on pure LCP2 and the blend was observed to be different. With ultrasonic treatment at an amplitude of 7.5 µm, the Young’s modulus of spun fibers of LCP2 was increased while that of 50/50 LCP1/LCP2 blends was decreased. This could be due to different structural changes occurring in LCP2 when processed in blends with LCP1.

The strength of LCP1, LCP2 and 50/50 LCP1/LCP2 blend versus DDR without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm is shown in Figure 9.24. Similar to the results of the Young’s modulus of fibers in this system, the strength was also highest for LCP1, and lowest for LCP2, with the 50/50 LCP1/LCP2 blend lying in
between. The strength of LCP1 was observed to increase strongly with DDR, while that of the blends increased less. On the other hand, the strength of LCP2 showed less change with DDR. The strength of LCP1 was observed to decrease with ultrasonic treatment at an amplitude of 10 µm. This indicated that ultrasound at this amplitude could have also caused degradation of LCP1. The strength of LCP2 was improved with ultrasonic treatment at an amplitude of 7.5 µm, due to improved orientation of LCP2 with treatment at this amplitude. The strength of LCP1/LCP2 blends was observed to decrease with ultrasonic treatment. This could be due to reduced fibrillation of LCP1 in the presence of ultrasonically treated LCP2.

![Graph showing strength vs. DDR for LCP1, LCP2 and 50/50 LCP1/LCP2 blend without (black filled symbols and lines) and with treatment at ultrasonic amplitudes of 7.5 µm (gray filled symbols and dashed lines), and 10 µm (open symbols and dotted lines).](image)

Figure 9.24. Strength vs. DDR for LCP1, LCP2 and 50/50 LCP1/LCP2 blend without (black filled symbols and lines) and with treatment at ultrasonic amplitudes of 7.5 µm (gray filled symbols and dashed lines), and 10 µm (open symbols and dotted lines).

The elongation at break of LCP1/LCP2 blend versus DDR without and with ultrasonic treatment at amplitudes of 7.5 and 10 µm is shown in Figure 9.25. The
elongation at break was observed to decrease with DDR, most significantly from undrawn fiber to a DDR of 45. The reduction in the elongation at break was greatest with LCP1. The elongation at break of undrawn LCP2 and 50/50 LCP1/LCP2 blend decreased with ultrasonic treatment at an amplitude of 7.5 and 10 µm. The elongation at break of drawn LCP2 fibers was higher than those of LCP1 and 50/50 LCP1/LCP2 blend. Ultrasonic treatment had no significant effect on the elongation at break of spun fibers.

![Elongation at break vs. DDR for LCP1, LCP2 and 50/50 LCP1/LCP2 blend without (solid symbols and lines) and with treatment at an ultrasonic amplitude of 7.5 µm (gray filled symbols and dashed lines), and 10 µm (open symbols and dotted lines).](image)

9.3. Morphology

The morphology of PEN/LCP1 fibers were studied due to findings that some mechanical properties of 90/10 PEN/LCP1 fibers were improved with ultrasonic treatment at an amplitude of 7.5 µm, indicating ultrasonically induced compatibilization.

Field emission SEM was used to study fibers without take-up and at a DDR of 45. The lower DDR range was studied as mechanical properties indicated that in-situ formed
copolymers could be displaced at high DDR. Also, low DDR fibers were easier to handle for sample preparation. Micrographs were captured at magnifications of 10,000x and 50,000x.

Figure 9.26. Field emission SEM micrographs at a magnification of 10,000x for undrawn fibers of PEN/LCP1 blends at concentrations of (a) 90/10 without treatment, (b) 90/10 with treatment at an amplitude of 7.5 µm, (c) 80/20 without treatment, (d) 80/20 with treatment at an amplitude of 7.5 µm.

Figure 9.26a-d shows the SEM micrographs at a magnification of 10,000x for undrawn fibers of 90/10 and 80/20 PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm. LCP1 phase was visible as droplets embedded in the PEN matrix without elongational flow introduced by fiber take-up at a DDR of 1. In all
micrographs, there was a broad distribution of LCP droplet size. Overall, the LCP droplet size was smaller in untreated and ultrasonically treated 90/10 PEN/LCP1 undrawn fibers (Figure 9.26a,b, respectively), than it was in untreated and ultrasonically treated 80/20 PEN/LCP1 undrawn fibers (Figure 9.26c,d, respectively). This indicated agglomeration of LCP1 phase to form larger droplets at the higher concentration without take-up.

Figure 9.27. Field emission SEM micrographs at a magnification of 50,000x for undrawn fibers of PEN/LCP1 blends at concentrations of (a) 90/10 without treatment, (b) 90/10 with treatment at an amplitude of 7.5 µm, (c) 80/20 without treatment, (d) 80/20 with treatment at an amplitude of 7.5 µm.

Figure 9.27a-d shows the SEM micrographs at a magnification of 50,000x for undrawn fibers of 90/10 and 80/20 PEN/LCP1 blends without and with ultrasonic
treatment at an amplitude of 7.5 µm. At this high magnification, individually aligned PEN fibers were also visible as small dots protruding from the surface. LCP1 domains were identified as droplets, and micrographs at this scale allowed the study of the interface between PEN and LCP1. While an interface with some degree of attachment of LCP1 droplets to the PEN matrix was observed, the interface appeared to be thicker and more persistent in the undrawn fiber of 90/10 PEN/LCP1 blends treated at an amplitude of 7.5 µm (Figure 9.27b).

Figure 9.28. Field emission SEM micrographs at a magnification of 10,000x for fibers at a draw down ratio of 45 for PEN/LCP1 blends at concentrations of (a) 90/10 without treatment, (b) 90/10 with treatment at an amplitude of 7.5 µm, (c) 80/20 without treatment, (d) 80/20 with treatment at an amplitude of 7.5 µm.
Figure 9.28a-d shows the SEM micrographs at a magnification of 10,000x for fibers at a DDR of 45 for 90/10 and 80/20 PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm. The size of droplets in untreated and ultrasonically treated 90/10 PEN/LCP1 blend was smaller and more uniform with take-up (Figure 9.28a-b) than without take-up (Figure 9.26a-b). 80/20 blends indicated a fibrillar structure without (Figure 9.28c) and with ultrasonic treatment (Figure 9.28d). As compared to 90/10 PEN/LCP1 blend, 80/20 PEN/LCP1 had significantly enhanced LCP1 fibrillation.

Figure 9.29. Field emission SEM micrographs at a magnification of 50,000x for fibers at a draw down ratio of 45 for PEN/LCP1 blends at concentrations of (a) 90/10 without treatment, (b) 90/10 with treatment at an amplitude of 7.5 µm, (c) 80/20 without treatment, (d) 80/20 with treatment at an amplitude of 7.5 µm.
Figure 9.29a-d shows the SEM micrographs at a magnification of 50,000x for fibers at a DDR of 45 for 90/10 and 80/20 PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm. Among the PEN/LCP1 blends drawn at a DDR of 45, a diffuse interface was present only in 90/10 PEN/LCP1 with treatment at an amplitude of 7.5 µm, as seen in Figure 9.29b. This indicated that the interface in untreated 90/10 PEN/LCP1 (Figure 9.29a), and both untreated and treated 80/20 PEN/LCP1 fibers (Figure 9.29c and d, respectively) was weaker, and collapsed with take-up.

In order to quantify the interfacial strength of PEN/LCP1 blends, image analysis of high magnification SEM micrographs was performed.

9.3.1. Interfacial tension

Interfacial tension in blends can be calculated from interfacial thickness between the phases in the blend. Use of a field emission SEM allowed capturing high magnification images clearly showing the interface in PEN/LCP1 blends. The interface in the extruded fibers (DDR=1) of 90/10 and 80/20 PEN/LCP1 blends without and with treatment at an amplitude of 7.5 µm were analyzed. This analysis was not carried out on PET/LCP1 fibers, which were shown to degrade while spinning due to the high processing temperature.

Wu’s relation was used for calculation of interfacial tension [320]:

\[ \gamma_{12} = 55a_i^{-0.86} \]  \hspace{1cm} (9.1)

where \( \gamma_{12} \) is the interfacial tension expressed in dyne/cm, and \( a_i \) is the measured interface thickness in Angstroms.
Figure 9.30 shows how the thickness of interface was measured in 90/10 PEN/LCP1 blends. This figure presents only an example of the measurements, of which at least 20 were performed from different droplets and micrographs at high magnification.

![Figure 9.30](image)

Figure 9.30. SEM micrographs indicating measurement of interfacial thickness ($a_I$) on undrawn fibers of 90/10 PEN/LCP1 blends, (a) without treatment, (b) with ultrasonic treatment at an amplitude of 7.5 $\mu$m.

Figure 9.31 shows measured interfacial thickness between LCP1 droplets and the PEN matrix in 90/10 and 80/20 PEN/LCP1 undrawn fibers, along with 95% confidence intervals presented by error bars. Without ultrasonic treatment, the PEN-LCP1 interfacial thickness in 90/10 and 80/20 PEN/LCP1 blends were 69 and 59 nm, respectively. With ultrasonic treatment at an amplitude of 7.5 $\mu$m, the average thickness of the interface increased substantially for 90/10 PEN/LCP1, while it remained constant for 80/20 PEN/LCP1. The presence of a thicker, diffuse interface indicated better interfacial attachment between PEN and LCP1 with ultrasonic treatment at an amplitude of 7.5 $\mu$m.

In a study by Song and Isayev, Wu’s relation (eq. 9.1) was also employed to determine interfacial tension between an LCP based on PET/HBA copolymer and PET and PBT...
droplets [198]. They measured the interfacial thicknesses by SEM as 80 nm between PET and LCP, and 280 nm between PBT and LCP. These interfacial thicknesses were in the same range as obtained for PEN/LCP1 of the present study.

Figure 9.31. PEN/LCP1 interface thickness in 90/10 PEN/LCP1 undrawn fibers without and with treatment at an ultrasonic amplitude of 7.5 μm, with the error bars indicating 95% confidence intervals.

The interfacial tension in PEN/LCP1 blends was quantified based on the measured interfacial thickness by using Wu’s relation, presented in Eq. 9.1. The interfacial tension and 95% confidence intervals were calculated and are presented in Figure 9.32.

Interfacial tension determined for untreated PEN/LCP1 blends in the present study were higher than that for PET/LCP and PBT/LCP blends reported by Song and Isayev, in which the LCP was a PET/HBA copolymer [198]. They reported values of 0.175x10⁻³ N/m for PET/LCP and 0.0597x10⁻³ N/m for PBT/LCP.
Figure 9.32. Interfacial tension of PEN/LCP1 blends without and with ultrasonic treatment at an amplitude of 7.5 µm, with the error bars indicating 95% confidence intervals.

While interfacial tension was similar for untreated 90/10 and 80/20 PEN/LCP1 blends, it was observed to decrease well below the range of error with in 90/10 PEN/LCP1 blend with ultrasonic treatment at an amplitude of 7.5 µm. Reduced interfacial tension in 90/10 PEN/LCP1 blends indicated improved interfacial adhesion with ultrasonic treatment due to the presence of a diffuse interphase. This interphase was formed with ultrasonic treatment, and would have improved adhesion to both PEN and LCP1. As ultrasound caused chain scission and recombination reaction during processing in the melt, any formed copolymer would already reside in the interface.

The effect of in-situ formed copolymer was expected to be largest when shear forces that could cause movement of the in-situ formed copolymer away from the melt were less intensive following ultrasonic treatment [5]. As mentioned in section (3.2.1.1), the additional mixing section in SONIC1 was replaced with screw flight for the ultrasonic
extrusion of PEN/LCP1 blends. Extruded pellets were packed by compression, pushed by a piston and hence experienced reduced shear during fiber spinning form the capillary rheometer than in the reciprocating screw injection molding process. Hence, it was anticipated that more copolymer would stay at the interface in melt spinning, leading to a more pronounced compatibilization effect.

Ultrasonic treatment was not observed to influence the interfacial tension of 80/20 PEN/LCP1 blends. As can be observed by comparing the morphologies of undrawn extrudates of 90/10 PEN/LCP1 (Figure 9.26a-b) and 80/20 PEN/LCP1 (Figure 9.26c-d) blends, the LCP1 domain size was larger at the greater LCP1 concentration. As ultrasonic treatment induced in-situ reactions, which were expected to generate copolymers in the interface of the two immiscible polymers in melt state, available surface area for reaction was determining parameter for reaction rate. As the total surface area for reaction would be higher with smaller LCP1 droplet size, greater ultrasonically induced copolymerization reaction could be expected at reduced LCP1 concentration, which resulted in less LCP1 agglomeration during processing. The difference in size of observed LCP1 droplets verified this effect.

9.4. Conclusions

Fibers spun from as-received PET became stiffer with increasing DDR, and did not lose strength. On the other hand, fibers spun from extruded PET could not be oriented with increasing DDR, and had low mechanical properties, due to their degradation at the processing temperature of 300°C. Mechanical properties of fibers spun from PET/LCP1 blends were also lower than expected due to the inability of the thermally degraded PET
matrix to deform the LCP1 phase. Blends with above 30% LCP1 content could be drawn stably and had greater orientation and strength with higher DDR.

Virgin and extruded PEN fibers were observed to become stiffer and their strength at break was observed to increase with increasing DDR. Fibers of PEN/LCP1 blends become stiffer with addition of 20% LCP1. Fibers of 90/10 PEN/LCP1 blends were brittle without ultrasonic treatment. With ultrasonic treatment at an amplitude of 7.5 µm, these fibers exhibited yielding behavior resembling that of PEN, at DDR of 45 and 76.5.

Interfacial tension of 90/10 PEN/LCP1 fiber compatibilized by ultrasound indicated a decrease of interfacial tension from $0.20 \times 10^{-3}$ N/m for untreated blend to $0.14 \times 10^{-3}$ N/m for ultrasonically treated blend. The improved ductility of PEN/LCP1 fibers at these conditions was attributed to in-situ ultrasonic compatibilization.

Fibers spun from 50/50 PET/PEN blends indicated increased stiffness and strength at break with increasing DDR. Their mechanical properties were not significantly affected by ultrasonic treatment at an amplitude of 7.5 µm. This was in contrast to the loss in mechanical properties of PEN fibers with ultrasonic treatment at an amplitude of 7.5 µm. These results indicate very different behavior of PET and PEN in their blends, as transesterification reactions dominated in this blend with ultrasonic treatment.

Undrawn fibers of LCP1 had greater elongation at break than undrawn fibers of LCP2. Increasing DDR ratio led to greater orientation in LCP1, while the Young’s modulus of LCP2 was observed to approach an asymptotic behavior with increasing DDR. The strength of LCP1 fibers was lower with ultrasonic treatment at an amplitude of
10 µm. The Young’s modulus and strength of LCP2 fibers were observed to increase with ultrasonic treatment at an amplitude of 7.5 µm, indicating greater orientation in the fibers, possibly thorough improved fibrillation by the action of ultrasound. The Young’s modulus and strength of fibers of LCP1/LCP2 blends were observed to decrease with ultrasonic treatment. The different effect of ultrasound on the mechanical properties of fibers of LCP1, LCP2 and their 50/50 blend, indicated the different effects of ultrasound on these systems. Unlike injection molding of LCPs, fibers of LCP1/LCP2 blends did not indicate a level of synergistic orientation that would increase the properties of blends above those of the pure components. This was attributed to the higher elongational flows in fiber spinning and the saturation of LCP2 orientation at low DDR.
A new ultrasonic extruder and extrusion process was developed and its efficiency in promoting fast in-situ compatibilization through copolymer formation in immiscible polymer blends was demonstrated. The effects of ultrasonic extrusion were evaluated on flexible chain polyesters, wholly aromatic thermotropic liquid crystalline polymers (LCPs), and their binary blends. The flexible chain polyesters studied were polyethylene terephthalate (PET), and polyethylene naphthalate (PEN); the LCPs studied were a copolymer of hydroxybenzoic and hydroxynaphthoic acid (LCP1), and a copolymer of dioxydiphenyl, terephthalic and isophthalic acid (LCP2). The effect of ultrasonic treatment was evaluated on binary blends of PET/PEN, PET/LCP1, PEN/LCP1, and LCP1/LCP2. The components and their blends were subsequently injection molded and spun into fibers. Ultrasonically induced compatibilization led to improvements in the mechanical properties of flexible chain polyester/LCP blends under certain conditions.

Effect of ultrasonic treatment at a frequency of 20 kHz on the components and their blends were studied at amplitudes of 0 to 10 µm at short residence times (7 and 14s). Residence time in the ultrasonic treatment zone was 7s in treatment of all components and blends except 80/20 PET/LCP1 blends, which was also studied at 14 s by reducing screw speed. 80/20 PET/LCP1 blends were also studied in an older generation ultrasonic extruder for comparison of properties. Process characteristic
(pressure and ultrasonic power consumption during extrusion) were measured, and rheological, thermal, spectroscopic, mechanical, and morphological characterizations of untreated and ultrasonically treated polymers were carried out. Optical transmission and oxygen barrier properties of molded films of PET/PEN blends were also determined.

PET underwent homopolymerization and degradation, respectively, at ultrasonic amplitudes of 7.5 \( \mu \)m and 10 \( \mu \)m, while PEN underwent degradation at all amplitudes, as indicated by their rheological and thermal properties. Greater amounts of hydroxyl and carboxyl terminated oligomers were observed in ultrasonically treated PET and PEN by MALDI-TOF mass spectroscopy, indicating their greater reactivity with treatment. Copolymer formation (transesterification) was observed in PET/PEN blends, which was enhanced with ultrasonic treatment, as indicated by \(^1\)H NMR and MALDI-TOF. The glass transition temperatures of ultrasonically treated blends determined by DSC correlated with those obtained for the blend by the Gibbs-DiMarzio equation, indicating random copolymer behavior in the treated blends. Viscosity of the blend was highest at an amplitude of 10 \( \mu \)m. Mechanical properties of the blend were not affected by ultrasonic treatment. Oxygen permeability of compression molded films of untreated and ultrasonically treated PET/PEN blends followed theoretical predictions for miscible blends. Ultrasonic treatment did not affect the optical transmittance of these films as they were above the critical level of transesterification required for optical clarity.

Ultrasonic treatment of LCP1 at amplitudes of 7.5 and 10 \( \mu \)m led to improved mechanical properties of its moldings. MALDI-TOF revealed chemical changes in LCP1 with treatment at these amplitudes. On the other hand, LCP2 underwent degradation with ultrasonic treatment, leading to its reduced mechanical properties. LCP1/LCP2 blends
were partially miscible, and indicated increasing shift in $T_g$ of LCP2 toward that of LCP1 with increasing LCP1 concentration. Synergistic fibrillation was observed in injection moldings, leading to mechanical properties superior to moldings of existing thermoplastics. A synergistic reinforcement was observed in the mechanical properties of injection molded blends. This was due to the LCPs enhancing each other’s orientation and the resulting intertwined microfibrillar morphology of the blend. Ultrasonic treatment of blends led to reduced mechanical properties in the blends due to degradation of LCP2 and reduced LCP fibrillation. Mechanical properties of spun fibers followed the rule of mixtures due to saturation of LCP orientation by the greater orientational flow experienced by the melt in fiber spinning.

PET/LCP1 and PEN/LCP1 blends became stiffer and stronger with increasing LCP1 content. LCP1 acted as a nucleating agent in 70/30 and 60/40 PET/LCP1, and 90/10 and 80/20 PEN/LCP1 blends. The blends exhibited greater shear thinning behavior with increased LCP1 content. The viscosity of 90/10 PET/LCP1 blends was below those of its components indicating that LCP1 acted as a processing aid. LCP fibrillation in moldings and spun fibers of these blends was controlled by the viscosity ratio of matrix polymer (PET, PEN) to LCP1. Ultrasonically induced copolymer formation was detected by MALDI-TOF in PET/LCP1 and PEN/LCP1 blends.

The ultimate strength, Young’s modulus, toughness and impact strength of 80/20 PET/LCP1 blend treated at an amplitude of 7.5 μm for 7 s, and the toughness of 90/10 PET/LCP1 blend treated at an amplitude of 10 μm were improved. These improvements were due to improved LCP1 fibrillation by PET homopolymerization in the blend at an amplitude of 7.5 μm, and improved interfacial adhesion, indicated by morphological
studies, due to copolymerization. Ultrasonic treatment for a residence time of 14 s for 80/20 PET/LCP1 blends led to large LCP domains with greater interaction with the PET phase due to the lower screw rpm and greater copolymer formation, as evidenced by MALDI-TOF. Ultrasonic treatment of 80/20 PET/LCP1 blends in an older generation extruder with a slit die ultrasonic attachment resulted in higher mechanical properties due to a shorter screw design but did not lead to improvements with ultrasonic treatment. Due to greater beneficial effects of ultrasound observed with the newly designed ultrasonic treatment zone geometry, the new extruder was used for all other studies.

Ultrasonic treatment of 90/10 PEN/LCP1 at an amplitude of 7.5 µm improved impact strength and elongation at yield of its injection moldings, and elongation at break of its spun fibers at intermediate draw down ratios (DDR). Interfacial tension was reduced with ultrasonic treatment of this blend due to presence of in situ created copolymer by ultrasonic treatment. The lack of improvement in elongation at break of treated fibers at a DDR of 125 indicated that high elongational stresses can negate the effects of in-situ compatibilization by disturbing the interphase between PEN and LCP1. While MALDI-TOF indicated greater copolymer formation at an amplitude of 10 µm, any of its beneficial effects were masked by reduced viscosity ratio of PEN to LCP1, which resulted in loss of LCP1 fibrillation and formation of LCP1 agglomerates in the blends with treatment at this amplitude.

The effect of adding transesterification catalysts (antimony trioxide and tetrabutyl orthotitanate) to 80/20 PEN/LCP1 blend without and with ultrasonic treatment was investigated. The catalysts induced degradation of PEN without and with ultrasonic treatment, leading to reduced LCP1 fibrillation, and therefore poor mechanical properties.
However, treatment of the PEN/LCP1 blend in the presence of catalyst at an amplitude of 10 µm did not result in the degradation of PEN observed without catalyst. This indicated greater copolymerization in the presence of catalysts, which led to higher mechanical properties of blends containing catalyst at an amplitude of 10 µm, as compared to the blends treated at 10 µm without catalyst.

In summary, the utility of ultrasonically-aided extrusion to induce in-situ compatibilization of immiscible polyester blends was demonstrated. Ultrasonic extrusion was shown to induce structural changes in pure components and in-situ copolymerization reactions in blends. The in-situ ultrasonic compatibilization of polyester blends proceeded through a chain scission and recombination mechanism. The properties obtained for ultrasonically treated binary blends were not a simple combination of those for ultrasonically treated pure components. The effects of ultrasonic extrusion on pure polymers and blends was found to depend on molecular structure of components, ultrasonic amplitude, pressure, temperature, residence time in extruder and in the sonication zone, degree of mixing, geometry of treatment zone, composition in blends and the presence of catalysts.

10.1. Recommendations

Based on the results obtained in this study for in-situ ultrasonic compatibilization of immiscible flexible chain and liquid crystalline polyester blends, the following recommendations are made:

- Choosing a material combination with low viscosity ratio of the dispersed LCP phase to the matrix polymer will allow achievement of finer LCP fibrillation.
- Effect of ultrasound on structure and properties of components should not be expected to be the same in their blends due to interchange reactions.

- In order to improve mechanical properties of flexible chain thermoplastic/LCP blends by ultrasonic treatment, amplitude and duration of ultrasonic treatment should be controlled to improve interfacial adhesion by in-situ copolymer creation, while preserving phase separation and high viscosity ratio of LCP to matrix required for LCP fibrillation.

- The degradation due to extrusion can be reduced by decreasing residence time in the ultrasonic extruder (lower L/D) while keeping the residence time in the sonication zone the same (longer ultrasonic horns), which will also reduce large changes in extent of mixing upon varying residence time in treatment zone.

- Optimization of the amount of transesterification catalyst in the ultrasonic treatment process could promote greater in-situ compatibilization while minimizing degradation.
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