MANUFACTURING OF HIGH PERFORMANCE POLYMER NANOCOMPOSITES
CONTAINING CARBON NANOTUBES AND CARBON NANOFIBERS USING
ULTRASOUND ASSISTED EXTRUSION PROCESS

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ABSTRACT

The major objective of this study was to investigate the effect of ultrasonic treatment on the state of dispersion and properties of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) in polymer matrices. In order to achieve this objective, an ultrasonic single screw extruder operating at a frequency of 20 kHz and an amplitude of upto 10 µm and an ultrasonic twin screw extruder operating at a frequency of 40 kHz and an amplitude of upto 6.0 µm, were used to process highly viscous materials and disperse these nanofillers homogeneously in a polymer matrix at residence times of order of seconds. High temperature thermoplastic resins including polyetherimide (PEI), liquid crystalline polymer (LCP) and polyetheretherketone (PEEK) were used. Multiwalled carbon nanotubes (MWNTs) and CNFs were used as reinforcing fillers. The effect of nanofiller loading and ultrasonic amplitudes on rheological, mechanical, electrical, thermal and morphological properties of the nanocomposites was studied. Ultrasonic treatment showed a tremendous decrease in die pressure. Morphological studies showed that ultrasonic treatment improved dispersion of CNFs and CNTs in polymer matrices.

PEI/CNFs and PEI/MWNTs nanocomposites were prepared using ultrasound assisted single and twin screw extruder, respectively. A permanent increase in the viscosity, storage and loss modulus and decrease in tan δ was observed with ultrasonic treatment. Ultrasonically treated PEI/CNFs nanocomposites showed a decrease in electrical percolation threshold value as compared to the untreated ones. Breakage of CNFs was observed primarily due to extrusion process alone. In case of PEI/MWNTs
nanocomposites, percolation threshold value was found to be between 1 and 2 wt% loading of CNTs for both treated and untreated samples.

LCP/CNFs nanocomposites were prepared using ultrasound assisted twin screw extruder with separate feeding of CNFs in the polymer melt. In contrast to behavior of PEI/CNFs and PEI/MWNTs nanocomposites, the rheological behavior of LCP/CNFs nanocomposites practically was not affected with the ultrasonic treatment due to a reduction in fibrillation of LCP matrix in the presence of CNFs. Similar to PEI/CNFs nanocomposites; ultrasonically treated samples showed a decrease in the electrical percolation threshold value as compared to the untreated ones. Due to reduction in fibrillation of LCP no improvement in the mechanical properties was observed on addition of CNFs. After introducing the orientation by fiber spinning of LCP/CNFs nanocomposites, a tremendous increase in the mechanical properties of fibers was observed with increase in the draw down ratio.

PEEK/MWNTs nanocomposites were prepared using ultrasonic single screw extruder. In contrast to PEI/CNFs and PEI/MWNTs nanocomposites, ultrasonically treated PEEK/MWNTs nanocomposites showed decrease in the complex viscosity, storage modulus. Loss modulus and increase in tan δ as compared to untreated ones. This could be due to the competition between increased dispersion of CNTs and a possible degradation of the polymeric chains in the presence of CNTs and a possible reduction of CNTs length on application of ultrasound. Due to above effects, ultrasonic treatment reduced the physical contacts between the CNTs and hence increased the volume resistivity near the percolation threshold. No degradation of pure PEEK matrix upon application of ultrasound was observed.
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I would also like to thank the faculty, staff, colleagues and friends who made my stay in Akron productive and memorable.

Finally, I want to dedicate this dissertation to my mother and my family for their love and support. Without them, I would not be the person I am today.
DEDICATION

I would like to dedicate this dissertation to my mother for her endless love, encouragement and having complete faith in me. I owe my all success and happiness to her. Without her struggle and hard work, I would not be the person I am today.
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CHAPTER I
INTRODUCTION

Fiber-reinforced composites have been widely used in the area of aerospace and military due to their light weight and improved mechanical properties. This reduced weight helps in higher speed and increased payload. The use of these fiber-reinforced composites on aerospace vehicles requires withstanding high temperature and should have improved mechanical properties to withstand the sudden changes in the external environmental conditions. Carbon fiber composites have already being used in many wings, fuselage and find applications in secondary structures of many commercial aircrafts. Till date, graphite fiber composites dominated the aerospace industry. There are some problems associated with the conventional fiber-reinforced composites such as the accumulation of electrostatic charge on their surface which can cause the local heating resulting in the catastrophic failure of the surrounding materials. Thus it is essential that the resin used should have sufficient electrical conductivity to dissipate the built up electrostatic charges. In recent years, the polymer/carbon nanotube composites have gained tremendous attention both in academia and industry [1,2,3,4,5,6,7]. Because of the exceptional mechanical, thermal and electrical properties along with their light weight [1,2], carbon nanotubes have the potential to surpass graphite fiber composite and overcome the problem associated with the conventional fiber-reinforced composites. Due
to the high aspect ratio (100-1000) of CNTs, it is possible to achieve the percolation threshold at very low loading of CNTs [4]. The biggest challenge in the manufacturing of high performance polymer nanocomposites containing CNTs and CNFs is the lack of dispersion of CNTs and CNFs in polymer matrices. During synthesis of CNTs and CNFs, nanotubes and nanofibers easily get agglomerated or form bundles due to strong intertube van der Waals attraction and hence limit the effective use of their exceptional properties obtained at the individual level [8,9,10]. Many researchers have tried different routes to disperse CNTs and CNFs; however, successful dispersion still remains a challenge as can be seen from the various review papers on the dispersion of CNTs and CNFs in a polymer matrix [11,12]. Currently commonly used methods for dispersion of nanotubes and nanofibers in a polymer matrix are: in-situ polymerization, mechanical and chemical treatment. Among these methods in-situ polymerization and chemical modification may not be commercially viable due to limitation in their scale up and their negative environmental impact. Prolonged sonication of the CNTs and CNFs in an ultrasonic bath using solvent is one of the most commonly used methods to disperse nanotubes. However, it introduces defects in CNTs and CNFs and results in reduced aspect ratio which is basis for many of their attractive properties. Melt processing, being more efficient, rapid and environmentally friendly method to disperse CNTs and CNFs in a polymer matrix, is one of the most preferred technique from industrial application point of view because of its easiness in scale up. However, a limited number of studies have been done on melt processing/extrusion of polymer-carbon nanotubes or polymer-carbon nanofibers composites.
From the above discussion, there is a clear need to develop a new method which is rapid, clean and commercially viable. In recent years, use of ultrasound to disperse nanofiller in a polymer matrix is gaining attention.

The objective of this study was to develop a novel ultrasonic extrusion process for preparing polymer nanocomposites containing carbon nanotubes and carbon nanofibers. A new approach to the use of high power ultrasound to disperse nanotubes and nanofibers in high performance polymer matrix, in short residence times, was developed and defined. Three different kinds of high performance polymer (polyetherimide, polyetheretherketone and liquid crystalline polymer) were studied. These polymers were reinforced by nanofillers (carbon nanotubes and carbon nanofibers) to improve their performance. The effects of ultrasonic energy on the state of dispersion of these nanofillers and on the resultant nanocomposites properties were studied. These high temperature materials were chosen because of their extensive use in composites for various industrial applications due to their desirable combination of mechanical and thermal properties. They have outstanding dimensional and thermo-oxidative stability with desired processability required for various applications.

This dissertation is composed of 8 chapters. In chapter II, literature survey and background deals with the current state of knowledge about carbon nanotubes based polymer nanocomposites. Chapter III describes the experimental procedures including materials used, design of ultrasonic extruder set up, processing instruments and conditions and different characterization techniques. In chapter IV, the effect of various processing conditions and ultrasonic treatment on the state of dispersion of CNFs in PEI matrix, processed using ultrasonic single screw extruder, has been reported and
discussed. Chapter V presents and discusses results of ultrasonic twin screw extrusion of PEI/CNTs nanocomposites. Results on the LCP/CNFs nanocomposites prepared by twin screw ultrasonic extrusion process have been presented and discussed in chapter VI. The results on PEEK/CNTs nanocomposites prepared using ultrasonic single screw extrusion process have been given in chapter VII. Finally, a summary of the research work has been presented in chapter VIII.
2.1. Carbon nanotubes

In this section a literature survey about history, synthesis, properties and applications of carbon nanotubes has been discussed.

2.1.1. History of carbon nanotubes

One of the most versatile elements in the periodic table is carbon. Its versatility results from its geniusness in creating different structures by bonding in many ways with different elements. Carbon has six electrons around its nucleus with four valence electrons in the outer orbital. These valence electrons can make up to four bonds with different hybridization mechanism. The two well known form of crystalline carbon are diamond and graphite, which results due to covalent bonding of valence electrons with other element with different hybridization mechanism involved in their formation [1,2].

When each sp³ hybridized carbon atom is bonded to four other atoms in a tetrahedral manner, it results in creating isotropic structure called diamond. Diamond is one of the hardest known substances, due to its strong network of carbon elements with excellent thermal conduction, electrical insulation and optical properties. In graphite, carbon atoms are bonded together in hexagonal network with sp² hybridization arrangement. Graphite is formed when only three valence electrons form bond with neighboring electrons.
leaving one electrons to be delocalized among all atoms. The delocalized fourth valence electron is free to move from one orbital to another forming $\pi$ bond network which results in higher electrical conductivity for graphite sheets. Diamond and graphite used to be considered the two allotropic form of carbon in solid state until fullerenes were discovered in 1985 by Smalley and coworkers [3]. Fullerenes having unique and distinct properties were immediately recognized as a new molecular form of carbon and termed as the third allotrope of carbon in the solid state. In fullerenes, all the carbon atoms are sp$^2$ hybridized but they are not arranged on a plane like in graphite. They consist of spheroidal or tubular molecules. The first discovered fullerenes has geometric shape like soccer ball called C$_{60}$ or bucky ball [1], where 60 carbon atoms are bonded together with 20 hexagons and exactly 12 pentagons. There could be many hexagons in fullerenes but exactly only 12 pentagons [1,2,3]. As fullerenes (an even number of carbon atoms starting at C$_{28}$) were made from planar hexagonal graphite lattice, so to provide the curvature some topological defects have to be introduced in the structure and this is done by creating pentagons on the surface [4].

While the concept of elongated fullerenes was proposed by Smalley and other scientists, however, experimental evidence of existence of nanotubes were reported by Iijima in 1991 [5]. The elongated fullerene with millions of hexagons but exactly 12 pentagons capped at both ends with fullerenes hemispheres corresponds to a nanotube.

The first image of tubes resembling single walled carbon nanotubes (SWNT) (Figure 2.1) was published in 1976, observing the growth of very small diameter filament during the synthesis of vapor grown carbon fibers [6], though not so claimed by the authors. But real advances in the area happened only when Iijima [5] reported the
formation of multi walled carbon nanotubes (MWNT) (Figure 2.2). In Figure 2.2, electron micrographs of microtubules of graphitic carbon are shown. Parallel dark lines corresponds to the (002) lattice image of the graphite. A cross section of each tubule is shown.

Figure 2.1. TEM images of tubes which could relate to SWNT [6].

Figure 2.2. TEM images of first reported MWNTs, (a) is the tube consisting of five graphitic sheets, (b), is two sheet tubes and (c), is seven sheet tube [5].

It was exceptional mechanical, electrical and thermal properties of SWNT and MWNT which stimulated the research in the area of fabrication of nanotubes based
composites. Being discovered in 1991, the progress in this area is really commendable and as it can be seen that in 1992 there were only 9 papers published containing word carbon nanotubes while in year 2004, there were 5000 publications containing the word nanotubes [1].

Carbon nanotubes can be classified in two categories, one is called single walled carbon nanotube (SWNT) and second one is called as multi walled carbon nanotube (MWNT). SWNT can be considered as the roll up of graphene sheet or also considered as close to the ideal fullerene fiber [7]. The properties will depend on how the graphene sheet being rolled. On the other hand, in MWNT there are concentric cylinders around a common central hollow one with spacing between layers at around 0.34 nm which is close to the interlayer spacing in graphite sheets [5].

2.1.2. Structure of carbon nanotubes

A SWNT can be considered as the roll up of graphene sheet in a cylindrical shape to make seamless structure. This open ended tube gets closed at ends by introducing defects called as pentagons during the growth process. The rolling up of graphene sheet can be done in many ways giving rise to different lattice orientation with respect to an arbitrary tube axis. The final properties of nanotubes will depend on the way graphene sheet rolled up to make nanotubes [1,2,8].

The circumference of the nanotube can be characterized by a chiral vector \( C_h \) and can be given as

\[ C_h = n \mathbf{a}_1 + m \mathbf{a}_2 \]

where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are basis vectors of graphite and \( n, m \) are two integers.
The tube generally designated by \((n,m)\) tube and chiral angle can be defined in terms of \(n,m\) as given by chiral angle \(\theta\):

\[
\theta = \tan^{-1}\left[3^{1/2}(n/2m+n)\right]
\]

and diameter of nanotube can be expressed as:

\[
d_t = 3^{1/2}\left[a_{c-c}(m^2 + mn + n^2)^{1/2}/\pi\right] = C_h/\pi
\]

Where \(C_h\) is the length of chiral vector \(C_h\) and \(a_{c-c}\) is the C-C bond length.

Based on chirality carbon nanotubes can be separated into three categories called as armchair, zig-zag and chiral as shown below in Figure 2.3 [1,2].

Figure 2.3. Schematic representation of chiral vector [4].

If integers are equal, i.e. if \(m = n\), then tubes are called as arm chair with \(\theta = 30^\circ\) and denoted as \((n,n)\) tubes. If \(m = 0\), and \(n>0 \ & \theta = 0^\circ\), then tubes are called as zig-zag tubes and designated as \((n,0)\) tubes. Whereas when \(0 < m < n\) and \(\theta < 30^\circ\), then these tubes are called as chiral tubes. Chiral angle also tell us about the electronic properties of
nanotubes. Armchair nanotubes are metallic in nature whereas zig-zag and chiral tubes can be semi-metallic if \( n - 3 = 3q \), with \( q \) being an integer and \( n \neq m \). This suggests that one third tubes are metallic and rest are semi conducting.

2.1.3. Synthesis of carbon nanotubes

Since their discovery by Iijima in 1991, a lot of research efforts have been directed towards the production of CNT on large scale with controlled dimensions, which can be seen from many review papers on the topic [4,9,10,11,12]. Though there are number of ways to produce CNTs, however, broadly there are mainly four popular methods to produce CNTs as mentioned below:

1. Arc discharge method
2. Laser ablation synthesis
3. Thermal synthesis
   - Chemical vapor deposition
   - High pressure carbon monoxide synthesis (HIPCO)
4. Plasma enhanced chemical vapor deposition method

Research has been directed around these above mentioned four methods at lab scale as well as at commercial scale.

2.1.3.1. Arc discharge method

Arc discharge method is one of the simple method to produce both multi walled and single walled nanotubes and was the first recognized method to produce MWNTs. Though method was used to produce fullerenes, however, MWNTs was formed as a by
product [5]. It was observed that needle like structure grow at the negative end of the electrode. Subsequent characterization reveals that each needle is made up of many coaxial tubes of graphite sheet with smallest tube observed was 2.2 nm in diameter and highest one was at 50 nm and upto 1 μm in length. It was observed that carbon atoms hexagons were arranged in a helical manner around needle axis suggesting the existence of helicity in the tubes which was most interesting discovery about structure of nanotubes. In arc discharge method, a high direct current (50 – 120 Amps) is used between two graphite electrodes separated by 1-4 mm wide gap, with low voltage. An inert gas such as He or Ar is used as atmosphere for the reaction at sub-atmospheric pressure. It has been found that nature of gas, pressure and DC current are important factor to maximize the yield of nanotubes. In the first reported publication, for synthesis of MWNTs, Ar gas was used at 100 torr pressure. Further research in the area optimized the condition for the higher yield and found that He or He:Ar gas mixture at ~ 500 torr pressure with modest voltage of 25 volt with current <100A are the best conditions for higher yield [4]. The schematic representation of arc discharge process is shown below in Figure 2.4 [11].

![Figure 2.4. Schematic figure of arc discharge process [11].](image-url)
In this process, an electric arc is struck between two graphite electrodes under inert atmosphere by using either He or Ar gas or their mixture and a voltage is applied. Once the pressure is stabilized, positive electrode which is movable brought closer to negative one until arcing occurs and once the arc gets stabilized, electrodes kept at distance of 1-4 mm gap. As the anode gets consumed, cylindrical deposits grow on cathode at a rate of 1-2 mm/min. A constant arc power and distance between electrodes is maintained by moving positive electrode and deposit has the same shape as the consumed anode electrode. The temperature between the electrodes is around 3500°C and rate of formation of nanotubes is very high as a MWNT of 5 nm dia. with 100 μm in length grows in $10^{-4}$s [13].

Iijima and Ichihashi [7] and Bethune et al. [14] in 1993, though separately in the same issue of Nature reported the formation of SWNT by covaporizing the graphite and metal in a composite anode. An axial hole is drilled in the anode and densely packed with mixture of metal and graphite powder. The nanotubes are occurred in a web like structure behind the cathode and not on anode as in case of MWNTs. Iijima use Fe as the metal catalyst whereas Bethune used Co as the metal catalyst. Subsequently many catalyst and their combinations have been tried however Ni and Y with graphite in a 15:5:80 weight ratio found to be best to obtain good yield of SWNT nanotubes [1,2,4].

2.1.3.2. Laser ablation

Laser ablation technique is used to produce both multi walled and single walled nanotubes. Its first use was to produce fullerenes, however, subsequent research in area helped to produce carbon nanotubes. Smalley and coworkers produced SWNTs on large
scale using this technique [1,15]. In this technique, a combination of Ni-Co metal (~1 wt%) with graphite composite as a target is placed in an oven at a temperature of 1200°C and ablated with laser in a controlled inert atmosphere. The graphite target vaporized with laser pulse and generated nanotubes and other nanoparticles were collected via condensation on water cooled target.

MWNT and fullerenes can be prepared when pure graphite is used. It has been observed that temperature plays an important role in yield and quality of MWNTs as both yield and quality of nanotubes decreased with decreasing temperature below 1200°C and at 200°C no nanotube formation was observed [2].

2.1.3.3. High-pressure carbon monoxide synthesis (HIPCO)

This process have received lot of interest as this technique has been adopted and commercialized by Carbon Nanotechnologies, Inc. (Houston,TX) to produce SWNT of high purity at large scale. Nikolev et al. [16] and Bronikowski et al. [17] used CO based CVD process to produce SWNT. In this process, CO gas injected into reactor at 900-1100°C and a very high pressure of about 30-50 atm. Disproportionation of CO takes place with the help of metal catalyst particles to produce SWNTs of high purity. The diameter of nanotubes can be controlled by catalyst composition and pressure in the reactor with highest yield at highest pressure [18].

2.1.3.4. Plasma enhanced chemical vapor deposition method (PECVD)

The PECVD technique has been used to produce both single walled and multiwalled nanotubes and has the ability to produce aligned array of carbon nanotubes with
controlled dimensions. PECVD’s first use was in the microelectronics field where high temperature of thermal CVD process was not suitable. In PECVD technique, plasma is excited with the help of either DC source [19] or microwave source [20]. For SWNT synthesis, substrate held at 550-850°C using a combination of CH₂-H₂ gas mixture at around 500 mTorr and plasma of 900 Watts power is applied along with an external magnetic field. As the feed stock in PECVD is in gaseous phase as a mixture of CH₄ and CO, hence there is no need for solid graphite source as in case of arc discharge or laser ablation methods.

2.1.4. Properties of carbon nanotubes

The C-C covalent bond, which is one of the strongest in nature, is the basic constitution of nanotube lattice. The whole range of superior properties of carbon nanotube is due to its combination of structure, dimensions and topology. Carbon nanotubes have in-plane properties of graphite such as very high conductivity, excellent mechanical properties, inertness and chemical resistance. The surface area of MWNT determined by BET techniques is around 10-20 m²/g, which is higher than that of graphite. Depending on the constitution of the samples, the densities of MWNT lies between 1 and 2 g/cm³ [4].

Due to their one dimensional structure, charge carriers can travel through the nanotubes without scattering resulting in ballistic electron transport at room temperature [21]. Kociak et al. [22] have shown that ropes of carbon nanotubes shows intrinsically superconducting behavior below 0.55 K where resistance drops by around 2 orders of magnitude. The in-plane of thermal conductivity of graphite (3000 W/m/K) has also been
observed in carbon nanotubes. Few studies [23,24] have shown the existence of ballistic conduction phenomena in nanotubes and thermal conductivity as high as 3000W/m/K has been measured [24].

In addition to the electronic properties, it is the exceptional mechanical property which makes nanotubes a fascinating material for use in various applications. The in-plane modulus of graphite is around 1.06 TPa [25] and nanotubes were expected to show the similar stiffness. In 1960, graphite whiskers fabricated by Bacon has the yield strength of around 20 GPa [26] whereas the Perepelkin [27] suggested the tensile strength of graphite around 130 GPa from the C-C bond properties. With this background, carbon nanotubes were materials of very high strength and stiffness. Overney et al. [28] calculated the modulus of SWNT to be 1500 TPa using computer simulations followed by some other studies predicting Young’s modulus for nanotubes close to 1 TPa [29]. Wong et al. [30] were the first one to do the direct measurement on nanotubes using AFM. Salvetat et al. [31] used an AFM tip to bend arc-MWNT to study their strength and flexibility and average modulus of 810 GPa was obtained.

At first nanotubes were considered to be chemically inert, however, subsequent studies shows that nanotubes can be oxidized at the ends surfaces and resulting in opening the tubes [32,33]. The ends are more reactive than cylindrical parts due to presence of pentagonal defects. It has also been shown that enhanced electron transfer was observed on nanotubes surfaces when they are used as electrodes in chemical reactions [34].
2.1.5. Applications of carbon nanotubes

Due to their remarkable properties, carbon nanotubes are gaining tremendous attention in academia and industry. A large part of research efforts are now in progress to harness these remarkable properties of carbon nanotubes for commercial applications. It has been predicted that nanotubes will play important role in future technology mainly based on nanotechnology area which is supposed to revolutionize any future technology.

Due to their remarkable electronic properties, carbon nanotubes already have significant impact on the field emission applications [2] and also qualify them to use as quantum wires [35]. Due to their high aspect ratio (100-1000), it is possible to achieve the percolation threshold at very low loading of CNTs [36,37]. The another major application area of nanotubes is in the fabrication of nanotubes based high performance composites materials due to very high strength and stiffness of the nanotubes along with their light weight. Due to their exceptional mechanical properties, they have potential to surpass graphite fiber based composites and overcome the problem associated with conventional fiber based composites.

Nanotubes under stress change their helicity which change their electronic character and make them useful in fabrication of nanotube probes or sensors [38]. Due to its superior mechanical properties coupled with its elastic behavior make them an excellent candidate as AFM tips [39]. Nanotubes have been successfully used in biochemical reactions as an electrode [40] and also as biosensors [2]. Another interesting use of nanotubes has been demonstrated in the area of hydrogen storage where nanotube acts as small gas cylinders [41,42].
2.2. Polymer-carbon nanotube nanocomposites

In this section various methods for preparation of carbon nanotubes based polymer nanocomposites has been discussed.

2.2.1. Methods of preparation

The exceptional mechanical, thermal and electrical properties of the carbon nanotubes along with their light weight make them ideal material as reinforcing filler in the polymer matrix \[4,37,43\]. Some attempts have also been made to develop metal \[44,45\] and ceramic- matrix composite \[46,47\] using carbon nanotubes as reinforcing filler, however, most efforts directed towards development of polymer-nanotubes composites.

There are many ways to incorporate nanotubes in the polymer matrix, however, successful uniform dispersion of carbon nanotubes in a polymer matrix and improved polymer –matrix interaction is still remains a challenge as can be seen from many review papers \[48,49\]. There are mainly three methods commonly used to prepare nanocomposites: solution processing, in-situ polymerization and melt processing. In this section we will discuss these methods.

2.2.1.1. Solution processing

Solution based method is one of the most common way for preparing polymer-nanotubes composites. This method has an advantage as due to low viscosities of solution it facilitates the mixing and dispersion of nanotubes. Many researchers have used this route to prepare both thermoset and thermoplastic polymer nanocomposites. In all
solution processing method, the basic scheme of mixing is almost same as either nanotubes dispersed in solvent or polymer solution by agitation or nanotubes mixed with polymer in solution by stirring and then followed by evaporation of the solvent to form a dry composite film. The agitation is provided by various means such as magnetic shearing, shear mixing, or sonication using sonication bath.

Shaffer and Windle [50], made composites films with varying loadings of carbon nanotubes. Aqueous solution of semi-crystalline polyvinyl alcohol (PVA) was mixed with various loadings of CVD-MWNT and subsequent composites films were prepared by casting and controlled water evaporation. The thickness of films was varied from 53 µm down to 44 µm following the increase in nanotubes loadings A very high nanotubes loading upto 60 wt% was used. In study [51], functionalized single walled nanotubes with multiple surface hydroxyl, called nanotubols, were used and mixed with semi-crystalline PVA as both are water soluble and subsequent composites films of nearly 200 µm were prepared with nanotube loading upto 1 wt%. In study [52], protein functionalized multiwall nanotubes were mixed with solution of PVA and resultant mixture was dried to form film.

Qian et al. [53] dissolved polystyrene and MWNT separately in toluene then mixed both solutions followed by solvent evaporation. Chang et al. [54] dissolved PS in O-dichlorobenzene (DCB) and mixed it with sonicated DCB solution of single walled nanotubes. Various concentration of polymer solution was used to study the effect of polymer concentration on CNT dispersion.

Stephan et al. [55] mixed the single wall nanotube powder and PMMA and dissolved the mixture in toluene and made composites by spin coating the solution.
PMMA and SWNT were dissolved in dimethylformamide (DMF) and mixed together followed by filtration to remove water to further make the nanocomposite films. The alignment to the nanotube was provided by melt spinning the fibers from suspension.

In study [56] treated MWNTs were subjected to thermal and freeze drying followed by mixing with PC. Then mixture was dissolved in tetrahydrofuran (THF) followed by solvent evaporation and finally films were made by pressing in hot press.

Park et al. [57] and Wise et al. [58] dispersed SWNTs in DMF or dimethylacetamide (DMAc), and used it as solvent for the synthesis of polyamic acid followed by either chemical or thermal imidization of SWNT-Polyamic acid to make SWNT-polyimide film. The unimidized SWNT-polyamic acid solution was found to exhibit excellent stability, remaining in solution state for over two years in sealed bottle under refrigeration [58].

Fournet et al. [59] used solution processing technique to remove the impurities together with dispersing nanotubes. CNTs interact with poly(m-phenylene-vinylene-co-2,5-dioctyloxy p-phenylene-vinylene)(PmPV), whereas the impurities settle out of solution.

This method is based on the efficient dispersion of the nanotubes in chosen solvent and generally the chosen solvent should be able to dissolve the polymer. However, nanotubes are not soluble in many solvents. To solve this problem some time surfactants have been used to disperse the nanotubes [60,61,62]. Sodium dodecyl sulphate (SDS) is one of the commonly used surfactant resulting in good dispersion of nanotubes in cast film.
Electrospinning is one another solution based process to provide alignment to the nanotubes. It is a simple process involving continuous production of one dimensional nanofibers. In this process a high voltage is applied to a polymer solution, the polymer solution overcomes surface tension and a fine jet stream ejected from the needle and gets deposited on the collector [63,64,65].

2.2.1.2. In-situ polymerization

In-situ polymerization is a method commonly used to improve the dispersion and compatibilization between different phases. The technique has an advantage as reinforcement is on molecular level and grafting of polymer molecules onto the walls of carbon nanotubes can be easily done. One can go to very high loading of nanotubes without any processing problem. This method has been mainly used for preparing insoluble or thermally unstable polymers.

In 1999, Jia et al. [66] prepared PMMA/MWNT composite by in-situ polymerization process. 2,2’-azobisisobutyronitrile (AIBN) was used as initiator to carry out the polymerization and it was observed that nanotubes consume AIBN reducing the amount of AIBN left for MMA molecules to get polymerized. It was also observed that AIBN opens the $\pi-\pi$ bonds of CNTs indicating that CNTs indeed participated in PMMA polymerization and form a strong interface between CNTs and PMMA matrix. Velasco – Santos et al. [67] also used AIBN as an initiator to prepare PMMA/MWNT composites. In another reported work [68], ultrasonic assisted in-situ emulsion polymerization technique was used to prepare stable poly(methyl methacrylate-co-n-butyl acrylate)(P(MMA-BA))/MWNT composite emulsion and resulting emulsion has very
good film forming property.

Polyimide/SWNT [69,70] composites were prepared via in-situ polymerization in the presence of sonication. A uniform dispersion of nanotubes in polymer matrix was observed resulting in optically transparent and conducting nanocomposite film. A non–ohmic behavior was observed with current–voltage measurement indicating quantum tunneling conduction mechanism.

Li et al. [71] synthesized the MWNT/poly (p-phenylene benzobisoxazole) (MWNT/PBO) nanocomposite by in-situ polymerization of dichlorides and diacids under sonication. With strong stirring, a stir opalescence formed indicating a nematic phase, and dry-wet spinning technique was used to spun composite dope.

In study [72], PU/MWNT composites were prepared by a sol-gel process. Carbon nanotubes were modified with coupling agents and introduced into polyurethane-urea system by chemical linkages and transparent membranes with self-crosslinkable PU/MWNT composites were prepared.

2.2.1.3. Melt processing

While solution processing and in-situ polymerization processes are quite popular and have gained a success upto certain extent in dispersing nanotubes in polymer matrix, however, these methods may not be commercially viable due to their limitation in scale up and their negative environmental impact. Melt processing, being more efficient, rapid and environmentally friendly method to disperse CNT in a polymer matrix, is one of the most preferred techniques from industrial application point of view because of its easiness in scale up. It is commonly used to process thermoplastic polymers. The
nanofiller or any additive added to the melt and homogenously mixed with application of shear mixing. A number of efforts have been directed towards dispersing nanotubes in polymer matrix using melt processing method. Jin et al. [73] used a miniature mixer molder to mix PMMA with up to 26 wt% MWNT. The extruded melt was compression molded under high pressure to make thin film samples. A good dispersion of nanotubes was observed under TEM even at high nanotubes loading. Many research groups [74,75,76,77,78,79] have studied PC/CNT composites prepared via melt processing method. In all these studies, a conical twin screw extruder was used with a circular die and composites with varying nanotubes concentration were prepared and a fair degree of dispersion was achieved in all the studies.

Injection molding has also been used very commonly in conjunction with extrusion to fabricate nanocomposites samples for further testing. HDPE/MWNT composites were studied by different groups [80,81]. In all cases, composite films and pellets were prepared via melt processing method using a conical twin screw micro extruder followed by samples fabrication using injection molding. Zhang et al. [82] developed a new method to disperse the nanotubes in a matrix and henceforth prepare the nanocomposites. They sprayed the aqueous solution of SWNT on the HDPE powders and then dried powder mixture was processed in a twin screw extruder and a uniform dispersion of nanotubes was observed in the resulting composites. In another work [83], LDPE/MWNT composites have been studied. In this study, mechanical mixer was used to mix nanotube powder and LDPE pellets. Mixed samples were compression molded under high pressure and cut into samples and again compressed under high pressure. This process repeated many times to improve the dispersion of nanotubes in a polymer matrix.
Siochi et al. [84] melt mixed SWNT powder and ULTEM (polyetherimide) powder in electrically heated Brabender mixer. The resulting material after grinding through 1 mm mesh screen passed through a single screw extruder especially designed by NASA Langley research centre.

2.2.2. Structural characterization

The dispersion of nanotubes in polymer matrix can affect the final properties of nanocomposites. To achieve the full potential of nanotubes in applications it is crucial to investigate and quantify the dispersion. This can be achieved by visualizing nanotubes themselves. However, characterization becomes difficult at nanoscale level. In case of emerging materials, characterization becomes important in understanding their basic chemical and physical properties.

2.2.1.1. Scanning electron microscopy (SEM)

Electron microscopy is one of the most popular techniques to study the structure of nanotubes and their state of dispersion in nanocomposites. The resolution of SEM is typically about 2 to 5 nm. High resolution scanning electron microscopy (HRSEM) allows one to image oriented growth of nanotubes [85], to image ropes of SWNT [86] and to see state of dispersion of nanotubes in a matrix. In the study on PCL/MWNT [65] and PA-12/MWNT [87] nanocomposites, SEM images technique was used to show (Figures 2.5 and 2.6), the state of dispersion of CNTs in a polymer matrix.
Figure 2.5. SEM images of fractured surface of PCL/MWNT (5 wt%) [65].

Figure 2.6. HRSEM image of nanocomposite fibers of polyamide-12 containing 5 wt% aligned catalytically-grown nanotubes [87].

In study [88], SEM micrographs shows the crack propagation in the matrix and it was observed, as shown in Figure 2.7, that nanotubes help in bridging the crack in the polymer matrix and could be considered as a way to increase the strength of the composites.
Figure 2.7. SEM image of microcrack connected by MWNTs sheathed with polymer in PA6 nanocomposites [88].

2.2.1.2. X-ray diffraction (XRD)

XRD has been a useful tool to study structure of various crystals. It is very useful in studying the intercalation of nanoclay in a polymer matrix by measuring the change in interlayer spacing in the clay layers [89]. It has found usefulness in characterizing the nanotube based nanocomposites.

XRD patterns of graphene sheets are very much similar to those of purified MWNTs, and at the same time outer shell patterns are similar to that of graphite rod. The wide d$_{002}$ spacing (0.34 nm) in MWNTs indicated by the shift of (002) and (004) peak positions of purified MWNTs to lower angles than those of the graphite rod [90]. The bundles of SWNT and MWNT have been investigated by XRD. In study [80], the state of dispersion of MWNTs in HDPE matrix has been investigated using XRD. It can be seen from the XRD patterns of MWNTs and HDPE/MWNT nanocomposites shown in Figure 2.8, that MWNTs exhibits a sharp Bragg reflection at $\theta = 26^\circ$ which is absent from XRD patterns of HDPE/MWNT nanocomposites and it greatly reduced for 10 wt% nanocomposites [80].
XRD has been used to study the effect of MWNT addition on the melting and crystallization of PA6 matrix and was found that effect was quite different from that of PA6/nanoclay system probably due to the different geometry or morphology of the nanofiller [88].

The orientation of nanotubes can be investigated by the XRD. The effect of stretching on the orientation of carbon nanotubes and in turn on the mechanical properties of composites has been studied in detail by various research groups using the XRD [91,92]. It was observed that as the orientation of nanotube increased, determined by Herman’s orientation factor, the Young’s modulus increased tremendously [92].
2.2.3. Nanocomposites properties

In this section reinforcement effect of carbon nanotubes loading on the mechanical, electrical, rheological and thermal properties on the polymer nanocomposites has been discussed.

2.2.3.1. Mechanical properties

In this section, mechanical properties of polymer-carbon nanotubes nanocomposites prepared by different methods have been discussed.

2.2.3.1.1. Melt processing

Fiber-reinforced composites have been widely used in many areas ranging from automotive to aerospace and military applications due to their light weight and improved mechanical properties. The idea of using filler as a reinforcing agent is not new and has been in practice since many centuries as straw has been used to reinforce mud bricks from a long time. Carbon fibers have shown the tremendous improvement in the mechanical properties (stiffness, strength etc.) of the polymer. Recently nanofillers (e.g. carbon nanotubes) have been very popular as a reinforcing agent in the polymers due to their exceptional mechanical properties. Carbon nanotubes proven to have a very high Young’s modulus (~1TPa) and strength (~100 GPa) as compared to all other carbon fibers. Due to exceptional mechanical properties along with their light weight, they have the potential to surpass all conventional fiber-reinforced composites. A lot of research [74,78,81,93] has been done in the area to effectively utilize the mechanical properties of nanotubes in a polymer matrix, however, still a long way to go till we get the proper
reinforcement as expected from nanotubes.

For any effective reinforcement, there are mainly four system requirements: high aspect ratio, good dispersion, interfacial stress transfer and alignment of nanofiller. However, the most challenging issue in nanotubes as filler is its dispersion to the level of individual tube in the matrix so that to enhance the load transfer capacity of the composite to the nanotube network. As already discussed many routes have been tried to disperse the nanotubes, however, found limited success.

The mechanical properties of melt processed carbon nanotube based composites for various thermoplastic polymers have been well documented. In study [93] of PC/MWNT composites a small increase (0.8 to 1.04 GPa) in the storage modulus was observed on 15 wt% nanotubes loading. In another study [78] no significant improvement in the Young’s modulus was observed for PC/MWNT composites for 2 wt% MWNT loadings. For PC/SWNT composites [74], a slight decrease in the Young’s modulus was observed and reason was attributed to the nanotubes weakening the coherence of the matrix.

HDPE is one of the mostly used thermoplastics material. It provides excellent chemical resistance, high impact strength, good fatigue and wear resistance, however, with moderate stiffness and rigidity. To improve these properties nanotubes can be used as a promising reinforcing agent. Tang et al. [81], used as received MWNTs and studied HDPE/MWNT composites films. They did punch test on the composites films. In this test, a small disk of material was clamped over a circular guide hole between two rigid dies. The specimen was then subjected to lateral indenter (tip of the indenter was hemispherical) moving at constant displacement rate through the guide hole and at the
same time indenter force and displacement was recorded. It was found that stiffness, peak load and work to failure increased by around 8%, 13% and 5%, respectively, on addition of 5 wt% MWNTs. In other study [80] on HDPE/MWNT composites, no significant improvement in mechanical properties was observed. However, modulus and strength was increased by 46% and 89%, respectively, for compression molded LDPE/MWNT composites at 10 wt% CNT loading [94]. In HDPE/SWNT study [82], nanotubes were dispersed with the help of surfactants and the aqueous solution was sprayed on the HDPE films, dried and then processed in a co-rotating twin screw extruder. The Young’s modulus and strength was increased by 50% and 65%, respectively, for HDPE/SWNT composites at 2.6 wt% CNT loading.

In early work on PMMA/MWNT composites, Jin et al. [73] reported the increase of the storage modulus of PMMA on addition of as received MWNTs (prepared with arc discharge method) with significant effect at higher temperature. The modulus increased by factor of 1.6-20 at 40°C whereas it increased by 5-27 times at 120°C with addition of upto 26 wt% nanotubes. The ratio of modulus at 120°C to that of 40°C is 0.03 for PMMA whereas it is 0.5 for PMMA/MWNT composites at 26 wt% nanotubes loading. The same group, Jin et al. [73], further used the PVDF coated MWNT (prepared by arc discharge method) to prepare PMMA/MWNT composites and found that the storage modulus increased significantly at low temperature with PVDF coated nanotubes where PVDF helped in dispersion of nanotubes and acted as a glue between PMMA and MWNT to increase the interfacial interaction.

For PET/MWNT composites, the tensile modulus and strength was increased by ~19% and ~11%, respectively, at 2 wt% nanotubes loading [95].
Amine functionalized nanotubes were used in study [96] to prepare Nylon 6/MWNT composites. A significant improvement in the tensile modulus and strength was obtained. The modulus and strength was increased by 87% and 69%, respectively, on addition of 1wt% nanotube loading. However, on further increasing the nanotubes loading upto 2 wt%, it was observed that modulus and strength decreased and was less than that at the 1 wt% loading and it was due to ineffective dispersion of nanotubes at high loading. The modulus and strength improvement at 2 wt% CNT loading was 58% and 55%, respectively, as compared to the pure material. The increase in mechanical properties was attributed to the better dispersion and interfacial adhesion due to functionalized nanotubes. In other studies [97,98], on Nylon/MWNT composites, Zhang and co-workers obtained three fold increase in the tensile modulus and around 160% improvement in the yield strength on addition of 2 wt% nanotubes. There was an almost 62% increase in the modulus for polyamide-6/MWNT composites at 12.5 wt% nanotubes loadings. However, it was accompanied by tremendous decrease in ductility [99].

In study [100], polystyrene was dissolved in THF solvent followed by mixing with nanotubes and then mixture was dried and fed into the extruder and processed nanocomposites were drawn as films with varying thickness. At low temperature the storage modulus was found to increase by 49% for drawn films as compared to randomly oriented composites for which increase was only 10% at 5 wt% MWNTs loading. The yield strength and ultimate strength was increased for drawn films as compared to un-reinforced polystyrene films. In another study [101], PS was dissolved in toluene to form clear solution followed by mixing with multi-walled nanotubes and then mixture was dried and obtained film was cut into small pieces and fed into extruder and composites
rods of 1mm diameter with nanotube loading varying from 0.1 to 2 wt% were obtained. At 0.1 wt% of nanotube loading, a moderate increase in stiffness ~2% and about 10% increase in the strength and 3% increase in the failure strain was observed. However, all these properties decreased with increasing nanotubes content suggesting a poor dispersion of nanotubes in a matrix.

PP/SWNT [102] composite were prepared via. melt processing in internal mixer. The Young’s modulus was increased from 0.85 GPa for neat PP to 1.19 GPa and the yield strength was increased by around 26% for PP/SWNT composites at 0.75 wt% nanotubes loadings. A slight decrease in the properties was observed at higher nanotubes loading. However, there was not any significant reduction in the deformation at break.

Siochi et al. [84] studied the PEI/SWNT composites prepared in a single screw extruder developed as NASA Langley research centre. No significant improvement in mechanical properties was observed for thin film samples; however, significant increase in tensile modulus and yield stress was observed when extrudate melt was drawn to thin fibers.

Recently [103], acrylic acid grafted metalloocene polyethylene-octene elastomers (POE-g-AA) were melt blended with purified MWNTs (acyl chloride as functional groups) in Brabender mixer with a blade type rotor to prepare the nanocomposites. The prepared nanocomposites were compression molded into 1 mm thick films and cut into specimens for further characterization. A three fold increase in the tensile strength was observed on addition of 5 wt% of nanotubes. However, no improvement in the strength was observed at 10 wt% nanotubes loading as compared to 5 wt% loadings.
2.2.3.1.2. Solution based system

A lot of studies [50,51,52,104] have been done to incorporate nanotubes in polymer matrix via different methods. Solution processing is one of the common methods studied for preparation of composites. Shaffer and Windle [50] made composites films with varying loadings of carbon nanotubes. Aqueous solution of semi-crystalline polyvinyl alcohol was mixed with various loadings of CVD-MWNT and subsequent composites films were prepared by casting and controlled water evaporation. The thickness of films was varied from 53 µm down to 44 µm following the increase in nanotubes loadings. A very high nanotubes loading upto 60 wt% was used and mechanical properties were tested using dynamic thermal analyzer (DMTA). The storage modulus increased from 6.3 to 12.6 GPa on addition of 60 wt% nanotubes. There was increase in modulus below the glass transition temperature; however, the better results were obtained above the glass transition temperature.

In study [51], functionalized single walled nanotubes with multiple surface hydroxyl groups were used and mixed with semi-crystalline PVA and subsequent composites films of nearly 200 µm were prepared with nanotube loading upto 1 wt%. The tensile modulus was increased by 79% from 2.4 to 4.3 GPa and the tensile yield strength was increased by 47 % (from 73 to 107 MPa) on addition of 0.8 wt% nanotubes. The improvement in mechanical properties was attributed to the improved nanotubes dispersion and increased matrix- nanotube interfacial interaction due to the hydrogen bonding between nanotube surface and the matrix as both have the hydroxyl groups on their surfaces.
Biological functionalization of nanotubes is gaining attention in recent years due to its diverse application areas. In study [52], protein functionalized multiwall nanotubes were mixed with solution of PVA and resultant mixture was dried to form film samples. The storage modulus was enhanced significantly at 1.5 wt% loading of nanotubes. Storage modulus increased from 3.46 to 7.22 GPa which is attributed to the better cross linking structure with covalent bonds between nanotubes and polymer matrix.

Chang et al. [104] studied the PS/SWNT composites and found that the flexural modulus, measured by DMTA analysis, increased by 20-30% on addition of 2 wt% of annealed and sonicated single wall nanotubes. However, data was significantly scattered over the entire measurement range. In another study [53] on PS/MWNT composites, sonicated nanotubes were mixed with dissolved PS (in toluene) and the mixture was subsequently casted to make a thin film of 0.4 mm with evaporation of solvent. Composite films shows that the tensile modulus and strength increased by 36-42% and 25%, respectively, on addition of 1 wt% multi walled nanotubes. In work on PS/MWNT composites [105], the modulus was increased from 1.53GPa to 3.4 GPa and the strength was increased from 19.5 MPa to 30.6 MPa for a 2.5 vol% nanotubes loading.

In study [106], copolymers of methyl and ethyl methacrylate (P(MMA-co-EMA) were mixed with octadecylamine functionalized multiwall nanotubes in a dichloromethane solvent followed by sonication. The resultant mixture was subsequently dried to remove solvent and further processed in a laboratory extruder to form a strip for further testing. The tensile modulus and strength increased by 135% and 49%, respectively, on addition of 10 wt% octadecylamine functionalized multiwall nanotubes. Octadecylamine functionalized nanotubes based composites showed little more
improvement in the mechanical properties as compared to the composites based on nanotubes which were simply purified using nitric acid treatment.

Cadek et al. [107] studied poly(vinyl alcohol) with different types of nanotubes and found that the reinforcement effect inversely changes with the diameter of the nanotubes suggesting that with low diameter nanotubes modulus enhancement is quite significant. Further Coleman et al. [108] studied the PVA/MWNT composites and found that besides the low diameter nanotubes, interfacial crystallinity has a large effect on the mechanical properties of the composites.

2.2.3.1.3. In-situ polymerization

Polymer–nanotubes composites prepared by in-situ polymerization are expected to have large interfacial shear strength due to strong polymer–nanotube interaction and depending on the reaction condition one can create covalent bonds between nanotubes and polymer matrix. In study [68], ultrasonic irradiated in-situ polymerization were carried out to prepare a stable poly (methyl methacrylate-co-n-butyl acrylate)(P(MMA-BA))/MWNT (purified nanotubes) composite emulsion. Composite films of thickness 0.2-0.5 mm show a significant improvement in the tensile modulus at 1 wt% nanotubes loading. The tensile modulus was increased from 124 to 289 MPa for 1 wt% nanotubes loading whereas the yield strength increased by 14% on addition of 0.5 wt% nanotube loadings. However, at higher loading mechanical properties were decreased as CNTs behave like floculants at higher loading and gets precipitated. In another study [72], MWNTs modified by coupling agents were used to prepare polyurethane-urea-carbon nanotubes composites film by sol-gel process. Due to cross linking between nanotubes
surfaces and polymer matrix, a significant improvement in mechanical properties was observed with addition of only 0.5 wt% of nanotubes. The tensile modulus and strength was increased by 400% and 150%, respectively, with 0.5 wt% nanotubes and without effecting elongation at break of the polymer matrix. Li et al. [71] first oxidized multi-wall nanotubes followed by dispersing it using ultrasonic method and further used to react with poly(p-phenylene benzobisoxazole) to prepare PBO/MWNT composites. The composites dope was further spun by dry wet spinning technique to make fibers. The tensile strength was increased by about 33% on addition of 5 wt% of nanotubes.

2.2.3.1.4. Thermosetting polymers

Thermoset materials have been quite popular for various industrial applications. Their composites with carbon nanotubes as fillers are gaining lot of attention in recent years. The first study on epoxy–CNT composites was done by Ajayan et al. in 1994 [109]. However, no quantitative measurements for the mechanical properties were done. In another study [110], fluorinated single walled nanotubes (FSWNT) were used to prepare epoxy-FSWNT composites. Storage modulus was found to increase by 20% with just 0.3 wt% of FSWNT. In study [111], load transfer mechanism in epoxy-CNT composites have been studied. The tensile and compression modulus was increased from 3.1 to 3.71 GPa and 3.63 to 4.5 GPa on addition of 5 wt% of multi-wall nanotubes. There was large scattering in the data believed to come from microstructural variability in samples. Yeh et al. studied [112], phenolic/MWNT composites and found that the tensile modulus and strength increased by ~47% and ~ 65%, respectively, on addition of 4 wt% of nanotubes.
2.2.3.2. Electrical properties

Fiber-reinforced composites have been widely used in the area of aerospace and military due to their light weight and improved mechanical properties. For these applications some electrical conductivity is also required to dissipate electrostatic charge and also some kind of EMI protection. Till date carbon black is quite popular as a reinforcing filler to provide the desired electrical conductivity. However, the volume fraction required by carbon black is quite high and at that high loading the matrix becomes more brittle with a significant reduction in strain to failure values. Recently, carbon nanotubes due to their exceptional mechanical, thermal and electrical properties are gaining tremendous attention both in academia and industry. Due to the high aspect ratio (100-1000) of CNTs it is possible to achieve the percolation threshold at very low loading of CNTs. Low level of loading coupled with the flexible nature of nanotubes makes it possible to maintain the fracture toughness and tensile properties of the matrix. Percolation threshold can be defined as a critical concentration of conductive filler where a three-dimensional network of filler formed resulting in creation of conductive path in the composites causing the material to behave like a conductor. With nanotubes it has been seen that one can get percolation threshold even at 0.0025 wt% nanotubes loading [37].

Zhang et al. [82] studied the HDPE/SWNT composites and found electrical percolation near 4 wt% of SWNT loading, whereas McNally et al. [80] studied HDPE/MWNT composites and found electrical percolation near 7.5 wt% loading which is usually higher than what has been observed for other polymers. In polyamide-6/MWNT nanocomposites [99], electrical percolation have been found to
be between 4-6 wt% nanotubes loading, whereas polyamide-6-ABS-MWNT blend nanocomposites shows reduced percolation threshold between 2-3 wt% of nanotubes loading due to the confinement of the conductive filler to one component of the blend.

A number of studies [74,76,93] have been done on polycarbonate–carbon nanotubes composites. Potschke et al. [76,93], did lot of studies on PC/MWNT composites. They found that for melt processed PC/MWNT composites the electrical percolation threshold lies between 1 and 2 wt% of nanotubes loadings. In PC/SWNT composites, two different kinds of nanotubes (prepared by HIPCO process and arc discharge method) were used. Melt processing and coagulation process were used to fabricate the PC/SWNT composites. It was observed that percolation threshold changes with the processing method. It was about 1.7 wt% for ArcD nanotubes with melt extrusion while with the coagulation method it stood at around 0.8 wt% of nanotubes loading. However, the percolation with both kinds of nanotubes was in the same range about at 0.5 wt% nanotube loading. In another study [56] on PC/MWNT composites prepared by solution process, a little higher percolation threshold was observed varying from 2 to 5 wt% of nanotubes content depending on the different kind of nanotubes.

Du and co-workers [113,114] studied PMMA/SWNT nanocomposites prepared via coagulation method. In coagulation method, PMMA was dissolved in a mixture of SWNT and DMF and the suspension formed was dripped in distilled water. PMMA precipitated immediately because of its insolubility in DMF and water mixture. The precipitating PMMA chains entrapped SWNT and prevent their reagglomeration. Electrical percolation was found to be at ~0.39 wt% (after purification nanotubes were dried) and around 1 wt% (wet nanotubes, after purification were used) of nanotubes
loadings in different studies [113, 114].

Epoxy is one of the most commonly used resins for manufacturing of fiber-reinforced composites for aircraft applications. A lot of work [37, 62] has been done to improve the electrical conductivity of epoxy composites using carbon nanotubes. Electrical percolation with multi-wall carbon nanotubes as filler in epoxy matrix has been reported as varying from 0.0021 to 0.04 vol% [37], whereas with single walled carbon nanotubes, percolation threshold has been reported as low as 0.074 wt% [36].

SWNT/polyimide nanocomposites [57] prepared by solution process and percolation threshold was found to be between 0.02 and 0.1 wt% of nanotube loadings. In different study [69] on SWNT/polyimide composites prepared by in-situ polymerization, the percolation found to be between 0.02 and 0.1 vol% of SWNT loadings.

Cheng and co-workers [54] studied the PS/SWNT composites prepared by solution process and used the annealed single wall nanotubes. A lower percolation threshold at around ~0.3 wt% was found as compared to the composite prepared by using raw single wall nanotubes (0.5 wt%).

A coagulation method was used to prepare PET/MWNT nanocomposites using purified nanotubes [115]. In this method, PET was added to the MWNT and ODCB-phenol suspension. After PET was dissolved, solution was precipitated in methanol. It was found that electrical percolation was about 0.9 wt% of nanotubes loading.

The electrical percolation threshold for PVA/MWNT composites prepared via solution process lies between 5 and 10 wt% of nanotubes loading [50].
2.2.3.3. Rheological properties

The rheological behavior of CNTs based composites can be used to determine the state of nanotube dispersion in the polymer matrix. A report on the PBT/clay nanocomposites [116] used the rheological behavior of nanocomposites to determine the state of extent of delamination of clay platelets stacks in the nanocomposites.

A number of studies [76,95,117] have been performed to understand the rheological behavior of various thermoplastic polymer/CNT composites while melt processing. For PC/MWNT [76] composites prepared by melt processing technique, rheological percolation found to be between 1 and 2 wt% of nanotubes loading. In case of PS/SWNT [117] composites prepared via solution process, rheological percolation lies between 1 and 2 wt% of nanotubes loading. In case of PET/MWNT composite prepared by melt processing [95] and coagulation methods [115] the rheological percolation lies between 0.5 and 1 wt% of nanotube loadings. A very low rheological percolation around 0.12 wt% of nanotubes loadings was observed for PMMA/SWNT composites prepared by coagulation process [113,114].

HDPE/MWNT [80] nanocomposite prepared by melt processing shows the rheological percolation around 7.5 wt% whereas HDPE/SWNT composites with modified nanotubes show percolation around 1.5 wt% of nanotubes loading [82]. For LDPE/MWNT composites, rheological percolation lies between 3 and 5 wt% of nanotubes loading [83].

In all the studies it has been observed that complex viscosity increased with the increase of nanotube content and it decreased with increasing frequency. The effect of nanotubes content on complex viscosity is more pronounced at low frequency region and
increase in viscosity is less in high frequency region. The nanocomposite shows a very strong shear thinning behavior as the nanotube content increase. The storage modulus and loss modulus continuously increased with nanotube content and with frequency with nanotube having more effect on the storage modulus. These studies found that on addition of nanotubes, the curves of log G’ vs. log G” (Cole-Cole plot) for different nanotubes loading, do not coincide indicating micro-structural changes taking place in the matrix.

2.2.3.4. Thermal properties

A number of various thermoplastics and thermoset nanocomposites have been studied to improve the thermal properties of the polymer with addition of CNTs. The glass transition temperature of polyimide (Ultem) did not change at all on addition of SWNTs whereas thermoxidative stability decreased slightly due to presence of impurities in nanotubes which accelerates the thermal degradation [84]. However, in case of another polyimide/pSWNT (purified SWNT) composites prepared by solution process, onset of thermal degradation temperature was increased by 35°C on addition of just 0.5 wt% of nanotubes [57]. The addition of low SWNT (< 1wt %) content in PP increase the crystallization rate without significant changes in melting point and crystalline structure of PP [118].

A very little or no significant change in glass transition temperature was observed on addition of carbon nanotubes in various matrix: PMMA [113], PET [95,115], epoxy [62] and PVA [50].
A significant improvement in the glass transition temperature, from 10-25°C, was observed for PVA [52], P(MMA-co-EMA)[106] matrices when functionalized nanotubes were used as the reinforcing filler. However, in few cases [110] a decrease in glass transition temperature was observed on addition of fluorinated single wall carbon nanotubes in matrix. However, a decrease in glass transition temperatures was also observed on addition of functionalized SWNT to epoxy matrix, the reason for that attributed to the non stoichiometry of the matrix on addition of nanotubes.

Carbon nanotubes are gaining lot of attention as a reinforcing filler to improve the thermal stability of the polymer matrix due to the higher thermal stability of nanotubes even at very high temperature. A significant retardation in the thermal degradation of the P(MMA-co-EMA) [106], PMMA [73], polyimide [69], POE-g-AA [103] matrices was observed on addition of carbon nanotubes. In study on PVA/MWNT [50], the onset of thermal degradation of PVA matrix was retarded on addition of carbon nanotubes at low loading, however, this stabilizing effect get negated at higher nanotube loadings because of oxidation of nanotube surfaces itself. As the content of multi-wall carbon nanotubes increased, a significant increase in the thermal degradation temperature of PET/MWNT composites was observed as compared to the PET matrix [95].

It is not necessary that addition of nanotubes always increase the thermal stability of the composites as can be seen from study on Nylon-6/MWNT composites [96] where amount of water in multi-wall nanotubes accelerated the hydrolysis of Nylon resulting in reduced thermal stability. In another study on epoxy/FSWNT [110] composites, on addition of functionalized SWNT to epoxy matrix, decomposition temperature of composite decreased and the reason for that attributed to the non stoichiometry of the
matrix on addition of nanotubes which result in lower cross link density and hence lower glass transition and degradation temperature.

The unusually high thermal conductivity of carbon nanotubes, which is around 3000 W/mK, makes them as an attractive filler to be used in polymer/carbon nanotubes composites to enhance their thermal properties [23]. The prediction of thermal behavior of nanocomposite materials is required to know the amount of heat dissipation from their surfaces. The interfaces and close proximity between CNTs and polymer matrix are very important for thermal conductance of the CNTs based composites [119]. Many studies [119,120,121] indicated that heat transport in CNT based composites is limited by small interface thermal conductance. This interface resistance results in lower thermal conductivity of the composites than the estimated value from the intrinsic high thermal conductivity of the nanotubes. Nan et al. [122] developed a very simple equation to predict the effective thermal conductivity of carbon nanotubes based polymer nanocomposites with interface resistance and it was observed that thermal conductivity was greatly affected by interface resistance. In study [121] PVDF/SWNT composites were prepared via solution process and thermal conductivity was found to increase by 130% at 49 vol% SWNT loading. However, the increase in thermal conductivity on addition of SWNTs was not upto the level required by heat sink applications [123]. It was also observed that thermal conductivity of the composites increased with increasing temperature from 25 °C to 50 °C [121]. The thermal conductivity of PP/MWNT [124] composites were increased with increasing temperature. Thermal conductivity increases by a factor of two on addition of 0.5 and 2 wt% of CNTs. In study [120] chemically modified multi-wall carbon nanotubes were used to prepare polydimethylsiloxane
rubber/MWNT composite. The thermal conductivity was increased by around 70% on addition of 2 wt% of CNTs. Choi et al. [125] magnetically aligned the CNTs in the epoxy-SWNT composites and found that thermal conductivity of the composites increased on application of magnetic field. Biercuk et al. [126] studied epoxy-SWNTs composites and found that thermal conductivity increased by 70% at 40 K and 125% at room temperature on addition of 1 wt% unpurified nanotubes. There was little or no improvement in the thermal conductivity of the epoxy-MWNT composite on addition of 0.5 wt% of CNTs [127].

Moisala et al. [127] found decrease in thermal conductivity of the SWNT-epoxy composites on addition of the nanotubes. The reason for decrease was assumed to be the dampening of phonon vibrations in the CNTs by the matrix interaction. The other possible reason was that there must be very large interface resistance to the heat flow associated with poor phonon coupling between stiff nanotubes and soft polymer matrix.

2.3. Ultrasound

In this section, basics about ultrasound and acoustic cavitation phenomena and application of ultrasound in polymeric systems have been discussed.

2.3.1. Ultrasound basics and acoustic cavitation

The range of human hearing varies from 16 Hz to 16 kHz. Ultrasound can be defined as any sound with a frequency above the upper limit of human hearing, i.e. 16 kHz [128]. The upper limit of ultrasonic energy is not clearly defined; however, generally it is accepted as 5 MHz for gases and 500 MHz for solids and liquids.
The use of ultrasound mainly falls in two areas. One is the use of ultrasound at high frequency level, with low power usually in milliwatt range, to determine the structure and conformation of polymers [128]. The effect occurred at physical level and is concerned with the effect of medium on the wave. The other more popular use of high frequency ultrasound in range of 1-10 MHz is in the navigation system such as SONAR and for the non destructive material testing in medical science and in medical techniques such as physiotherapy and scanning.

The other area is the use of ultrasound at low frequency levels in range of 20-500 kHz, with high power upto several hundred watts. It is mainly used for ultrasonic cleaning, plastic welding and in medical science where kidney stones are broken by short bursts in lithorpsy [129].

It has been observed that low frequency ultrasound operated with high power influenced the chemical reactions; however, ultrasound itself does not have any direct action on chemical bond. In most of sonochemical experiments under usual conditions, the acoustic field has an energy density of $10^{-10}$ eV per atom ($1\text{ eV} = 1.602 \times 10^{-19}\text{J}$). As there is no direct interaction exists between wave and matter, we need some kind of indirect phenomena to start or induce the reaction. This indirect phenomena is termed as cavitation. Alternating pressure waves can be characterized by its two main properties: frequency and amplitude. Whenever any liquid media is subjected to an acoustic field, the sonic wave passes through the medium as alternating series of longitudinal compression and refractions causing a variation in acoustic pressure ($P_a$) with time ($t$).

This pressure will be applied to system in addition of ambient hydrostatic pressure which is already acting on the medium. A simplified form of the pressure $P_a$ at any given
point in a medium (solid, liquid or gas) can be described as:

\[ P_a = P_{\text{max}} \sin (2\pi ft + \phi) \]

where \( P_{\text{max}} \) is the pressure amplitude of the wave, \( \phi \) the phase, and \( f \) is the frequency of the pressure wave with \( f \geq 20 \text{ kHz} \) for ultrasound and \( t \) is the time. The intensity of wave, \( I \), can be given by

\[ I = \frac{(P_{\text{max}})^2}{2\rho c} \]

where \( \rho \) is the fluid density and \( c \) the speed of sound in fluid.

Due to attenuation by viscous forces, the intensity varies with distance, \( d \), from the source according to the following:

\[ I = I_o \exp (-2\alpha d) \]

where \( \alpha \) is the absorption coefficient which depends on frequency of sound, density, viscosity and thermal conductivity of medium.

Whenever the ultrasonic wave passes through the liquid media, it compresses and stretches the liquid molecules due to the action of alternating pressure waves of high power ultrasound. The liquid is subjected to tensile stresses during the negative half of the cycle, called as refraction. When refraction wave is powerful enough to overcome the cohesion forces between neighboring molecules, then voids formed (cavitational bubbles) at the weak points in the structure of liquid which grow and collapse with releasing a large amount of energy. By introducing defects in the lattice structure, one can create the cavitation phenomena in the gas free liquids.

The cavitation mechanism consists of mainly three steps: formation, growth and collapse of bubbles as schematically represented in Figure 2.9.
When sound waves with sufficient high intensity applied to a medium, bubbles or cavities are formed during the expansion half of the wave. These bubbles then expand and contract alternately and steadily grow in size in the range of 100-200 $\mu$m where it comes in resonance with applied sound field and undergo rapid expansion and collapse. The intensity experienced by individual bubble is not constant due to surrounding bubbles forming and resonating around them. Due to this some bubbles suddenly reach an unstable size and collapse violently releasing tremendous amount of heat and pressure. It is this tremendous amount of energy release in this process which becomes the source for activation of chemical reactions. During collapse these bubbles mechanically focus the low energy density of the sound field by more than 11 orders of magnitude. Dissolved gases in the liquid media or solvent vapors can enter bubbles and prevent its complete collapse during the refraction cycle.

Noltingk and Neppiras showed on the basis of assumption of adiabatic collapse of bubbles on microsecond scale, the final temperature ($T_f$) and pressure ($P_f$) generated as:

$$T_f = T_o[P_m(\gamma - 1)/P] \quad \text{and} \quad P_f = P[P_m(\gamma - 1)/P]^{\gamma/(\gamma - 1)}$$

where $T_o$ is the bulk temperature of the liquid, $P$ and $P_m$ are pressure before and after the bubble collapse, respectively, and $\gamma$ is the ratio of specific heats of the vapor or any dissolved gases. These empirical relations predict the final temperature and pressure values in the range of 4000-6000K and 1000-2000 bar, respectively, depending on the conditions and liquid media used.
2.3.2. Effects of ultrasound on polymers

Ultrasounds can effects polymers both physically as well as chemically. Acoustic streaming from ultrasound irradiated liquid mainly causes only physical changes such as rapid mixing and bulk heating. Though cavitation is not always required for these changes, they almost always accompany cavitation. The dispersion of filler in base polymer, polymer encapsulating the inorganic particles and modifications of the particle size in polymer powders, welding of thermoplastics are few examples of physical changes induced by ultrasound in the polymer systems. On the other hand, ultrasound also induces structural and chemical changes in the polymer systems as result of cavitation process [131].

Figure 2.9. Ultrasound cavitation bubble growth and collapse [130].
2.3.2.1. Sonochemical synthesis of polymers

Cavitational phenomena occur on application of ultrasound which in turn creates a number of free radicals which can be used to initiate the reaction in a controllable manner. Despite a number of studies to search for new polymerization techniques, vinyl monomers still get polymerized using radical initiation. Although the molecular weight of the radical initiated polymers can be controlled using chain transfer agents, however, there is little control over the stereochemical structure of the resulting polymer [130]. It has been observed in case of AIBN initiated polymerization of styrene that high molecular weight polymer formed on application of ultrasound to the polymerizing media [130]. High ultrasonic intensity was used to polymerize MMA [130] and it was found that no polymerization occurred in absence of initiator. In another study [132], it was found that decomposition of initiator can be accelerated on application of ultrasound results in high yield of polymers.

Ultrasound is quite beneficial in emulsion and solution polymerization processes where it could be used to form and stabilize the suspension and emulsions as sonication is effective way of mixing and dispersion alongside the cleaning of the equipment. In addition the radical produced due to sonication in aqueous phase can be used as initiator and could reduce the use of emulsifiers and initiators [133]. It has been seen that sonication reduces the agglomeration of particles or sticking them to the wall of container and minimized the heat build up in the reactor and prevent the run away reactions. There have been very few reports [134] on the use of ultrasound in condensation polymerization. However, it has been observed that sonication gave higher yield of polymer with higher inherent viscosities in formation of polyformals [134].
2.3.2.2. Ultrasonic degradation of polymers

It has to be noted that most of the work on degradation of polymer under sonication effect was studied in solutions [135,136,137,138,139]. Here the meaning of degradation is simply to mean a lowering of molecular weight. From these earlier works [135,136,137,138], it has been found that degradation process is faster in higher molecular weights and it approaches a limiting value below which no further degradation takes place. As the rate of degradation is molecular weight dependent, so as the polydispersity of the polymer. While studying the effect of ultrasound on polymers in solutions, the changes in solution viscosity was observed. Therefore, it is useful to find out the reason for these changes: whether they are permanent or thixotropic effects. It was observed that there was breakage of macromolecular chains leading to lowering of molecular weight. The breakage of molecular chains under thermal, chemical or photo-degradation process is random whereas in case of ultrasound degradation, chain scission or chain cleavage is more specific. A number of studies [140,141] have shown that cleavage occurs near the centre of the chain and the best fit of data was observed when breakage was distributed in Gaussian manner within ±15% of centre of chain. The precise reason for degradation is still not clear, however, it has been shown that it is due to the cavitation phenomena. If cavitation is suppressed there will be no degradation. Irrespective of the centre of breakage, the end result is formation of macro radicals [142], the existence of which has been confirmed spectroscopically using radical scavengers such as diphenyl picrylhydrazyl (DPPH).
Figure 2.10. Schematic representation of polymer degradation due to cavitation [130].

In absence of radical scavengers, the radicals are free to combine in any manner, disproportionation or combination with the former leading to smaller sized macromolecules while the latter will give a distribution depending on the size of combining fragments.

2.3.2.3. Compatibilization of polymer blends with ultrasound

To improve the compatibility of two incompatible blends has been an area of research since many decades [143]. Ultrasonic energy has been proved to be very useful tool in increasing the interfacial adhesion between two different incompatible and immiscible blends. The prolonged application of ultrasound on the polymer solutions induced the stresses due to cavitation phenomena which results in homolytic cleavage of polymeric chains and results in decrease of molecular weight [144,145]. Ultrasonic energy creates the long chain radicals by breaking the C-C bond which further combined with other long chain radicals from another polymer and leads to formation of copolymer [146].
Hong and Isayev [147] studied the effect of ultrasound on blends of devulcanized ground tire rubber with HDPE. It was found that the blends of HDPE and GRT mixed with twin screw extrusion and later on passed through ultrasonic devulcanization extruder has better mechanical properties (tensile properties and impact properties) than the blend of GRT which was first devulcanized before mixing with HDPE and passing through ultrasonic devulcanized extruder. This is due to better mixing in twin screw extrusion and specific reaction occurring between rubber and plastics phases during devulcanization.

Feng and Isayev [148], studied In-situ compatibilization of PP/EPDM using ultrasound assisted extrusion process. It was observed that the ultrasonic treatment induced the thermo-mechanical degradation and also shows the possibility of increased molecular transport and chemical reaction at the interface. More stable morphology after annealing and improved mechanical properties indicated that ultrasonic energy led to the In-situ compatibilization of the blends.

Oh et al. [149] developed a continuous process for in-situ compatibilization of PP/NR blends. PP/NR blends of various concentrations were prepared using twin screw extruder and passed through specifically designed ultrasound assisted extruder where they were subjected to intense ultrasonic energy. Treated blends shows significant improvement in mechanical properties than the untreated ones. Microscopic studies (SEM, AFM) revealed that domain size in treated blends was smaller than untreated ones. Treated blends show improved interfacial adhesion between PP and NR with creation of thin interfacial layer in treated blends as compared to untreated ones. It is believed that this is due to the formation of in-situ PP/NR copolymer at the interface of two immiscible
blends subjected to ultrasonic treatment.

In another study on PP/PA6 blends [150], ultrasonically treated samples for certain blend ratios shows a significant improvement (around double) in the tensile toughness and impact strength as compared to the untreated one. A competition between degradation and in-situ compatibilization was observed for treated PP/PA6 blends. However, full in-situ compatibilization was not achieved due to lack of selectivity of highly reactive radicals for coupling reactions. It was also observed that during ultrasonic treatment, polymerization and degradation of PA6 polymeric chains occurred simultaneously.

Isayev and Hong [151] were issued a patent in 2003 for developing a continuous ultrasound assisted extrusion process for manufacturing polymers blends and copolymers by ultrasonic treatment. Ultrasonic treatment believed to enhance the interfacial interaction between two immiscible and incompatible polymers with the end products having better mechanical properties as compared to the untreated blends.

Zhang et al. [152] used the ultrasonic energy to functionalize the polyolefins (HDPE, LDPE, PP and EPDM) with maleic anhydride (MAH) in melt state and compared with the method of peroxide initiation. It was observed that the percentage of grafting was increased in case of ultrasonic initiation. However, due to degradation of PP under ultrasonic treatment, the grafting of PP with MAH was not achieved in melt state.

2.3.2.4. Application of ultrasound in filled polymer systems

Most of the time, various kinds of fillers or additives are added to the polymer matrix to improve its different properties and make it suitable to the desired applications.
Ultrasound has found applications in the filled polymer system as it helps in breaking the agglomeration of various fillers and disperses them throughout the polymer matrix. The performance of tires can be significantly improved by using silica filled rubber. However, due to their tendency to get agglomerated and due to their strong polarity it is difficult to achieve the good dispersion of silica filler in rubber which would help in getting the best performance properties of rubber/silica vulcanizates. It has been found that ultrasound helps in dispersion of silica in EPDM rubber as can seen from the decrease in the particle size of silica (0.3µm) in ultrasonically treated samples as compared to untreated one (0.7µm) [153]. Ultrasonically treated samples showed the increase in viscosity and yield stress than the untreated ones. This was due to the increase in surface area of silica which is in contact with the EPDM rubber. At the same time the viscosity and yield stress of samples prepared by ultrasonic extrusion process is higher than the prepared by internal mixer or two roll mill with the silica agglomeration size less in samples prepared with ultrasonic extruder [153]. The ultrasonically treated samples also shows the lowest die swell behavior indicating the reduced elasticity of the mixture due to possibility of EPDM chain degradation on application of ultrasound.

A number of studies [154,155,156] have been done on use of ultrasound in nanocomposite preparations. Nickel-polystyrene composites [154], polyaniline-nanosilica [155], PP-clay [156] and HDPE –clay [157] nanocomposites have been prepared with the aid of high power ultrasound.

Lapshin and Isayev [158] developed a continuous ultrasound assisted extrusion process to prepare PP-clay nanocomposites. It has been observed the ultrasound helps in rapid intercalation and exfoliation of clay in the polymer matrix without any chemical
modification of the matrix. The spacing in clay galleries (d-spacing) was increased from 2.4 nm to 3.5 nm for ultrasonically treated samples (10 μm) obtained at a feed rate of 0.25 g/s. Ultrasonically treated nanocomposites samples shows improved elongation at break and toughness as compared to the untreated ones.

Lapshin and Isayev [159,160] further studied the PP-clay nanocomposites prepared by ultrasound assisted extrusion process using two different methods. They compared two stage method (a co-rotating twin screw extruder followed by single screw extruder attached with ultrasonic die attachment was used to prepare nanocomposites) and single stage method (a single screw extruder having mixing elements and an ultrasonic die attachment was used to prepare nanocomposites) and found that single stage process led to less degradation of the polymer matrix under ultrasound treatment. Effects of various feed rates, mode of feeding and die gap size on the nanocomposites properties were studied. It was observed that flood feeding and smaller gap size helps in higher intercalation of clay. Elongation at break and toughness were further improved for the nanocomposites prepared by single stage process as compared to two stage process.

Swain and Isayev [157,161] used ultrasound assisted extrusion process to prepare HDPE/clay nanocomposites. Ultrasonically treated samples shows improved clay dispersion with the increase in elongation at break, toughness, complex viscosity and storage modulus for nanocomposites at certain clay concentrations and ultrasonic amplitudes. The addition of clay and ultrasonic treatment substantially decreased crystallinity and oxygen permeability of HDPE as compared to the untreated samples. Swain and Isayev [162] also studied PA6/clay nanocomposites prepared using ultrasound assisted extrusion process. The most significant observation was that oxygen
permeability tremendously decreased with increasing the clay concentration.

2.3.2.5. Ultrasonically devulcanization of rubbers

Ultrasonic devulcanization is believed to be due to the same phenomena “cavitation” which leads to degradation of polymeric chains in solution. In devulcanization, cavitation occurs in solid body. The presence of cavitational bubbles in solid polymer has been verified experimentally [163,164,165]. As discussed earlier, cavitation can be induced by presence of voids, cavities, density fluctuations in solid polymers. Whenever ultrasound is applied to rubber in the melt state, during the negative half of pressure cycle, the micro voids expanded and surrounding material experienced tensile stress. During the positive half of pressure cycle, material experiences compression. Due to this pulsating force cavitational bubble expand and contract releasing a large amount of energy which leads to the rupture of intermolecular bonds due to fatigue.

Over the last two decades extensive work has been done by Isayev and co-workers at University of Akron, on the ultrasonic devulcanization of rubber. They have demonstrated that ultrasonic devulcanization is rapid, clean, solvent free and effective technique for recycling and reprocessing the waste tires and other rubber products. The three-dimensional network of crosslinked rubber breakdowns in seconds and the devulcanized rubber can be revulcanized in the same manner and can retain or sometime the better mechanical properties than the virgin rubber.

To understand the ultrasonic devulcanization mechanism a number of experiments have been carried out on various kinds of rubbers including GRT, sulphur cured SBR
rubber/plastic blends, NR, silicone rubber, EPDM rubber. The exact mechanism of ultrasonic devulcanization of rubber is still not clearly understood, partially due to number of competing effects taking place simultaneously. However, it has been shown that devulcanization of rubber using high power ultrasound requires local energy concentration, as uniformly distributed ultrasonic energy among all chemical bonds is not capable of breaking the 3-D network of vulcanized rubber.

It has been observed that in addition to the break up of three-dimensional networks, the ultrasonic devulcanization process also leads to break up of C-C bonds in the main macromolecular chains.

2.4. Conclusions from the literature survey

The exceptional mechanical, thermal and electrical properties of carbon nanotubes along with their light weight make them ideal materials as a reinforcing filler in a polymer matrix. These exceptional properties of carbon nanotubes have stimulated research all over the world to study theoretically and experimentally the preparation and properties of carbon nanotubes based materials and most efforts have been directed towards development of polymer-nanotubes composite. Major application of polymer-carbon nanotubes composites are in the field of aerospace and military due to their light weight and improved mechanical and thermal properties.

There are many methods to prepare CNT and CNF based polymer nanocomposites, however, irrespective of the method of preparation, there are two fundamental challenges associated with translating the unique and exceptional properties of the nanotubes and...
nanofibers to a polymer matrix.

i) The biggest challenge in effective use of CNTs and CNFs is lack of their dispersion in a polymer matrix. Due to the strong Van der Waals forces, the nanotubes and nanofibers get easily aggregated or form bundles during the synthesis process. The existing technologies lack in the ability to break up the bundles of CNTs and CNFs and disperse them in a polymer matrix during the preparation of the composites.

ii) The second is the lack of interfacial interaction between the nanotubes and the polymer matrix. For effective use of nanotubes and nanofibers, the load applied to the polymer matrix should get transferred to the nanotube and nanofibers. Few studies have been done to modify the surface of CNTs and CNFs to improve the interfacial interaction, however, found limited success.

The existing technologies are either not commercially viable or they have negative environmental impacts. There is a clear need to develop a new method which is rapid, clean and commercially viable.
CHAPTER III
EXPERIMENTAL

In this chapter, the materials used in this research work and experimental procedure have been explained in detail. The design of novel ultrasonic extruders and various processing operations for preparation of samples for testing purpose have been discussed.

3.1. Materials

High performance and high temperature thermoplastics polyimide, polyetherether ketone and liquid crystalline polymer were used. Carbon nanotubes and carbon nanofibers were used as the reinforcing filler material. The chosen polyimide was polyetherimide (PEI) made by GE under trade name ULTEM 1000P. The chosen liquid crystalline polymer has marketed by Ticona under trade name Vectra A 950. PEEK under trade name VICTREX 450P made by Victrex Inc. was used.
3.1.1. Polyetherimide (PEI): ULTEM 1000 P, GE

PEI is high temperature high performance thermoplastic resin in powder form. It was made by GE under trade name ULTEM 1000P and was used as received. It is commercially used in fabrication of advanced materials for aerospace applications. ULTEM 1000P is an amorphous polymer with glass transition temperature around 217°C.

3.1.2. Liquid crystalline polymer (LCP)

Vectra is a high performance polymer used for many applications ranging from domestic appliances to multiway electrical connectors, automobile and components in computer hardware. Vectra A 950 was developed by Hoechst Celanese in 1985, and is currently marketed by Ticona. It is wholly aromatic polyester containing 27% HNA and 73% HBA. It has melting temperature of around 275°C.
3.1.3. Polyetheretherketone (PEEK)

PEEK in coarse powder form made by Victrex Inc. under trade name VICTREX 450P was used as received. The multiwalled carbon nanotubes (MWNT) under trade name Baytubes ® C 150 P were provided by Bayer Material Science, and were used as received. The MWNT had an outside mean diameter of ~13 nm and length >1 μm.

These high temperature materials were chosen because of their extensive use in composites for aerospace applications due to their desirable combination of mechanical and thermal properties. They have outstanding dimensional and thermo-oxidative stability with desired processability required for space applications.

3.1.4. Multi-wall carbon nanotubes (MWNT)

Multi-wall carbon nanotubes, regularly entangled grade were obtained from two different sources. The first batch of multi walled carbon nanotubes were provided by Nanostructured and Amorphous Materials Inc., Houston, TX, US. The outside diameter was 10-20 nm whereas the inside diameter was 5-10 nm with the length range of 0.5-200 μm. Multi-wall nanotubes has specific surface area, SSA > 200 m²/g and the bulk density of the nanotubes was 0.04-0.05 g/cm³ whereas true density was ~2.1 g/cm³. The second batch of multi walled carbon nanotubes, Baytubes ® C 150 P was provided by Bayer Materials Science, Pittsburgh, PA. The multi walled carbon nanotubes had a mean outside diameter of ~13 nm and length >1 μm.
3.1.5. Carbon nanofibers (CNFs)

Carbon nanofibers, Pyrograf-III, PR-19-HT grade were obtained from Applied Sciences, Inc., Cedarville, OH, US. They were approximately 70-200 nm in diameter and 50-100 \( \mu \)m in length. These nanofibers were vapor grown and subsequently heated to temperatures up to 3000 °C to increase their electrical conductivity.

3.2. Nanocomposites preparation

Both the polymer resins (PEI) and nanofiller (carbon nanotubes and carbon nanofibers) were in powder form. Polymer was dry mixed with MWNTs and CNFs using a ball mill for 24 hours. The loading of MWNTs was varied from 0 to 10 wt% in case of PEI/MWNT nanocomposites and loading of CNFs was varied from 0 to 20 wt% in case of PEI/CNF nanocomposites. The mixtures were dried for at least 24 hrs at 110°C in vacuum oven prior to processing. The bundles of MWNTs and CNFs were dispersed in the matrix due to the milling effect.

LCP pellets were vacuum dried for at least 24 hrs at 110°C in vacuum oven prior to processing. Vacuum dried LCP pellets were fed to the extruder in the feeding zone using co-rotating twin screw feeder, whereas CNFs were added to the molten LCP stream using a separate precision feeder. The loadings of CNFs were varied from 0 to 20 wt% in the compound.

PEEK pellets were vacuum dried for at least 24 hrs at 110°C in vacuum oven prior to processing. Vacuum dried PEEK pellets were premixed with MWNTs in a plastic bag with manual shaking and the mixture was fed to the extruder in the feeding zone through the hopper.
3.2.1. Extrusion

For processing of the polymer nanocomposites, two different ultrasonic extruder set-up, one single screw extruder with different screw design and second a continuous intermeshing co-rotating twin screw extruder without and with separate feeding mechanism, were used. The details of ultrasonic extrusion process, screw and die design have been discussed in this section.

3.2.1.1. Ultrasonic single screw extruder

Two different ultrasonic single screw extruders having different screw design were used to study the effect of mixing on the properties of the prepared nanocomposites. In the first extruder, the ultrasonic attachment was on the barrel surface and screw was designed in a way that it was extended after the ultrasonic treatment zone. In this design, screw has a distributive melt star mixing (MSM) element after the ultrasonic treatment section. The purpose of this additional mixing element is to uniformly distribute the dispersed bundles of nanofillers in polymer melt due to previously subjected ultrasonic treatment. In the second screw design, the MSM element was replaced with conveying screw flights in order to reduce the breakage of the carbon nanofibers and carbon nanotubes due to intensive shear mixing action.

In both configurations, the screw diameter is 1” with L/D ratio of 33:1. It was built based on a Killion extruder with L/D of 24. The extruder screw had a variable diameter along its length. The total length of the screw was 838 mm. The diameter of the screw was 25.4 mm for the first 624.5 mm, corresponding to the extruder mixing section before the ultrasonic treatment zone. Before the ultrasonic treatment zone, the screw
diameter was enlarged to 38.1 mm till location of the pressure transducer. The length of this section was 60.2 mm. Following this section, the diameter of the extruder screw was reduced to 33.0 mm. This section had no flights in the vicinity of the horns in order to provide the 2.54 mm gap for ultrasonic treatment. The length along this section was 85.1 mm. The diameter of the screw after the ultrasound horns was 25.4 mm. A schematic graphical representation of the ultrasonic extruder is shown in Figure 3.1.

Figure 3.1. Schematic representation of ultrasonic single screw extruder.

In the first design, the extruder screw had Union Carbide (UCM) and melt Star mixing sections along the screw before the ultrasonic treatment zone and another melt Star mixing section at the end of the screw just before the die, as shown in Figure 3.2. The UCM section was 53.8 mm long, while both Melt Star mixing sections were 63.5 mm long. The first melt star mixing section was located 70 mm after the first mixing
section. A converging circular die with exit diameter of 3.0 mm was connected to the extruder. The die diameter converged from 25.4 mm to 3.0 mm along a length of 51.7 mm and after that it maintained at 3.0 mm diameter along a length of 12.7 mm. This screw was used to process and prepare PEI/CNF nanocomposites.

![Diagram of the converging die](image1.jpg)

Figure 3.2. Design of 33:1 screw with two mixing section before the ultrasonic treatment section and a melt star mixing element after it.

In the second screw design, melt star mixing section was replaced with conveying screw flights as discussed earlier to reduce the breakage of carbon nanofibers and carbon nanotubes. This screw, as shown in Figure 3.3, was used to process and prepare PEEK/CNT nanocomposites.

![Diagram of the screw with conveying flights](image2.jpg)

Figure 3.3. Design of 33:1 screw with two mixing section before the ultrasonic treatment section and a conveying screw flights after it.

For ultrasonic treatment, two 6 kW ultrasonic power supplies (2000bdc, Branson, Danbury, CT), were connected to two fan cooled ultrasonic converters (Branson H.P.
101-135-124) to generate ultrasonic waves at a frequency of 20 KHz. Each converter was connected in series to a 1:1 titanium booster (Branson 101-149-096) and a water-cooled titanium horn, which was inserted into the barrel. The tip of the ultrasonic horn was in contact with the molten compound. The amplitude of ultrasound was varied from 5 to 15 \( \mu m \). This allowed us to study the effect of increasing ultrasound power on the dispersion of CNFs in PEI melt.

The barrel surface in the ultrasound treatment zone was streamlined in such a way that the compound melt was forced to flow in gaps between the horns and the screw. This prevented creation of a dead zone in the flow domain.

Cylindrical ultrasound horns of 25.4 mm diameter were used. The horns were provided with curved tips to match the curvature of the barrel surface. The horn tips had a radius of curvature of 18.4 mm. They were precisely aligned with the curvature of the barrel to maintain a constant gap thickness. For all ultrasonic experiments, both the horns were operated simultaneously. The gap opening for the flow of compound in ultrasonic zone was kept at 2.54 mm. Seals made of 40% graphite filled Vespel® were used to prevent the flow of melt along the lateral clearance between the barrel and horn in the ultrasound treatment zone. A pressure transducer of maximum pressure 34.5 MPa (PT435A, Dynisco, Franklin, MA) was mounted on the barrel before the ultrasonic treatment zone. The barrel temperature of the ultrasonic extruder was controlled by several heaters connected to temperature controllers. Three temperature control zones were located on the original extruder within the conveying, compression and metering sections. In the ultrasonic barrel attachment following the original extruder, four additional temperature control zones were made available. Zone 1 was located at the
transition region from the original extruder to the ultrasonic attachment. It had one heater controlled by the shim stock thermocouple. Zone 1 also had a nozzle thermocouple monitoring the melt temperature. Feedback from nozzle type thermocouple was used to control the temperature in zone 2. Zone 2 had one heater located at the end of the mixing section within the ultrasonic treatment zone. Temperature of Zone 3 was controlled using the nozzle type thermocouple. Shim stock thermocouple was used to control the temperature in zone 4, corresponding to the die section.

In compounding, independent process variables are flow rate and gap thickness in the ultrasonic treatment section (which measure the mean residence time in the treatment zone), shear rate (screw speed), temperature and ultrasonic amplitudes. Ultrasonic power consumption and pressure in the treatment zone are dependent process variables. All the independent and dependent process variables were recorded. The single screw extruder is equipped with a laptop computer and the data acquisition system (DI-715-U, Dataq instruments, Akron, OH) based on National Instrument software were used to record the dependent variables.

The ultrasonic power imposed to the polymer melt was controlled by adjusting the amplitude dials on the ultrasonic power supplies. The ultrasonic amplitudes at the tip of horns were calibrated in air, and a plot of ultrasonic amplitude versus amplitude setting is shown in Figure 3.4.
To determine the zero power consumption of the horns, power consumption with no material present under the horn was measured. It is shown below in Table 3.1.

Table 3.1. Zero power consumption of ultrasonic horns in single screw extruder

<table>
<thead>
<tr>
<th>Ultrasonic amplitude</th>
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<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>
3.2.1.2. Ultrasonic twin screw extruder

A commercially available continuous co-rotating intermeshing twin screw micro-extruder (PRISM USA LAB 16, Thermo Electron Corp., UK) was used to prepare PEI/CNT and LCP/CNF nanocomposites. It was modified by addition of ultrasonic treatment sections at the exit of the micro-extruder as shown in Figure 3.5. Ultrasonic treatment section was designed by Todd M. Lewis.

![Figure 3.5. Schematic representation of ultrasonic twin screw extruder.](image)

The intermeshing co-rotating twin screws having a diameter of 16 mm with an L/D = 25, is shown in Figure 3.6. The ultrasonic slit die of 4.5 x 0.677 x 0.157 in³ dimension was designed and connected to the exit of the micro-extruder through a die connector.
Figure 3.6. Design of 25:1 intensive co-rotating screws of the twin screw extruder.

A pair of 800W ultrasonic power supply (Branson Ultrasonics Corp., Model 2000 bdc 40:0.8, Danbury, CT) generated ultrasound at 40 kHz frequency. Each ultrasonic power supply is connected in series to a converter (Branson Ultrasonic Corp., Model no. BUC 116, Danbury, CT), 1:1 booster (Branson Ultrasonics Corp., Model no. 109-041-1P, Danbury, CT) and the water cooled titanium horns which are in direct contact with the polymer melt. Horns were cooled using tap water at room temperature. The horns provide the longitudinal vibrations in the direction perpendicular to the flow direction. Both horns were symmetrically mounted on the slit die and both were operated simultaneously for all ultrasonically treated samples. The ultrasonic horns have square cross section with 19.05 x 19.05 mm² (0.75 x 0.75 in²) tip area. The imposition of high intensity ultrasonic waves on the flowing polymer melt was digitally controlled from the ultrasonic power supplies. The horn tips were calibrated in air for ultrasonic amplitude in range of 0-8 μm. A range of ultrasonic amplitude, varying from 0-6.0 μm was applied to molten compound to study the effect of increasing ultrasonic power on the dispersion of the CNTs in a polymer melt.

The gap size between the horns creates a channel with clearance of 4 mm for flow of polymer melt. 40% by weight graphite filled polyimide (Vespel SP-22) seals were used to prevent the flow of polymer melt along the side of the horn in the ultrasonic treatment zone.
Heating elements were installed on slit die and on the transition part connecting the micro-extruder with the slit die. Temperature controllers and thermocouples were used together with the heating elements to allow die temperature and die connector temperature to go from room temperature to 400 °C during extrusion.

Two pressure transducers (TPT 412-5M-6/18, Dynisco Instruments, Franklin, MA) of maximum pressure of 5000 psi, to measure the melt temperature and pressure, were placed in the slit die zone before and after the ultrasonic treatment zone. The pressure, temperature and power consumption were recorded by data acquisition system (Dataq Instruments, DI-715-U, Akron, OH).

The ultrasonic power imposed on the polymer melt was controlled by adjusting the amplitude dials on the ultrasonic power supplies. The ultrasonic amplitudes at the tip of horns were calibrated in air, and a plot of ultrasonic amplitude versus amplitude setting is shown in Figure 3.7.

![Ultrasonic Amplitude Calibration Curve](image)

Figure 3.7. Calibration curve for ultrasonic horns in twin screw extruder.
To determine the zero power consumption of the horns, power consumption with no material present under the horn was measured. It is shown below in Table 3.2.

Table 3.2. Zero power consumption of ultrasonic horns in twin screw extruder

<table>
<thead>
<tr>
<th>Ultrasonic amplitude</th>
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<th>Bottom</th>
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<tbody>
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<td>32</td>
</tr>
<tr>
<td>6</td>
<td>79</td>
<td>52</td>
</tr>
</tbody>
</table>

For PEI/CNT nanocomposites, premixed dried powder of PEI/CNT was fed through the hopper in the feed zone.

For LCP/CNF nanocomposites, a separate feeder for CNF was designed to feed CNF in the polymer melt. The separate feeder was used to reduce the breakage of the CNF in the shear intensive feed zone. The schematic representation of the micro extruder with separate feeder for LCP pellets and CNF powder is shown in Figure 3.8.

![Figure 3.8. Design of 25:1 intensive co-rotating twin screw extruder with two feeder mechanism.](image)
In compounding, independent process variables are flow rate and gap thickness in the ultrasonic treatment section (which define the mean residence time in the treatment zone), screw speed, temperature and ultrasonic amplitudes. Ultrasonic power consumption and pressure in the treatment zone are dependent process variables. All the independent and dependent process variables will be recorded. The micro extruder is equipped with a laptop computer and the data acquisition system based on National Instrument software. It was used to record the dependent variables.

3.2.2 Moldings

In this section preparation of the samples, for various characterization purposes, using compression and injection molding machines have been discussed.

3.2.2.1 Compression molding

The pellets of extruded nanocomposites are compression molded into discs of 25 mm diameter and 2.2 mm thickness under compression pressure of around 3-5 MPa using the compression molding press (CARVER 4122, Wabash, IN, US) for rheological measurements. The material was placed between heated parallel plates and squeezed and then excess material was removed from the sides to remove and boundary effects. A high temperature mold release agent (Frekote HMT2) was used to spray on the plates and mold and Kapton ® polyimide film was placed between the preheated plates and the mold. Different temperatures were used for different materials according to their processing temperature range for preparing the samples. Pellets were preheated in the mold for three minutes and subsequently squeezed at a force of 1 ton for 2 minutes and
released to remove any trapped air bubbles. The melt was further squeezed at 3 ton for 2 minutes and released and again at 5 ton for four minutes. The mold and hot metal plates were removed from the compression molding press and allowed to cool for 10 minutes. The prepared sample discs were then removed from the mold. The samples for electrical conductivity measurements were also compression molded in a same way as for the rheological samples, using Carver 4122 compression molding press, into discs of 90 mm diameter and 1 mm thickness.

3.2.2.2. Injection molding

A mini-jet piston injection molder (HAAKE, Thermo Electron Corp. Germany) was used to prepare samples for tensile testing measurements. This mini jet piston injection molding machine was used to prepare tensile bars of size (63.5 x 9.53 x 3.34 mm³, ASTM D-638), as this mini-jet require very less amount of material. Material was filled in the heated barrel at different temperature for different materials and allowed to melt for five minutes. The mold was sprayed with high temperature mold release agent (Frekote HMT2) before use. Different injection pressure was used to inject the different materials in the mold. After waiting for 10 seconds, mold was removed from the mini –jet and it was opened to collect the prepared tensile bar sample.

3.3. Characterization

Prepared nanocomposites were characterized using different characterization techniques. In this section, procedures used for the characterization purpose has been discussed.
3.3.1. Rheological measurements

The rheological measurements of CNTs and CNFs based composites can be used to study the effect of ultrasound and CNTs or CNFs loading on the rheological behavior of nanocomposites. It can also be used to determine the state of dispersion of carbon nanotubes and carbon nanofibers in a polymer matrix. Wagener et al. [130] used rheological measurements to determine the extent of delamination of clay platelets stacks in the PBT/clay nanocomposites. The rheological properties of the nanocomposites are studied by using an Advanced Rheometric Expansion System (Model ARES LS, TA Instruments). A 25 mm parallel plate geometry in oscillatory shear mode with dynamic frequency sweep test, with frequency range of 0.03 to 100 s\(^{-1}\), is used at 340°C for PEI/MWNT and PEI/CNF nanocomposites, 280°C for LCP/CNF nanocomposites and 360°C for PEEK/MWNT nanocomposites, for a fixed strain amplitude of 2%. Before zeroing the fixture (the contact between upper and lower plates and set the zero position), the gap size was kept 3 mm, the sample is inserted slowly between the plates and pushed it to the centre of the plates. The gap between the plates reduced slowly to compress the material properly so that it touches the plates. Excess material from the plate sides is removed using brass tools to avoid the boundary effects and the test was started. The complex viscosity, storage modulus, loss modulus and loss tangent as a function of frequency was measured.
3.3.2. Mechanical properties

Fillers are added to polymer matrix to improve its mechanical properties (stiffness, strength, etc.) for desired applications. Recently, due to its exceptional mechanical properties carbon nanotubes are gaining popularity as a reinforcing agent.

3.3.2.1. Tensile test

Tensile measurements were done to study the effect of carbon nanotubes and carbon nanofibers loading on the mechanical properties of polymer. Tensile measurements on injection molded samples were carried out using an Instron test machine (Model 5567, Instron Corp., Canton, MA, US). Tests were carried out on minimum five samples according to ASTM D 638 test method at cross head speed of 5 mm/min using a 30 kN load cell and extensometer for PEI/CNF, PEI/MWNT nanocomposites and 10 kN load cell for LCP/CNF and PEEK/MWNT nanocomposites. All the results were the average of minimum five measurements.

From the recorded engineering stress-strain curves, the tensile strength, Young’s modulus, elongation at break and toughness were determined. The engineering tensile strength is defined as

$$\sigma = \frac{F}{A_0}$$

where F is the instantaneous force and A_0 is the cross-sectional area of the unstrained sample. The elongation \( \varepsilon \) is defined as

$$\varepsilon (\%) = \left( \frac{l-l_0}{l_0} \right) \times 100$$

where \( l \) is the observed length of the extended specimen and \( l_0 \) is the extensometer gauge length.
3.3.3 Electrical resistivity

Fiber-reinforced composites are popularly used in aerospace applications due to their light weight and improved mechanical properties. However, there are some problems associated with conventional fiber-reinforced composites such as an accumulation of electrostatic charge on their surface which can cause the local heating resulting in the catastrophic failure of the surrounding materials. For these applications some electrical conductivity is required to dissipate this accumulated static charge and also some kind of EMI protection. Carbon nanotubes and carbon nanofibers being highly conductive have been gaining popularity as conductive fillers. A Keithley electrometer (Model 6517A, Keithley Instruments, Cleveland, OH) equipped with an 8009 test fixtures was used to measure the volume and surface resistivity of the prepared nanocomposites in accordance with the ASTM D 257 method. The prepared nanocomposites were compression molded into disc shape having 90 mm diameter and 1mm thickness.

3.3.4 Morphological studies

In this section experimental procedure to investigate the morphological behavior of prepared polymer nanocomposites using scanning electron microscope and optical microscope has been discussed.

3.3.4.1 Scanning electron microscopy (SEM)

The biggest challenge in effective use of CNTs and CNFs is their lack of dispersion in a polymer matrix. During synthesis of CNTs and CNFs, nanotubes and nanofibers easily aggregate or form bundles due to strong intertube Van der Waals
attraction and hence limit the effective use of their exceptional properties obtained at the individual nanotube or nanofiber level and affect the final properties of the nanocomposites. Hence it becomes crucial to investigate and quantify the dispersion of nanotubes and nanofibers which can be achieved by visualizing nanotube or nanofiber themselves. HRSEM is one of the most popular techniques to study the state of dispersion of nanotubes and nanofibers in a polymer matrix. Surface morphology and dispersion of CNTs and CNFs were investigated on cryofractures injection molded bar and compression molded discs samples using a field emission high resolution scanning electron microscope (Model JEOL JSM-7401 F, JEOL, Peabody, MA) for PEI/MWNT and PEEK/MWNT nanocomposites and scanning electron microscope (Hitachi S-2150 SEM at a voltage of 20kV) for PEI/CNF and LCP/CNF nanocomposites. Before the image process start, all samples for morphological study was mounted on the aluminum sample holders with double sided conductive copper tape. In order to increase the conductivity along the sample and to provide more secure mounting on the sample was covered at the opposite edges with two thin strips of single sided copper tape. The samples were sputter coated with silver coating of thickness 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 mA for 60 s.
3.3.4.2 Optical microscopy

Optical microscope was used to study the macro size dispersion and distribution of nanofiller in a large scale at low magnification (x50-100). For optical microscopy study, specimens were prepared using a microtome (MS1B, microstar Technologies) at room temperature. Thin sections with a thickness of 0.5-1 μm were cut and collected on a glass slide to be analyzed under the optical microscope.

3.3.5 Thermal studies

Carbon nanotubes and carbon nanofibers due to their high thermal stability even at very high temperatures are used to enhance the thermal stability of a polymer matrix. The effect of CNTs and CNFs addition on the thermal stability of a polymer matrix was studied using Dupont 951 Thermogravimetric Analysis (TGA 2050, TA instruments, New Castle, DE, US) at heating rate of 20 °C per minute, from 30 °C to 900 °C under nitrogen atmosphere. Each time about 12-20 mg of sample size was used.

The effect of CNTs loading on the melting behavior and on the crystallinity of the polymer matrix was studied using a differential scanning calorimeter (DSC, TA instrument). The experiments were run at a heating rate of 10°C/min from room temperature to 370°C under N₂ atmosphere. Between 5-7 mg of sample cramped in an aluminum hermetic pan was used in each run. Two consecutive heating runs were performed to eliminate any thermal history. Between the two heating runs, samples were cooled at controlled heating rate of 10°C/min.
CHAPTER IV

ULTRASOUND ASSISTED SINGLE SCREW EXTRUSION PROCESS FOR
DISPERSION OF CARBON NANOFIBERS IN POLYETHERIMIDE POLYMER
MATRIX

The present chapter describes preparation of PEI/CNF nanocomposites obtained by means of an extrusion process in a novel ultrasonic single screw extruder. Mechanical, electrical, and thermal properties and rheological and morphological behavior of the obtained nanocomposites were studied.

4.1. Introduction

Recently, polymers containing CNFs have gained considerable attention both in academia and industry due to their superior mechanical, electrical and thermal properties as compared to conventional fiber-reinforced composites and are suitable for a wide variety of potential applications [180]. Among them, PEI/CNF nanocomposites have been studied because polyimide is one of very highly thermally stable polymer and is one of the most reliable thermoplastic polymers for use in high temperature environment [181]. The exceptional electrical, mechanical and thermal properties of CNFs along with their light weight positioned them for electronic structures, electro-statically dissipative materials, polymer nanocomposites and biological systems [180]. The CNF’s are
produced by vapor grown carbon method, based on the catalytic decomposition of hydrocarbons in the vapor phase at 500-1500°C [182]. However, as result of manufacturing process, CNFs are easily aggregated and bundle together or entangled due to strong interfiber attraction which is the main obstacle for their use in many applications [183]. Currently, the biggest challenge for the effective use of CNFs is the lack of their dispersion in the polymer matrix.

The commonly used methods to disperse CNFs are mechanical, chemical and plasma treatment [184,185,186]. Among these methods ultrasonication of CNFs in solutions for a prolonged time (minutes and hours) is one of the most commonly used methods for their dispersion [187]. This is a batch process that is typically carried out in an ultrasonic bath. However, the prolonged ultrasonication introduces defects in CNFs by shortening them and hence resulting in the reduced aspect ratio which is responsible for many of their attractive properties [188]. Also, melt processing of the high viscosity polymer/CNF mixtures is utilized using high shear mixing in extruder [184,189,190,191,192,193,194] and internal mixer [184,195,196,197,198]. These methods have advantages as they are solvent free processes. Plasma coating is also used to enhance the dispersion of the CNFs in the polymer matrix [186]. In-situ polymerization is also one of the methods used to keep bundles of CNFs dispersed in the polymer matrix [199]. As reviewed in [43], some other methods have been attempted for enhancing dispersion, like in-situ production of CNFs, but found a limited success.

From the above discussion, there is a clear need to develop a new method which is rapid, clean and commercially viable.
Recently, use of high power ultrasound in extrusion process was proposed to disperse nanosize fillers in polymers at the residence time of the ultrasonic treatment of a few seconds. In particular, it was found that ultrasound assists in better silica filler dispersion in rubber [153] and nanoclay intercalation and exfoliation in polypropylene [158,160] and polyethylene [157] matrices in an extrusion process.

The present study described the preparation of PEI/CNFs nanocomposites prepared by means of an extrusion process in a novel ultrasonic single screw extruder. Effect of processing parameters and various ultrasonic amplitudes on the state of dispersion of CNFs in PEI matrix and the resultant effect on their mechanical, electrical and thermal properties were discussed.

4.2. Experimental

In this section, ultrasonic extruder, experimental procedure to prepare polymer nanocomposites, processing conditions and characterization methods have been discussed.

4.2.1. Ultrasonic extruder

A single screw ultrasonic compounding extruder having a screw diameter of 25.4 mm and L/D ratio of 33:1 was used. It was built based on a Killion extruder with L/D of 24. Three mixing sections and the ultrasound treatment zone were made along the barrel. Two mixing sections were before the ultrasonic treatment zone and one mixing section after the ultrasonic treatment zone. A schematic drawing of the ultrasound extruder is shown in Figure 3.1.
The amplitude of ultrasound was varied from 5 to 10 μm. Ultrasonic horns were cooled using tap water at room temperature. This allowed us to study the effect of increasing ultrasound power on the dispersion of CNFs in PEI melt.

The barrel surface in the ultrasound treatment zone was streamlined in such a way that the compound melt was forced to flow in gaps between the horns and the screw. This prevented creation of a dead zone in the flow domain. The mean residence time in the ultrasonic treatment zone was 7 s at a flow rate of 15 g/min.

The gap opening for the flow of compound in ultrasonic zone was kept at 2.54 mm. A pressure transducer was mounted on the barrel before the ultrasonic treatment zone, as shown in Figure 3.1. The details of ultrasonic extruder have been presented in section 3.2.1.1.

4.2.2. Preparation of nanocomposites

The PEI powder, prior to processing, was premixed with various CNF contents (3, 5, 8, 11, 15, and 20 wt%) using ball milling process for 24 hrs. The premixed powder was subsequently dried in a vacuum oven at 120 °C for a minimum of 24 hrs prior to processing. The premixed PEI/CNF nanocomposites of various CNF contents were processed using a single screw ultrasonic extruder with and without ultrasonic treatment. The ultrasonic treatment was carried out at amplitudes of 5, 7.5 and 10 μm to study the effect of increasing ultrasonic power on the state of dispersion of CNF in a polymer melt. Pure PEI, without any CNF content, was also processed using the same procedure, to produce a control sample. The extrusion temperature was varied from 320 to 340°C from the feed zone to the die. Different screw speed of 30, 60 and 100 rpm was chosen to study
the effect of shear rate on state of dispersion of CNFs. Flow rate of 15 g/min was chosen to prepare the nanocomposites. Extrudates were quenched at a room temperature in water bath and then pelletized.

4.2.3. Characterization

For rheological measurements an Advanced Rheometric Expansion System (ARES, Rheometrics Scientific) was used in the dynamic mode with parallel fixtures of diameter of 25 mm and a gap of 2 mm. The complex viscosity, loss tangent, storage, $G'$, and loss, $G''$, moduli were obtained at a fixed strain of 2% in dynamic frequency sweep experiments as a function of an angular frequency, $\omega$, ranging from 0.1 to 100 rad/s at a 340°C temperature. The dynamic measurements provide information about nanocomposites in their original state without destroying their structure and require short testing time as compared to the steady-state conditions that take longer testing time and also could destroy the structure of the nanocomposites. Data acquisition was carried out with the aid of a microcomputer interfaced with the rheometer. All experiments were conducted under nitrogen environment to prevent oxidation of the samples.

The volume and surface resistivity of an insulator can be measured by using a power source of known voltage by measuring the resulting current, and calculating the resistivity according to the Ohm’s law. The volume resistivity is calculated from the value of resistance and the physical dimensions of the test sample. Disks with a thickness of 1 mm and a diameter of 60 mm were prepared by compression molding. An electrometer, Keithley Instrument Model No.6517A, attached to an 8009 test fixture was used to measure the volume and surface resistivity of the sample in accordance with
ASTM D257 method. A constant voltage of 10V was applied for 60 s in the test. It should be noted that the application of higher voltages led to different values of resistivity (conductivity). Moreover, at high loadings of CNFs, resistivity readings became unstable and electrometer got tripped off.

Specimens for tensile tests according to ASTM D638 were prepared by a HAAKE mini-jet piston injection molding machine at a melt temperature of 340°C and a mold temperature of 120°C. Pellets of a total weight of 6 g were loaded into the cylinder and melted for 180 s to make 2 g dumbbell shaped samples. The injection pressure was 65 MPa in each case. Instron tensile testing machine (Model 5567, Instron Corp.) was used to carry out tensile tests at room temperature. The ASTM D638 method was followed. Samples were clamped in the jaws of the testing machine and put under tension at a crosshead speed of 5 mm/min. A 30 kN load cell was used to register the force values against displacement. An extensometer with 7.62 mm gauge length was used to record the displacement data. For each condition, a minimum of 5 specimens were tested. The yield stress, yield strain, stress at break, strain at break, Young’s modulus and toughness (area under the stress-strain curve) were measured. The average and standard deviation of these values were calculated.

The quality of the mixing is an important parameter to quantify dispersion of CNFs. Therefore, microscopic analysis was conducted by means of a scanning electron microscopy (SEM) to identify the level of dispersion of CNFs in melt at different processing conditions. The morphologies of samples were observed using Hitachi S-2150 SEM at 20kV. For this purpose, injection and compression molded specimens were
prepared. The specimens were cold fractured in liquid nitrogen. The fractured surfaces were sputter coated with silver.

To determine the CNFs aspect ratio in the composites, selected PEI/CNF nanocomposites were dissolved in N-methyl-2-pyrrolidinone solvent. The solution was filtered through a poly(tetrafluoroethylene) membrane disk filter (Gelman, 0.2 mm pore size) to separate CNFs. Afterwards, CNFs were washed several times with N-methyl-2-pyrrolidinone to completely remove the residual polymer. CNFs removed in this process were observed using the SEM.

4.3. Results and discussion

The results obtained after the characterization of the PEI/CNFs nanocomposites have been discussed in detail in this section.

4.3.1. Process characteristics

The entrance pressure and temperature of the ultrasonic treatment zone as a function of ultrasonic amplitude is presented in Figure 4.1. It is seen that the overall level of the entrance pressure during this process is very low (below 1 MPa). The entrance pressure of the ultrasonic treatment zone is substantially reduced as the ultrasonic amplitude is increased leading to improved processability of melts. This decrease of die pressure can be explained as a result of acoustic cavitation leading to permanent and thixotropic changes in the melt [200] and thixotropic changes recovered after ultrasonic treatment. The degradation of polymer chains during ultrasonic treatment may become more pronounced in the presence of CNFs. This may lead to permanent reduction of
matrix viscosity, as indicated by the observed slight reduction of viscosity of pure PEI after the treatment as can be seen in Figure 4.5. In addition, ultrasonic waves may also enhance shear thinning behavior of the melt leading to a temporary decrease of melt viscosity that recovers after treatment (thixotropic effect). It is also noted from Figure 4.1 that the temperature at the ultrasonic treatment zone increases with increasing ultrasonic amplitude. This behavior can be attributed to the effect of energy dissipation of the ultrasonic wave in a viscoelastic melt causing melt temperature rise by conversion of mechanical ultrasonic energy to thermal energy. In addition to heating effect, reduced friction of polymer melt along horn surfaces due to ultrasonic vibrations may also lead to decrease in die pressure.

It is also evident from Figure 4.1 that the pressure increases with increasing CNF concentration. It is interesting to note that the pressure is increased linearly up to 8 wt% CNF loading. This linear increase of pressure slows down at 11 wt% (for the purpose of clarity these data were not shown in Fig. 4.1) and 15 wt% loading. Then a significant increase of pressure was observed at 20 wt% CNF content, suggesting a possibility of formation of interconnected network of CNFs. Such a behavior can be attributed to the presence of the rheological percolation threshold in the melt between 15 and 20 wt% loading of CNFs under ultrasonic treatment.

Ultrasonic power consumption during ultrasonic treatment of PEI containing 3 wt% and 11 wt% of CNFs as a function of ultrasonic amplitude at different screw rotation speeds is shown in Figure 4.2. The measured power consumption is the total power that is consumed due to oscillations of the horn and propagation of ultrasonic waves in the polymer melt leading to heat dissipation. Unfortunately, the power loss due to the heat
dissipation and power used by ultrasonic wave propagation through the melt cannot be separated. The only energy losses that can be measured are the initial power consumption when horn works without any loading. The results presented in Figure 4.2 are obtained after subtracting of these losses from total power consumption.

Figure 4.1. Entrance die pressure in front of ultrasonic treatment zone and melt temperature in the ultrasonic treatment zone as a function of amplitude at various CNF concentrations at 60 rpm.

It is seen that the power consumption increases with increasing ultrasonic amplitude. The power consumption is also seen to continuously increase as screw rotation speed decreases. This is due to an increase of the pressure at lower rotation speeds. The latter is due to the fact that a decrease of the screw rotation speed leads to a lower shear rate in the melt causing an increase of its viscosity.

The ultrasonic power consumption during ultrasonic treatment of PEI at various CNF concentrations as a function of ultrasonic amplitude is shown in Figure 4.3. This set of data is obtained at 60 rpm. On increasing the CNF content from 0 to 20 wt%, an increase of the power consumption was observed with an increase of amplitude. An
increase of power consumption with CNF concentration is evidently due to the higher energy required to disperse CNFs in melt as have seen in case of PP-clay composites [158].

Figure 4.2. Ultrasonic power consumption as a function of ultrasonic amplitude at flow rate of 15 g/min and various rpm for (a) 3 wt% CNF and (b) 11 wt% CNF.
4.3.2. Rheology

Figure 4.4 shows the dependence of complex viscosity at 0.2 s⁻¹ frequency on ultrasonic amplitude at various screw rotation speeds for PEI containing 3 wt% of CNFs. It is observed that the complex viscosity of the composites processed at rotation speeds of 30 rpm and 60 rpm reach their maximum values at ultrasonic amplitude of 10 µm. The presence of the viscosity maximum is a result of a competition between the viscosity increase due to the increased surface area with better dispersion of CNFs at higher ultrasonic amplitude and the viscosity decrease due to a possible breakup of molecular chains by high power ultrasound during melt extrusion [153]. The viscosity of material at rotation speed of 100 rpm decreases with increasing ultrasonic amplitude and does not show a maximum. This is because the degradation of polymer is apparently dominates at
the higher rotation speed leading to the viscosity reduction. In addition, the observed viscosity reduction is due to the breakage of CNFs which is more pronounced at the higher rotational speed, as indicated by the microscopic analysis which can be seen below from Figure 4.14. As shown below, viscosity of ultrasonically treated pure PEI is reduced only slightly. However, due to the presence of CNFs and multiple interfaces in nanocomposites, it is expected that PEI matrix degradation would be more enhanced.

![Figure 4.4](image.png)

Figure 4.4. Complex viscosity at frequency of 0.2 s⁻¹ as a function of ultrasonic amplitude for 3 wt% PEI/CNF nanocomposites obtained at various screw rpm.

The complex viscosity as a function of frequency for the untreated and ultrasonically treated PEI/CNF nanocomposites containing 0 to 20 wt% CNFs is shown in Figure 4.5. It was observed that there is tremendous increase in complex viscosity of PEI/CNF nanocomposites with the increase of CNFs content. It is clearly observed that
viscosity of ultrasonically treated nanocomposites samples is consistently higher compared to that of the untreated ones. This increase in complex viscosity due to ultrasonic treatment is attributed to an improved dispersion of the CNFs in polymer matrix, as indicated by the SEM studies reported below in section 4.3.4. It has also been observed that viscosity of virgin PEI slightly decreases with ultrasonic treatment. This is due to a possible breakup of macromolecular chains under the action of ultrasonic amplitude. The viscosity of nanocomposites obtained at an amplitude of 10 μm shows slightly lower values than those at amplitudes of 5 μm and 7.5 μm. This is not only because of the thermo-mechanical degradation of polymer, but also because of a possibility of breakage of carbon nanofibers during ultrasonic treatment. This explanation is supported by experimental results of the length of CNFs extracted from nanocomposites, as shown below in Figure 4.11. This observation is also in agreement with values of the Young’s modulus of nanocomposites containing 11 wt% of CNFs, also indicated below (see Figure 4.18). As seen in Figure 4.5, it was observed that for low loadings of CNFs, a Newtonian plateau, similar to that of virgin PEI occurs in the low frequency region. Complex viscosity of the nanocomposites exhibits more frequency dependence at low frequencies (in the range from 0.1 to 1 s⁻¹) as the CNFs concentration is increased. Also, such a strong frequency dependence and, therefore, shear thinning is especially pronounced for ultrasonically treated nanocomposites at concentrations of 15 and 20 wt%. This strong shear thinning behavior can be attributed to a greater degree of polymer-CNF interactions and due to better dispersion of the CNFs and formation of continuous CNFs network. Also, a steep rise in viscosity for treated nanocomposites at concentration above 15 wt% is an indication of rheological percolation threshold. This
can be better understood by plotting complex viscosity vs. CNFs concentration at a
frequency of 0.2 s\(^{-1}\) as shown in Figure 4.6. From this figure it is difficult to judge the
presence of rheological percolation threshold for untreated nanocomposites at the
concentration range studied. Possibly, the percolation threshold lies at higher
concentration. Therefore, this suggests that ultrasonic treatment leads to the reduction of
the rheological percolation threshold in nanocomposites. It means that the viscosity curve
is a possible tool for identifying the presence of the percolation threshold for these
composites, as earlier shown in [198]. This percolation threshold is evidently created by a
better dispersion of CNFs by ultrasonic treatment.

Figure 4.5. Complex viscosity as a function of frequency for untreated and ultrasonically
treated PEI/CNF nanocomposites containing 0 to 20 wt% CNFs obtained at various
ultrasonic amplitudes at 60 rpm.
Figure 4.6. Complex viscosity at a frequency of 0.2 s\(^{-1}\) as a function of CNF concentration for untreated and ultrasonically treated nanocomposites obtained at various ultrasonic amplitudes at 60 rpm.

The improved dispersion of CNFs due to ultrasonic treatment can further be substantiated by an increase in the storage and loss moduli for the treated nanocomposites (Figure 4.7). Both the storage and loss moduli increase with ultrasonic amplitude and CNFs content with more effect seen in G’ than in G”. The value of G’ also increases with frequency. However, the effect is more pronounced at low frequencies, as compared to high frequencies. Based on these data one can conclude that nanocomposites at CNF concentrations above 15 wt% exhibit a dramatic increase in the storage modulus with ultrasonic treatment, indicating an existence of the rheological percolation threshold. Furthermore, the effect of CNFs and ultrasonic treatment on the structural differences between polymer and nanocomposites can be seen from the logarithmic plot of G’ vs. G” (Figure 4.8), which is similar to so-called Cole-Cole plot [201]. Such a plot was used by
Figure 4.7. Storage $G'$ (a) and loss $G''$ (b) moduli as a function of frequency for untreated and ultrasonically treated PEI/CNF nanocomposites containing 0 to 20 wt% CNF obtained at various ultrasonic amplitudes at 60 rpm.
many researchers [202,203] to study the dynamic properties of materials in the melt state. From Figure 4.8 it is clear that at given $G''$ value, $G'$ increases more significantly with CNF content. This is in accordance with behavior reported for PC/MWNT nanocomposites [76]. Clearly, ultrasonically treated composites show increase in $G'$ at given $G''$ for all CNFs loadings indicating a stronger network structure due to the better dispersion of CNFs in a polymer matrix.

Figure 4.8. Storage modulus versus loss modulus for ultrasonically treated and untreated nanocomposites at different carbon nanofibers concentrations.

The effect of CNFs loadings and the ultrasonic treatment on the damping characteristics of PEI/CNF nanocomposites was explained by plotting $\tan \delta$ versus frequency for various CNFs loadings as can be seen from Figure 4.9. It was observed that $\tan \delta$ decreased with an increase of CNFs content. It was also observed that ultrasonically...
treated nanocomposites shows significantly lower tanδ than those untreated ones indicating the improved dispersion of CNFs due to the application of ultrasound. Also, the curve becomes more flat in the low frequency region indicating that CNFs affect the relaxation behavior of polymer chains such that the storage modulus increases more with ultrasonic treatment than the loss modulus (see Figure 4.7). This results in lowering tan δ of nanocomposites.

![Figure 4.9](image-url)

Figure 4.9. Tan δ as a function of frequency for untreated and ultrasonically treated PEI/CNF nanocomposites containing 0 to 20 wt% CNFs obtained at various ultrasonic amplitudes at 60 rpm.

4.3.3. Electrical and thermal conductivity

The electrical conductivity of composites is generally dependent on the carbon fiber volume fraction. At low fiber loadings, the conductivity of the composite is still very close to that of the pure insulating polymer matrix. At some critical loading, corresponding to the electrical percolation threshold, the conductivity increases by
several orders of magnitude with very little increase in the fiber amount. At the percolation threshold, fibers begin to form continuous conductive networks throughout the composite and conductivity increases sharply. After this drastic increase, the conductivity once again levels off and assumes values close to that of the conductive particles.

Figure 4.10 shows electrical volume resistivity of nanocomposites as a function of CNF concentration. For ultrasonically treated composites, the resistivity at the 15 wt% of CNFs loading dropped by about 2 orders of magnitude. At the same time, a similar drop in the resistivity of composite extruded without ultrasonic treatment occurs at 17 wt% CNF loading. Evidently, these concentrations correspond to the onset of percolation with and without ultrasonic treatment. Volume resistivity is dependent not only on fiber concentration, but also on fiber length and dispersion. Evidently, high power ultrasonic treatment leads to better interconnected network of CNFs with improved dispersion of CNF even with reduction in aspect ratio of CNFs. Both these effects are indicated by the results shown below. Clearly, the ultrasonic amplitude has an effect on the electrical percolation threshold. The results for electrical percolation threshold of treated nanocomposites are in agreement with rheological percolation threshold. It was observed that both fall in between the 15 and 20 wt % of CNFs concentration. In earlier study on PP/CNF [197,198], prepared by melt processing, both rheological and electrical percolation threshold lies in same range of 10 and 20 wt% of CNFs loadings. In another study on PC/MWNT [76] nanocomposites, prepared by melt processing, it was observed that both rheological and electrical percolation lies in the same range of 1 and 2wt% of MWNTs loading. However, in some other studies [113,115] concentrations corresponding
to rheological and electrical percolation threshold have found to be different, with electrical percolation values being higher than the rheological one.

The aspect ratio of the CNFs also plays an important role on the concentration of fibers necessary to achieve percolation. It is seen from Figure 4.10, that composites prepared by ball milling show percolation threshold at much lower CNF concentration (4 wt %). This is due the presence of long and aggregated fibers in these composites.

![Graph of Volume resistivity vs. CNF concentration](image)

Figure 4.10. Volume resistivity of PEI/CNF nanocomposites versus CNF concentration for various ultrasonic amplitude obtained at 60 rpm.

Surface resistivity of the prepared nanocomposites as a function of CNF concentration is shown in Figure 4.11. It can be seen that surface resistivity follows the same trend as that of the volume resistivity (Figure 4.10). A sharp decrease in surface resistivity was observed between 15 and 20 wt% of CNFs loading. Surface resistivity of
nanocomposites decreased by more than four orders of magnitude on addition of 20 wt% of CNFs. It was also observed that decrease in surface resistivity was less as compared to the volume resistivity as can be seen from Figure 4.10 where volume resistivity decreased by more than 5 orders of magnitude on addition of 20 wt% of CNFs. This sharp decrease in surface resistivity suggests the existence of electrical percolation threshold between 15 and 20 wt% of CNFs loading. It can also be seen that ultrasonically treated samples shows lower surface resistivity as compared to the untreated samples. For the same CNFs loading level at 15 wt%, ultrasonically treated samples shows more than an order of magnitude decrease in surface resistivity as compared to the untreated ones. This indicates that high power ultrasonic treatment leads to better dispersed interconnected network of CNFs.

Figure 4.11. Surface resistivity of PEI/CNF nanocomposites versus CNF concentration for various ultrasonic amplitude obtained at 60 rpm.
Figure 4.12 shows the thermal conductivity of PEI/CNF nanocomposites as a function of CNF concentration. It was observed that the thermal conductivity of nanocomposites increases from 0.23 to 0.52 W/mK as the CNF concentration increases from 5 wt% to 20 wt%. The thermal conductivity of CNFs is 20 W/mK, as reported by Applied Sciences, Inc. Although the thermal conductivity increases by more than two times with the addition of the CNFs, the prepared nanocomposites do not show a percolation threshold based on these measurements. This is because heat transport mainly occurs through the polymer matrix at fiber concentrations used. It is interesting to note that the thermal conductivity of 20 wt% PEI/CNF composites increases with increasing ultrasonic amplitude. This observation could be a result of the continuously improved dispersion of CNFs by increasing ultrasonic power consumption.

![Graph showing thermal conductivity of PEI/CNF nanocomposites vs. CNF concentration for various ultrasonic amplitudes](image)

Figure 4.12. Thermal conductivity of PEI/CNF nanocomposites versus CNF concentration for various ultrasonic amplitude obtained at 60 rpm.
4.3.4. Morphology

Figure 4.13 (a) shows SEM micrographs of CNFs as received. This figure indicates the presence of bundles of CNFs. As received CNFs have large aspect ratios (> 100) with diameters varying from 70 nm to 200 nm. Size of CNF bundles is seen to be in the range from 10 \( \mu \)m to 50 \( \mu \)m. Some catalyst impurity and amorphous carbon may also be present in these samples [198]. After ball milling of CNFs with PEI powder and subsequent molding, the CNF bundles still remain in molding, as shown in Figure 4.13 (b). Therefore, a poorly dispersed mixture is obtained. Interwoven bundles and aggregates of CNFs up to 50 \( \mu \)m in size were observed in SEM micrographs (Figure 4.13 b). These bundles of entangled CNFs make the dispersion of the fibers into the polymer matrix more difficult. However, as seen in Figure 4.10, these aggregates help to induce electrical conductivity due to easier charge transfer along bundles of CNFs, due to longer fiber length and better interconnected fiber network [204]. Possibly, if the extrusion process can be carried out without a breakage of CNFs along with improved dispersion, one would observe a lower electrical percolation threshold.

To evaluate the dispersion of CNFs in a PEI matrix, examination of the surface of injection molded samples broken in the liquid nitrogen was carried out by SEM. In particular, Figure 4.14 shows the SEM micrographs of fractured surface of the 3 wt% PEI/CNF nanocomposites before (a) and after (b) ultrasonic treatment at amplitude of 10 \( \mu \)m. It cannot be visually verified at this concentration if CNFs are better dispersed in PEI matrix after ultrasonic treatment since the CNFs at this low concentration are already dispersed very well throughout the samples even without ultrasonic treatment. Free individual fibers are clearly seen from SEM micrographs. They are apparently not wetted.
Figure 4.13. SEM micrographs of CNFs as received (a) and cryofractured surface of nanocomposite containing 3 wt% CNFs prepared by ball mill milling and injection molding (b).

Figure 4.14. SEM micrographs of cryofractured surface of injection molding of 3 wt% PEI/CNF nanocomposites obtained without (a) and with (b) ultrasonic treatment at an amplitude of 10 μm at 60 rpm.
by the polymer due to poor adhesion and fiber-matrix interaction. This observation is in agreement with results on the strength of PEI/CNF nanocomposites which do not vary with increasing CNFs loading, as shown in section 4.3.5.

Figures 4.15 and 4.16 depict SEM micrographs of fractured surfaces of the 15 wt% and 20 wt% PEI/CNF nanocomposites without (a) and with (b) ultrasonic treatment at ultrasonic amplitude of 10 μm. There is a higher possibility of overlapping of fibers throughout the PEI matrix at 20 wt% CNF composition compared to 15 wt % of CNF content. The CNFs are clustered in the matrix with about 2~5 μm diameter in untreated composites and resin rich part without CNFs is also evident, as indicated by arrows. There is a sharp contrast between the resin clumps without and with fibers. In the treated nanocomposites, CNFs are not clustered but still in contact with each other. The latter could be the reason why the percolation threshold is achieved at a concentration of about 15 wt% in ultrasonically treated nanocomposites.

Figure 4.17 shows the SEM micrographs of CNFs extracted from untreated 11 wt% PEI/CNF nanocomposites at 60 rpm. As seen from this figure, fiber length is significantly reduced from the initial length of 30~100 μm reported by Applied Sciences, Inc. to 2 ~10 μm. The degradation of fiber length is not only attributed to the high shear in extruder [43] but also to the action of high power ultrasound. In particular, Figure 4.18 shows the length distribution of CNFs in nanocomposites obtained without and with ultrasonic treatment, respectively. In Figure 4.18(a), effect of screw rotation speed is presented in the absence of ultrasound. With screw rotation speed, the longer fibers are broken. This is caused by higher stresses acting at high screw rotation speed. The average
Figure 4.15. SEM micrographs of cryofractured surface of injection molding of 15 wt% PEI/CNF nanocomposites obtained without (a) and with (b) ultrasonic treatment at an amplitude of 10 μm at 60 rpm.

Figure 4.16. SEM micrographs of cryofractured surface of injection molding of 20 wt% PEI/CNF nanocomposites obtained without (a) and with (b) ultrasonic treatment at an amplitude of 10 μm at 60 rpm.
value of CNF length was determined using Image analysis software (ImageJ) at 30 rpm is found to be 5.4 \( \mu \text{m} \). At 60 rpm this length is decreased to 4.4 \( \mu \text{m} \). Another factor considered in assessing fiber damage was the effect of ultrasound. Figure 4.18(b) shows length distribution of CNFs in nanocomposites obtained without and with ultrasonic treatment at a screw rotation speed of 60 rpm. Only slight decrease in the fiber length due to ultrasonic treatment is observed.
Figure 4.18. Effect of screw rpm on length distribution of CNFs for 11 wt% PEI/CNF nanocomposites without ultrasonic treatment (a) and effect of ultrasound on length distribution of CNFs for 15 wt% PEI/CNF nanocomposites at 60 rpm (b).
4.3.5. Mechanical properties

Typical stress-strain curves of the PEI/CNF composites at various CNF contents ultrasonically treated at amplitude of 5 µm are presented in Figure 4.19 (a). As the CNF concentration is increased, the nanocomposites become more brittle. At concentrations above 11 wt%, the PEI/CNF nanocomposites exhibit no yielding behavior indicating a lower toughness with increase CNF concentration. It is also seen that the Young’s modulus of the nanocomposites significantly increases with increasing CNF concentration.

The stress-strain curves of PEI/CNF nanocomposites containing 11wt% CNFs ultrasonically treated at various amplitudes are given in Figure 4.19(b). The yield stress is not affected by ultrasonic treatment, while the elongation at break is reduced. The reduction in the elongation at break and toughness with ultrasonic treatment is possibly due to the scission of polymeric chains at high ultrasonic amplitude resulting in increased brittleness of material. As PEI/CNF nanocomposites do not yield at high levels of CNF loading, the terms the yield stress and strength are used interchangeably in this study. The strength of PEI/CNF nanocomposites showed little change with ultrasonic treatment and CNF concentration as can be seen from Figure 4.20 (a). It is seen from Figure 4.20 (a) that the strength of nanocomposites does not change up to 15 wt% loading and then slightly decreases. This behavior is attributed to the lack of adhesion between CNFs and PEI matrix. The explanation is supported by the detachment of fibers seen in SEM micrographs depicted in Figure 4.14. The average values of mechanical properties of PEI/CNF composites are summarized in Table 4.1 along with the standard deviation in measurements. Figure 4.20 (a) also shows the strength of composites obtained after ball
Figure 4.19. Stress vs. strain curves of PEI/CNF nanocomposites ultrasonically treated at an amplitude of 5 μm at various concentrations (a) and 11 wt% PEI/CNF nanocomposites obtained without and with ultrasonic treatment at different amplitudes (b) at 60 rpm.
Figure 4.20. Strength (a) and Young’s modulus (b) vs. CNF concentration of PEI/CNF nanocomposites obtained without and with ultrasonic treatment at different amplitudes at 60 rpm and after ball milling.
milling. These composites indicate inferior values of the strength in comparison with those of extruded nanocomposites.

Ultrasonic treatment at amplitude of 5 and 7.5 μm leads to an increase in the Young’s modulus of the nanocomposites, as can be seen from Figure 4.20 (b). The modulus of PEI/CNF nanocomposites containing 11 and 15 wt% CNFs is increased by 17% and 13%, respectively, upon ultrasonic treatment at ultrasonic amplitude of 5 μm. Figure 4.20 (b) also shows values of the modulus of samples after ball milling. The values of modulus of these nanocomposites are typically lower than those of extruded nanocomposites.
## Table 4.1. Mechanical properties of PEI/CNF composites

<table>
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<tr>
<th>CNF (wt%)</th>
<th>Ultrasonic Amplitude (μm)</th>
<th>Strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>Elongation at yield (%)</th>
<th>Elongation at break (%)</th>
<th>Toughness (MPa)</th>
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4.4. Conclusions

PEI/CNF nanocomposites with contents up to 20 wt% have been prepared by means of an ultrasonic single screw compounding extruder. Based on rheological and electrical conductivity measurements, the estimated percolation threshold in ultrasonically treated PEI/CNF nanocomposites is found to be at about 15 wt% of CNF loading which is lower than those of untreated nanocomposites showing the higher percolation threshold. Furthermore, it was established that high power ultrasound is effective in obtaining relatively homogeneous dispersion with improved electrical and thermal conductivity in the PEI/CNF nanocomposites, in comparison with extruded untreated ones. However, the sample prepared by ball milling and without extrusion showed much lower electrical percolation threshold.

An increase of the Young’s modulus in PEI/CNF nanocomposites was recorded under ultrasonic treatment, without reduction in the tensile strength up to 15 wt% CNF loading. A decrease in the tensile strength at higher loadings is attributed to the lack of adhesion between the CNFs and PEI matrix.

SEM micrographs of dry-mixed PEI/CNF composites by ball milling indicated the presence of CNF bundles. However, the CNF bundles are absent after compounding using an ultrasonic single screw extruder with ultrasonic treatment indicating good dispersion of CNFs in PEI matrix. SEM micrographs of fibers extracted from nanocomposites show a breakage of the CNFs during extrusion. The breakage is strongly affected by the screw rotation speed and slightly affected by ultrasonic amplitude.
A novel method and apparatus for the continuous dispersion of CNTs in a polymer matrix has been discussed in this chapter. In particular, an ultrasound assisted twin screw extruder was used to prepare PEI/MWNT nanocomposites. The effects of ultrasonic energy on state of dispersion of CNTs in PEI polymer matrix were studied. The obtained nanocomposites were characterized based on their rheological, morphological mechanical electrical and thermal properties

5.1. Introduction

High performance fiber-reinforced composites have been widely used in various engineering applications due to their light weight and high mechanical properties. Till date, carbon- and glass-fiber composites dominate the industry. There are some limitations associated with the glass-fiber reinforced composites such as the accumulation of electrostatic charge on their surface which can cause local heating resulting in the catastrophic failure of the surrounding materials. In recent years [11], the polymer/CNT composites have gained tremendous attention both in academia and industry. While the
first image resembling nanotubes was published in 1976 [6] major advances in the area happened after the formation of MWNTs was published by Iijima in 1991 [5]. Because of the high aspect ratio (100-1000) of MWNTs and exceptional electrical properties along with their light weight [4,43], it is possible to achieve the percolation threshold at very low loadings [37]. The biggest challenge in effectively using MWNTs is their lack of dispersion in a polymer matrix. During synthesis of MWNTs, nanotubes easily aggregate or form bundles due to strong intertube van der Waals attraction and hence limit the effective use of their exceptional properties obtained at the individual nanotube level. Many researchers [69,205] have tried different routes to disperse MWNTs. However, successful dispersion still remains a challenge as can be seen from the recent reviews on dispersion of MWNTs in a polymer matrix [12,48].

Melt processing is more efficient, rapid and environmentally friendly method to disperse MWNTs in a polymer matrix. It is one of the most preferred techniques from an industrial application point of view because it can easily be scaled up. A number of studies have been done on melt processing/extrusion of polymer/CNT composites[73,76,77,80,96].

To our knowledge, there has been no work done to improve the dispersion of CNTs in polyimide matrix with the help of ultrasound assisted extrusion process. This work presents a novel method and apparatus for the continuous dispersion of CNTs in a polymer matrix. In particular, an ultrasound assisted twin screw extruder was used and the compounding of the PEI/MWNT was carried out. PEI was chosen because of its extensive use in composites for various industrial applications due to its desirable combination of mechanical and thermal properties. Moreover, PEI has desired
processability and outstanding dimensional and thermo-oxidative stability. In the present study, the effects of ultrasound on die pressure, electrical conductivity, rheological, morphological and mechanical properties were studied.

5.2. Experimental

In this section, ultrasonic twin screw extruder, experimental procedure to prepare polymer nanocomposites, processing conditions and characterization methods have been discussed.

5.2.1. Ultrasonic extruder

For melt processing, a commercially available continuous co-rotating intermeshing twin screw micro-extruder (PRISM USA LAB 16, Thermo Electron Corp., UK) having a diameter of 16 mm with a L/D = 25, was used. It was modified by addition of ultrasonic treatment sections at the exit of the micro-extruder as shown in Figure 3.5. The ultrasonic slit die of 4.5 x 0.677 x 0.157 in³ dimension was designed and connected to the micro-extruder through a die connector.

A range of ultrasonic amplitude, varying from 0-6.0 μm was applied to molten compound to study the effect of increasing ultrasonic power on the dispersion of the CNTs in a polymer melt. The gap size between the horns creates a channel with clearance of 4 mm for flow of polymer melt. Two pressure transducers (TPT 412-5M-6/18, Dynisco Instruments, Franklin, MA) of maximum pressure of 5000 psi, to measure the melt temperature and pressure, were placed in the slit die zone immediately before and after the ultrasonic treatment zone. The pressure, temperature and power consumption were
recorded by data acquisition system (Dataq Instruments, DI-715-U, Akron, OH). The
details of ultrasonic twin extruder have been presented in Section 3.2.1.2.

5.2.2. Preparation of nanocomposites

The PEI powder was mixed prior to processing with 1, 2, 5, and 10 wt% MWNT
loadings by ball milling for 24 hrs. The MWNTs were provided by Nanostructured &
Amorphous Materials, Houston, TX, and were used as received. The MWNTs had an
outside diameter of 10-20 nm with lengths of 0.5-200 μm. The premixed mixture was
then dried for a minimum of 24 hrs at 110 °C in a vacuum oven prior to processing. The
premixed PEI/MWNT nanocomposites powder was fed in the feed zone of twin screw
extruder for processing with and without ultrasonic treatment. The ultrasonic treatment
was carried out at amplitudes of 2.5, 4.0, 5.0 and 6.0 μm. The temperature in the barrel
section was set from feed zone to die zone as 280 °C, 340 °C, 350 °C, 360 °C, 360 °C.
The temperatures were digitally controlled by several heaters connected to temperature
controllers. The screw speed was set at 50 rpm. A feed rate of 0.5 lb/hr was controlled by
a feeder (Brabender Technology MT-2, Germany). The mean residence time of the melt
in the ultrasonic treatment zone was 29 s. The extrudate was collected, dried and
pelletized in a grinder (Weima America Inc., Fort Mill, SC).

5.2.3. Characterization

The rheological properties of the nanocomposites were studied using an advanced
rheometric expansion system (Model ARES LS, TA Instruments). Prepared
nanocomposites were compression molded into discs of 25 mm diameter and 2.2 mm
thickness at 300 °C using a compression molding press (CARVER 4122, Wabash, IN) for the rheological measurements. A 25 mm parallel plate geometry in the oscillatory shear mode with dynamic frequency sweep test was used at 340 °C and a fixed strain amplitude of 2%. The frequency range was 0.03 rad/s to 100 rad/s. The material was placed between the heated parallel plates and squeezed and then excess material was removed from the sides to avoid any boundary effects. The dynamic measurements provide information about nanocomposites in their original state without destroying their structure, as would occur in case of the steady state measurements.

For electrical volume and surface resistivity, the samples were compression molded into discs of 90 mm diameter and 1 mm thickness. A Keithley electrometer (Model 6517A, Keithley Instruments, Cleveland, OH) equipped with an 8009 test fixture was used to measure the volume and surface resistivity of the samples in accordance with the ASTM D257 method using applied voltage of 0.1V. It was difficult to measure the resistivity at higher voltages for all the samples since at high CNT loadings, the material becomes highly conductive and it caused the short circuiting in the electrometer. Therefore, the voltage of 0.1V was selected to measure the volume and surface resistivity of all the nanocomposites samples for comparison. It is due to the fact that the different voltage can lead to different resistivity values as conductivity shows dependence on applied voltage. The readings were taken 60 s after the applied voltage to get the stabilized values.

For tensile tests, samples were prepared according to ASTM D-638 using the mini-jet piston injection molder (HAAKE, Thermo Electron Corp., Germany) at a melt temperature of 360 °C, a mold temperature of 130°C and injection pressure of 740 bars.
Tensile measurements on injection molded samples were carried out using an Instron test machine (Model 5567; Instron Corp., Canton, MA). Tests were carried out according to ASTM D 638 test method at a cross head speed of 5 mm/min using a 30 kN load cell and an extensometer. The highest standard deviation for Young’s modulus and tensile strength was 12% and 5% respectively.

The state of dispersion of MWNTs in a polymer matrix can be studied by visual inspection of the nanotubes using micrographs obtained by high resolution microscopy. Therefore, microscopic analysis was carried out to study the morphology and state of dispersion of MWNTs in a polymer matrix using field emission high resolution scanning electron microscope (HRSEM, Model JEOL JSM-7401 F, Tokyo, Japan). The cryofractured surfaces of injection molded impact bar specimens without and with silver sputter coating were used for the HRSEM investigation. The image analysis software (ImageJ) was used to determine the distribution of diameters of nanotubes from the HRSEM micrographs.

5.3. Results and discussion

The results obtained after the characterization of the PEI/MWNTs nanocomposites have been discussed in detail in this section.

5.3.1. Process characteristics

The entrance die pressure for various loadings of MWNTs as a function of ultrasonic amplitude during the extrusion of PEI/MWNT composites is shown in Figure 5.1. The pressure is measured before the ultrasonic treatment zone. A continuous decrease
in the pressure with increasing ultrasonic amplitude was observed. This could be due to occurrence of acoustic cavitation phenomenon in the melt leading to both permanent and thixotropic changes in the melt. Typically, cavitation can cause the scission of the molecular chains resulting in degradation of the polymers which could be seen from reduction in viscosity. However, no such reduction in viscosity was observed for neat polymer as shown in Figure 5.3. So reduction in the die pressure cannot be explained on the basis of degradation of polymer under action of ultrasound but can be attributed to thixotropic changes in the melt. However, it should be noted that due to the presence of MWNTs, degradation of the polymer matrix cannot be completely ruled out since the possibility of a local energy density at the interfaces between polymer and MWNTs exists. In addition to the thixotropic effect produced by ultrasound, the decrease in die pressure is due to heating from dissipated ultrasonic energy, reduction in friction at horn surfaces due to ultrasonic vibrations and possible shear thinning effect created by ultrasound waves. The die pressure increases with the increasing MWNT loading, as expected, due to increase in viscosity caused by an increase in MWNT content. Due to the ultrasonic treatment a tremendous decrease in die pressure at high amplitudes leads to improved processability of polymer melts, allowing one to achieve a faster extrusion rate. In case of a twin screw extrusion, the higher feed rate will lead to build up of the higher die pressure. Therefore, without imposition of ultrasound the die pressure may become prohibitively high. However, with imposition of ultrasound the pressure will be reduced allowing one to increase the feed rate.

The ultrasonic power consumption, as a function of ultrasonic amplitudes for various CNTs concentrations is shown in Figure 5.2. The measured power consumption is
the total power consumption during the treatment of nanocomposites, a part of which is
dissipated as heat and the rest is exerted to disperse nanotubes in melt and potentially
increasing the polymer-nanotube interaction.

Figure 5.1. Die pressure versus ultrasonic amplitude at different MWNT loadings.

Figure 5.2. Ultrasonic power consumption versus amplitude at different MWNT loadings.

It was observed that power consumption increased with the increase of ultrasonic
amplitude and MWNT loading, indicating more energy was transmitted from the horns to
the polymer melt. However, the highest value of power consumption is below 100 Watts.

5.3.2. Rheology

The effect of ultrasound on the complex viscosity of nanocomposites as a function of frequency at different MWNT loadings is shown in Figure 5.3. There is tremendous increase in the complex viscosity of nanocomposites with the increase of MWNT loadings and ultrasound. However, at high loadings the effect of ultrasound on viscosity is masked by its high value. Viscosity increased by an order of magnitudes in comparison with that at low loadings. In other words, the relative change of viscosity at high loadings is less than that at low loadings, but absolute changes are very large. The effect is more pronounced in the low frequency region with minimal increase in the high frequency region. The increase in complex viscosity due to ultrasound is attributed to better dispersion of nanotubes in the polymer matrix with enhanced polymer-nanotube interaction. It has been observed that for low loadings of MWNTs, up to 2 wt%, a Newtonian plateau, similar to that of pure PEI, occurs in the low frequency region. However, this plateau disappears as the MWNT loading is increased beyond 2 wt%. Viscosity increases with MWNT loading and a stronger shear thinning behavior observed at high MWNT loading. This is in accordance with earlier studies done on PC/MWNT [76], HDPE/MWNT [80] and clay-based nanocomposites [206,207,208]. The increase in viscosity observed in the present study at high frequency is similar to that observed in study [76]. However, this increase is more pronounced for 5 wt% loading than in study [76]. At 2 wt% MWNT loading there was a sudden increase in the complex viscosity showing the possibility of a typical rheological percolation between 1 and 2 wt% loading.
This could be better understood by plotting complex viscosity vs. MWNT loading at low (0.03 rad/s) and high (75.35 rad/s) frequencies, as shown in Figure 5.4. It has been observed that at low frequencies, viscosity increase is a strongly nonlinear function of MWNT loading. At high frequency, viscosity is also a nonlinear function of the MWNT loading but this nonlinearity is weak. At the low frequency, there is sharp increase in viscosity at 2 wt% MWNT loading clearly suggesting the existence of a typical rheological percolation between 1 and 2 wt % MWNT loading. This increase in viscosity is more significant in the ultrasonically treated nanocomposites. Evidently, the latter effect is due to the improved dispersion of MWNTs by ultrasonic treatment. The improved dispersion of nanotubes can further be substantiated by the increase in the storage modulus (G’). Both storage (G’) and loss (G”) moduli increase with MWNT loadings with a greater increase in G’ than G” (Figure 5.5). The storage modulus was increased by many orders of magnitude with the increase of MWNT loading. The value of G’ also increases with frequency but the effect is more pronounced at low MWNT loading as compared to high MWNT loading (Figure 5.5a). At higher loadings, the dependence of G’ on frequency becomes very weak almost approaching the plateau region. This indicates the existence of solid like behavior of nanocomposites suggesting that the MWNTs cause the restriction of motion of the polymer chains. In other words, microstructure changes occurred in the polymer restricting the long range dynamics of the polymer chains. The terminal behavior disappears with MWNT loadings further suggesting the formation of a nanotube network with enhanced elasticity of the nanocomposites.
Figure 5.3. Complex viscosity as a function of frequency at different MWNT loadings for untreated and ultrasonically treated nanocomposites at an amplitude of 6 µm.

Figure 5.4. Complex viscosity versus MWNT loading at frequencies of 0.03 and 75.35 rad/s for untreated and ultrasonically treated nanocomposites at an amplitude of 6 µm.
Figure 5.5. Storage (a) and loss (b) moduli versus frequency at different MWNT loadings for untreated and ultrasonically treated nanocomposites at an amplitude of 6 μm.
The effect of MWNT loadings and ultrasound on the structural differences between polymer and nanocomposites can be seen from the logarithmic plot of $G'$ vs. $G''$ (Figure 5.6) which is similar to the Cole-Cole plot [201] used by various researchers [202,203,209] to study the dynamic mechanical properties of polymers in the melt state. At a given $G''$ value, the $G'$ increased significantly with nanotube content and is in accordance with the behavior reported for PC-MWNT composites [76]. It was observed that ultrasonic treatment increases $G'$ at given $G''$ for nanocomposites at all loadings. The increase in the storage modulus with ultrasonic treatment further indicates improved polymer-nanotubes interaction and better dispersion of MWNTs.

![Figure 5.6. Storage modulus versus loss modulus at various MWNT loadings for untreated and ultrasonically treated nanocomposites at an amplitude of 6 μm.](image-url)
The effect of ultrasound and MWNT loading on the damping characteristics of the nanocomposites can be explained by plotting tan δ vs. frequency at various MWNT loadings as shown in Figure 5.7. It is observed that tan δ decreases with nanotube content. The curve becomes more flat in the low frequency region indicating that the nanotubes strongly affect the relaxation behavior of polymer chains. As can be seen, the storage modulus increases more with ultrasonic treatment than the loss modulus resulting in a lower tan δ value. The decrease in tan δ with MWNT loading is more significant at low frequency than at high frequency. At high loading, the value of tan δ is seen to be higher at high frequency than that at low frequency. But it is opposite at low loadings. In comparison with the untreated samples, the ultrasonically treated nanocomposites show a lower value of tan δ indicating the improved interaction between nanotubes and polymer matrix under action of ultrasound.

5.3.3. Electrical resistivity

The volume resistivity of nanocomposites as a function of MWNT loading at different ultrasonic amplitudes is plotted in Figure 5.8. The volume resistivity decreased by almost 7 orders of magnitude at 10 wt% MWNT loading. A sharp reduction in resistivity was observed at 2 wt% MWNT content indicating the percolation threshold lies between 1 and 2 wt% MWNT loading. In other words, a critical concentration existed between 1 and 2 wt% MWNTs, such that nanotubes form a network resulting in creation of conductive path causing the material to behave like a conductor. These results are in accordance with the percolation threshold reported for PC/MWNT nanocomposites prepared by melt processing method [76]. It has to be noted that all the measurements
Figure 5.7. Tan δ versus frequency at various MWNT loadings for untreated and ultrasonically treated nanocomposites at an amplitude of 6 µm.
Figure 5.8. Volume resistivity as a function of MWNT loading for untreated and ultrasonically treated nanocomposites at various ultrasonic amplitudes.
were done at a constant voltage of 0.1V. The application of different voltages can lead to different values of resistivity as conductivity shows dependence on applied voltage. At high MWNT loading nonlinear current-voltage behavior was observed [70] due to tunneling mechanism where electron hopping can occur that could change the value of percolation threshold. No significant change in resistivity occurred with further nanotube loading, up to 10 wt%, and with ultrasonic treatment. The enhancement of dispersion of nanotubes in ultrasonically treated samples is expected to cause a reduction of number of contacts between the nanotubes, leading to an increase of the resistivity. However, since percolation threshold, where the volume resistivity varies by many orders of magnitude, was already achieved, minor changes in the electrical conductivity due to improved dispersion cannot be detected. Apparently, rheological properties are more sensitive to variation in dispersion of MWNTs than the electrical conductivity.

Surface resistivity of nanocomposites as a function of MWNTs concentration is shown in Figure 5.9. It was observed that surface resistivity of nanocomposites decreased by more than 4 orders of magnitude on addition of 10 wt% of MWNTs. A sharp decrease in the surface resistivity for both untreated and ultrasonically treated samples was observed on addition of 2 wt% of MWNTs loading. A further decrease in surface resistivity was observed with increasing MWNTs loading up to 5 wt%. However, no significant decrease in resistivity was observed with further addition of MWNTs loading up to the 10 wt%. No significant change in resistivity occurred with ultrasonic treatment. This is due to the fact that since percolation threshold was already achieved, a minor change in resistivity due to improved dispersion of MWNTs cannot be detected. This is in comparison to the volume resistivity result as shown in figure 5.8.
Figure 5.9. Surface resistivity as a function of MWNT loading for untreated and ultrasonically treated nanocomposites at various ultrasonic amplitudes.

5.3.4. Comparison of rheological and electrical percolation

From comparison of Figures 5.4 and 5.8, it was observed that both rheological and electrical percolations are in the same range. At low frequencies a sharp increase in complex viscosity was observed at 2 wt% MWNT loading. This transition is considered as the rheological percolation. Earlier study [76] also reported that electrical and rheological percolation for PC/MWNT composites prepared by melt processing fall in same concentration range of MWNT loading. For PP/MWNT nanocomposites, study [210] indicated that electrical percolation and composite firmness, defined as a reciprocal value of tan δ, were in the concentration range of 0.25 to 1.0 vol% of MWNTs. In another study [198], PP/CNF composites, prepared by melt processing, showed the same concentration range for both electrical and rheological percolations.
In study [80], PE/MWNT composites, also prepared by melt processing method, showed both the rheological and electrical percolations at 7.5 wt% MWNT loading. However, it is interesting to note that in many other studies [113,115,211] the rheological and electrical percolations were found to be different such that the concentration corresponding to the electrical percolation was higher than that of the rheological percolation. Generally, it is observed that the electrical percolation strongly depends on materials and processing method used. In particular, thermoset materials generally exhibit percolation at lower loading than thermoplastics materials [37,212,213]. Moreover, it was generally observed that concentration corresponding to the percolation increased with the alignment of the CNTs [214]. When CNTs are aligned, the number of contacts between them is reduced, destroying the CNT network. Therefore, it is difficult to make conductive path at low CNT loading. However, study [125] reported a slight increase in the conductivity with SWNT alignment.

5.3.5. Mechanical properties

In this section effect of CNTs loading, processing conditions and compatibilizer on the mechanical properties of the polymer nanocomposites has been discussed.

5.3.5.1. Mechanical properties without use of compatibilizer

The typical stress-strain curves for the PEI/MWNT nanocomposites at various loadings at constant ultrasonic amplitude of 2.5 μm are shown in Figure 5.10. From the figure, one can see that at amplitude of 2.5 μm the addition of nanotubes does not affect the shape of the stress-strain curves. In particular, the ability to exhibit the yielding
behavior of the PEI matrix was retained. This is in contrast to conventional composites that typically become brittle upon addition of fibers.

![Stress-strain curves](image)

Figure 5.10. Typical stress-strain curves of PEI and nanocomposites at various MWNT loadings treated at an ultrasonic amplitude of 2.5 μm.

The Young’s modulus, tensile strength and yield strain are presented in Figure 5.11. The elongation at break was not reported here due to significant scatter in the data. The values are also summarized in Table 5.1. From Figure 5.11, it is observed that the addition of MWNTs have a significant effect on values of the mechanical properties of nanocomposites. In addition, ultrasonic treatment has also some effect on mechanical properties of nanocomposites. Improvement in the Young’s modulus is seen to be more significant at higher MWNT loading, as seen from Figure 5.11(a). In particular, the Young’s modulus of untreated nanocomposites at 10 wt% MWNT loading is about 70% higher than that of untreated pure PEI. It is also observed that at 10 wt% MWNT loading the nanocomposite treated at an amplitude of 5.0 μm shows 86% increase in the Young’s
Figure 5.11. Young’s modulus (a), tensile strength (b) and yield strain (c) versus ultrasonic amplitude for PEI and nanocomposites obtained at different MWNT loadings.
modulus, as compared to the untreated PEI matrix. It should be noted that studies [95,96] found a greater improvement in mechanical properties at lower MWNT loadings than at higher loadings possibly due to a lack of dispersion of MWNTs at higher loadings. However, the present study convincingly shows that the Young’s modulus consistently increased with loading. This implies that dispersion of MWNTs was achieved. As indicated by Figure 5.11(b), the tensile strength of the samples increased from 108 MPa for untreated PEI to 115 MPa for PEI nanocomposite at MWNT loading of 10 wt%. A further increase in the tensile strength was observed for the ultrasonically treated samples. In particular, at an amplitude of 4 μm, the tensile strength increased from 102 MPa for pure PEI to 123 MPa at loading of 10 wt%. The latter clearly indicates that, in addition to a better dispersion of MWNTs, ultrasonic treatment evidently results in increasing the interfacial interactions between polymer matrix and MWNTs. However, for the samples with loadings of 5 and 10 wt%, the tensile strength drops significantly at amplitude greater than 4 μm. This is possibly due to the introduction of defects in both the matrix and MWNTs under action of high amplitude ultrasonic waves. Figure 5.11(c) shows that the yield strain of untreated samples and ultrasonically treated samples at low amplitudes insignificantly affected by MWNT loading. However, the yield strain decreases significantly at high amplitudes due to the introduction of defects in both the matrix and MWNTs.

Earlier studies indicated that the Young’s modulus was increased by about 12% for HDPE/MWNT composites at 5 wt% MWNT loading [81], about 19% at 2 wt% MWNT loading for PET/MWNT composites [95] and 30% for PS/MWNT composites at 5 wt% MWNT loading [9]. Contrary to [81], no significant improvement in mechanical
properties was observed for HDPE/MWNT composites [80]. However, the modulus and strength were increased by 50% and 65%, respectively, for HDPE/SWNT composites at 2.6 wt% SWNT loading [82]. Furthermore, a 62% increase in the modulus was obtained for polyamide 6/MWNT composites at 12.5 wt% MWNT loading [99]. In the present study, PEI, being the high performance thermoplastic, exhibits a modulus and strength much higher than those of polymers discussed above. However, even in this case a significant increase in both the Young’s modulus and tensile strength were obtained. This indicates the effectiveness of ultrasonic assisted extrusion developed in the present study. However, it should be noted that the increase of the mechanical properties such as Young’s modulus (about 5.2 GPa) at 10 wt% of MWNTs loading was not large as expected from the composite rule of mixture [215]. It could be expected to be as high as 31 GPa assuming density of polymer matrix is 1.27g/cc and true density of MWNT as 2.1 g/cc with modulus of polymer matrix is 3 GPa and of the nanotube as 600 GPa. A number of ways was suggested to improve the mechanical properties of the nanotube-based nanocomposites. A common method to improve the mechanical properties of the nanocomposites is to provide orientation or alignment to the CNTs. This is commonly done by melt spinning at high draw ratio to make fibers with CNTs oriented along the fiber axis [87]. Studies [216,217] have shown that the increased alignment provides better mechanical properties. However, in those cases CNT concentration corresponding to electrical percolation was higher due to the alignment of CNTs [125]. In study [218], PMMA/SWNT composites were melt spun to make fibers at various draw ratios. A significant improvement in mechanical properties was observed. In addition, Fornes et al. [219] prepared melt spun fibers from PC/MWNT which resulted in the increase in the
Young’s modulus and tensile strength by 75% and 50%, respectively, at 5 wt% MWNT loadings. Also, PP/SWNT [220] fibers were post drawn after spinning. An increase in the modulus from 6.3 to 9.8 GPa was observed at a loading of 1 wt%. In another study [104], PP/SWNT fibers showed improvement in the modulus from 0.4 to 1.4 GPa, i.e. more than threefold increase in the strength at 5 wt% SWNT loading. In the present study no alignment or stretching was performed and the die section is of constant rectangular cross section without any converging flow. Hence, the observed enhancement of properties in PEI/MWNT nanocomposites is not due to orientation nanotubes. In fact, they are randomly distributed in PEI matrix as indicated by HRSEM pictures reported below. However, providing orientation to MWNTs by stretching is expected to further enhance the mechanical properties of PEI/MWNT nanocomposites.

From many studies [118,221], it has been observed that CNTs cause nucleation resulting in increased crystallinity of the material. Accordingly, it becomes difficult to find whether the increased mechanical properties are due to increased crystallinity or due to the reinforcement effect of nanotubes. However, in the present study the polymer matrix, PEI, is an amorphous polymer. Therefore, any improvement in mechanical properties can be attributed to only MWNT reinforcement caused by improved dispersion or increased nanofiller-matrix interactions.

Generally, it is believed that CNTs with larger aspect ratios will yield higher mechanical properties. However, in the case of PC/SWNT fibers Fornes et al. [219] observed little improvement of the mechanical properties above an aspect ratio of 300. At an aspect ratio of ~ 2000 a further increase in reinforcement was not observed. Another way [52,106] to improve the mechanical properties could be the functionalization of
MWNTs to achieve good interaction with the matrix. However, few studies have been carried out to investigate the effect of functionalization on the mechanical properties [51,72].

5.3.5.2. Effect of compatibilizing agent on the mechanical properties

The compatibilizer can be used to enhance the mechanical properties of the nanocomposites. In this study, a separate feeder was used to add the CNTs in the melt state of polymer to reduce the breakage in the high stress feed zone. The titanium based compatibilizer from Kenrich under trade name Ken-React® CAPOW® NZ® 37/H was used to enhance the compatibilization between CNTs and the PEI polymer matrix. The compatibilizer was used in the concentration range of 0.5, 1 and 2 wt %. Compatibilizer was thoroughly premixed with the powder of CNTs before adding to the polymer melt. The screw speed of feeder used to fed PEI powder and the another high precision feeder used to fed premixed mixture of CNTs and compatibilizer, was adjusted to get a fixed flow rate of 0.5 lb/hr. The screw speed was set at 50 rpm. The CNTs loading was 5 wt%. The effect of addition of different concentration of compatibilizer on the mechanical properties can be seen from Figure 5.12.

It was observed that there was not much effect of compatibilizer loading on the mechanical properties of the prepared nanocomposites. There was no significant improvement both in the Young’s modulus and tensile strength of the nanocomposites was observed. This could be due to the fact that compatibilizer gets degraded at such a high processing temperature as can be seen from the thermal degradation curve as shown in Figure 5.14.
Figure 5.12. Young’s modulus (a), tensile strength (b) versus compatibilizer loading for PEI/MWNT nanocomposites at 5 wt% MWNT loading without ultrasonic treatment.
Table 5.1. Mechanical properties of PEI and PEI/MWNT nanocomposites obtained at various ultrasonic amplitudes

<table>
<thead>
<tr>
<th>MWNT (wt%)</th>
<th>Ultrasonic Amplitude (µm)</th>
<th>Young's Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Yield Strain (%)</th>
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<tr>
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</tbody>
</table>
5.3.6 Thermal gravimetric analysis

The thermal stability of the prepared nanocomposites was studied using thermal gravimetric analysis. The degradation curves for pure PEI and nanocomposites containing different wt% loadings of carbon nanotubes have been presented in Figure 5.13. It can be seen from Figure 5.13 that at around 875°C the residual amount in all prepared nanocomposites is approximately 46% or more of the initial weight. There was not much improvement in the thermal stability of the prepared nanocomposites on addition of the carbon nanotubes. The TGA curve for compatibilizer is shown in Figure 5.14. From figure 5.14, it can be seen that compatibilizer lost most of its weight below 200 °C temperature with further loss in weight at high temperature. This indicates that it was not enough thermally stable at the processing temperature of the nanocomposites to provide any compatibilizing effect between carbon nanotubes and polymer matrix.

![TGA curves for PEI/MWNT nanocomposites with various loadings of multi-walled carbon nanotubes without and with ultrasonic treatment.](image)

Figure 5.13. TGA curves for PEI/MWNT nanocomposites with various loadings of multi-walled carbon nanotubes without and with ultrasonic treatment.
Figure 5.14. TGA curve for Ken-React® CAPOW® NZ® 37/H compatibilizer.
5.3.6. Morphology

Figure 5.15 shows HRSEM micrographs of surfaces of the as-received MWNTs (a), cryofractured moldings of untreated (b) and ultrasonically treated (c) nanocomposites filled with 2 wt% MWNTs. Image analysis of micrographs of the as-received MWNTs allowed us to determine distribution of their diameters. It was found that their diameters varied from 9 to 28 nm with the average diameter being 18 nm. Images in Figure 5.15 b and c clearly distinguish nanotubes that are randomly oriented and uniformly dispersed. However, the untreated nanocomposite sample shows the presence of entangled MWNT bundles as large as 1 µm. Nanotubes in the treated sample were found to be completely unentangled after treatment at an amplitude of 6 µm. This sample does not show even a single MWNT bundle. The images show that the nanotubes were dispersed to a level of 50 nm diameter, which is higher than diameters of 9-28 nm of MWNTs as-received. This suggests that there are two possibilities. First, PEI matrix was coated or wrapped around the MWNTs. This may be a further indication of the existence of interfacial interactions between MWNTs and PEI matrix. Second, the observed increase in diameters of nanotubes could be due to the silver sputter coating used in preparation of the nanocomposite samples for the HRSEM studies. This effect is further explained in detail.

Figure 5.16 shows micrographs of the untreated (a, c) and ultrasonically treated (b, d) nanocomposites at 10 wt% MWNT loading and an amplitude of 5.0 µm at low (a, b) and high (c, d) magnifications. Due to very high loading, at low magnification, it is difficult to detect whether dispersion of nanotubes is at the individual level in both the untreated and treated samples. However, one can see that the untreated sample shows the
Figure 5.15. HRSEM micrographs of as received MWNTs (a), surface of cryofractured moldings of untreated nanocomposite (b) and ultrasonically treated nanocomposite (c) at 2wt% MWNT loading and an amplitude of 6 μm.
Figure 5.16. HRSEM micrographs of sputter coated surface of cryofractured moldings of untreated (a, c) and ultrasonically treated (b, d) nanocomposites at 10 wt% MWNT loading and an amplitude of 5 μm. (a,b): low magnification; (c,d): high magnification.
resin rich part along with a network of nanotubes, whereas the treated sample seems to indicate dispersed nanotubes forming the network all over the polymer matrix. Another interesting observation can be made about the length of the nanotubes. It has been observed that the treated sample shows longer nanotubes than the untreated one. This can be seen from comparison of Figure 5.16 (c) and (d) obtained at high magnification. However, why this occurs is not clear. One possible reason could be the tremendous decrease in die pressure with ultrasonic treatment as compared to the untreated samples (see Figure 5.1). The lower pressure may lead to a reduction of the breakage of nanotubes.

Figure 5.17 shows a typical HRSEM micrograph of ultrasonically treated nanocomposites at loading of 10 wt% and an amplitude of 5 µm obtained without the silver sputter coating. The image analysis of various micrographs was performed. An interesting observation was made from the comparison of the micrographs that were obtained with (Figure 5.16d) and without (Figure 5.17) the silver sputter coating. Nanotube diameters appear to be bigger with the sputter coating. In particular, nanocomposites without sputter coating show the diameter of nanotubes ranging from 10 to 64 nm with an average diameter of 30 nm. This is a clear indication of PEI matrix getting coated or wrapped around the MWNTs and a further proof of the existence of interfacial interactions between MWNTs and PEI matrix. However, the mechanism of nanotube interaction with polymer matrix is not clear at this stage. Further work needs to be done to understand this phenomenon. At higher MWNT loadings, due to high aspect ratio and large surface area, nanotubes formed an interconnected network.
Figure 5.17. HRSEM micrograph without sputter coating surface of cryofractured moldings of ultrasonically treated nanocomposites at 10 wt% MWNT loading and an amplitude of 5 μm.

5.4. Conclusions

A new ultrasound assisted twin screw extrusion process was developed for manufacturing PEI/MWNT nanocomposites with excellent dispersion of nanotubes in a polymer matrix. This process is solvent free and uses no surface modification of the nanotubes. The rheological behavior of the nanocomposites was studied in the oscillatory shear mode. The rheological behavior was considered as an indirect way to determine the dispersion state of MWNTs. The tremendous increase in the complex viscosity and storage modulus of PEI was observed with MWNT loading. In addition, the rheology was affected by ultrasonic treatment. In particular, the ultrasonically treated nanocomposites show an increase in the viscosity, storage modulus and reduced damping characteristics, as compared to the untreated ones. This indirectly indicates the presence of better dispersion of nanotubes in PEI under ultrasonic treatment. At low MWNT loading, the
shear thinning behavior of nanocomposites is similar to that of the matrix. At high nanotube loading, nanocomposites show very strong shear thinning behavior. Data on mechanical properties shows that MWNT loading and ultrasound has an effect on the tensile strength and Young’s modulus of the nanocomposites. In particular, the Young’s modulus of the treated nanocomposites shows some increase in values at loadings of 5 and 10 %. Also, the strength of nanocomposites increased from 115 MPa for the untreated sample to 123 MPa for the treated sample at 10 wt% MWNT loading and amplitudes of 2.5 and 4 μm. However, reductions in the tensile strength and yield strain were observed in nanocomposites treated at higher amplitudes. The rheological and electrical percolations were found to be between 1 and 2 wt% MWNT loading. Rheology was found to be more sensitive to MWNT dispersion than the electrical conductivity. HRSEM results show that ultrasound helps in dispersion of nanotubes as a result of breakage of MWNT bundles.
CHAPTER VI

ULTRASOUND ASSISTED TWIN SCREW EXTRUSION PROCESS FOR PREPARATION OF LCP/CNF NANOCOMPOSITES WITH SEPARATE FEEDING OF CARBON NANOFIBERS IN THE MELT STAGE

In the present chapter, the preparation of LCP/CNF nanocomposites using ultrasound assisted twin screw extrusion process has been studied. In contrast to the previous chapter where polymer resin was physically premixed with the carbon nanotubes and then fed to the extruder, in this study, a separate feeder was used to feed the CNFs in the molten LCP stream. This was done to reduce the breakage of the CNFs in high stress feed zone. Rheological, mechanical, electrical, thermal and morphological characterizations were carried out to investigate effect of ultrasonic treatment on the state of dispersion of CNFs in LCP matrix.

6.1. Introduction

LCPs attracted a lot of attention due to their excellent mechanical and thermal properties with low oxygen/water permeability and making them promising material for high performance molding, optoelectronics and photonic devices [222,223]. LCP materials are characterized by long, rigid, rod like molecules that get aligned in the elongational flow resulting in superior mechanical properties. LCP has very low
conductivity, preventing their use in high performance applications where EMI shielding is desired. CNFs have been incorporated in many thermoplastics [194,198] to improve their electrical conductivity. However, a limited studies has been done on LCP/CNF [224,225] and LCP/multiwalled carbon nanotube (MWCNT) [226] nanocomposites.

From the literature review, it has been observed that to achieve the homogenous dispersion of CNFs in high performance and viscous materials is a challenging task. So there is a clear need to develop a new clean, rapid and environment friendly method which can process highly viscous materials.

In the previous chapter, polymer was physically premixed using ball milling process with carbon nanotubes before feeding to the twin screw extruder. In this work, ultrasound assisted twin screw extrusion of LCP/CNF has been carried out by feeding CNF into molten LCP stream to reduce the breakage of the CNFs in high stress feed zone area. It was done by using the separate feeder for the CNFs.

To our knowledge, there has been no work done to improve the dispersion of CNFs in LCP matrix with the help of ultrasound assisted extrusion process. Therefore, this work presents a novel method for the continuous dispersion of CNFs in a polymer matrix. Ultrasound assisted twin screw extrusion of LCP/CNF has been carried out by feeding CNF into molten LCP stream. LCP was chosen because of its excellent chemical resistance, mechanical and thermal properties. They have outstanding dimensional and thermo-oxidative stability with desired processability required for space applications.

In this work the effects of ultrasound on die pressure, electrical conductivity, rheological, morphological and mechanical properties were studied.
6.2. Experimental

In this section, ultrasonic extruder, experimental procedure to prepare polymer nanocomposites, processing conditions and characterization methods have been discussed.

6.2.1. Ultrasonic extruder

For melt processing, a continuous co-rotate twin screw extruder equipped with high power ultrasonic die attachment was used as shown in Figure 3.7. The details about the design of ultrasonic slit die and ultrasonic attachment can be found in section 3.2.1.2. In contrast to the earlier study where a physical mixture of the polymer and nanofillers were fed into feed section of the extruder, whereas in the present study LCP was fed into feed section while CNFs were fed into LCP stream after melting. The micro extruder (PRISM USA LAB 16, Thermo Electron Corp., UK) has diameter of 16 mm with L/D = 25. Two pressure transducers (TPT 412-5M-6/18, Dynisco Instruments, Franklin, MA) of maximum pressure of 5000 psi, were placed in the die zone immediately before and after the ultrasonic treatment zone. The die pressure and temperature were recorded by data acquisition system (Dataq Instruments, DI-715-U, Akron, OH). Two horns oscillating at a frequency of 40 kHz were attached to the die zone having a 4 mm gap size for flow of polymer melt. The molten compound was continuously subjected to amplitudes ranging from 0 to 3.2 \( \mu \)m. Dried LCP pellets were fed to the extruder using a twin screw feeder (K-Tron Soder, Model K2V-T20, Pitman, NJ, USA). A separate high precision feeder (Brabender Technology MT-2, Germany) was used to add the CNFs in the melt to reduce the breakage of nanofibers due to high stresses in the feed zone. The temperature in the
barrel section was set from feed zone to die zone as 300 °C. The screw speed was set at 150 rpm. The feed rate of LCP pellets and CNFs were adjusted to give output of 1 lb/hr of nanocomposites.

6.2.2. Preparation of LCP/CNF nanocomposites

LCP used was wholly aromatic copolyester containing 73% HBA (1,4-dihydroxybenzoic acid) and 27% HNA (2,6-dihydroxynaphthoic acid). It has the melting temperature of 275 °C. The CNFs, Pyrograf-III, were provided by Applied Sciences, Inc., Cedarville, OH. They were used as received.

The LCP pellets and CNFs were dried separately in a vacuum oven at 110 °C for at least 24 hrs prior to processing. The dried LCP pellets were fed to the feed zone of the twin screw extruder while CNFs were separately added to the LCP stream after melting. The ultrasonic treatment was carried out at amplitudes of 1.0, 2.5 and 3.2 μm. The temperature in the barrel section was set from feed zone to die zone as 300 °C. The screw speed was set at 150 rpm. The feed rate of LCP pellets and CNFs were adjusted to give output of 1 lb/hr of nanocomposites. The residence time in the ultrasonic treatment zone was 12 seconds. The extrudate was collected, dried and pelletized in a grinder (Weima America Inc., Fort Mill, SC).

6.2.3. Characterization

For the rheological measurements prepared nanocomposites were compression molded into discs of 25 mm diameter and 2.2 mm thickness at 300 °C using the compression molding press (CARVER 4122, Wabsah, IN). Advanced Rheometric
Expansion System (Model ARES LS, TA instruments) was used to study the rheological properties of the nanocomposites. A 25 mm parallel plate geometry in oscillatory shear mode with dynamic frequency sweep test was used at 300 °C and a fixed strain amplitude of 2%. The studied frequency range was 0.03 rad/s to 100 rad/s. The complex viscosity, storage modulus, loss modulus and loss tangent were obtained as a function of the angular frequency. The disc shaped sample was placed between the heated parallel plates and squeezed and then excess material was removed from the sides to remove any boundary effects. Data acquisition was carried out with the aid of a microcomputer interfaced with the rheometer.

For electrical conductivity measurements, the samples were also compression molded at 300 °C into discs of 90 mm diameter and 1 mm thickness. An electrometer, Keithley Instrument (Model 6517 A, Keithley Instruments, Cleveland, OH) attached to an 8009 test fixture was used to measure the volume and surface resistivity of the prepared samples in accordance with ASTM D257 method. The measurements were done at a constant voltage of 1.0 and 0.1 volt. The readings were taken 60 s after the applied voltage to get the stabilized values. At high applied voltage, materials having high CNFs loadings become very conductive and cause the short circuiting of the electrometer. Hence, it was difficult to measure the volume and surface resistivity for all samples at same high voltage. The low voltage of 1.0 and 0.1 volt was chosen for the comparison purpose and to show the effect of voltage on percolation threshold value as different voltages can lead to different percolation threshold values.

For tensile tests, specimens were prepared according to ASTM D-638 using the HAAKE mini-jet piston injection molder (HAAKE, Thermo Electron Corp., Germany) at
a melt temperature of 290 °C and mold temperature of 80 °C. The injection pressure was 420 bars in each case. High temperature mold release agent (Frekote HMT2) was sprayed before injecting the material.

The oriented fibers of LCP/CNF nanocomposites were prepared using capillary rheometer (Rosand 2000). The barrel temperature of 300 °C was used to produce the fibers. As the rod like strand comes out of the capillary die of a diameter of 2 mm and L/D=32, it was stretched and collected at ambient air cooling using a cylindrical take up device. The distance between die exit and take up device was 46cm. Three different draw down ratios (DDR) were used to produce the fibers of different diameters at a flow rate of 15 g/min. The three DDR used were 30, 51 and 75. The fibers of LCP/CNF nanocomposites up to 5 wt% CNFs loadings were melt spun; however the higher CNFs loadings fibers were difficult to prepare due to melt fracture and high viscosity of the polymer melt.

Instron tensile testing machine (Model 5567, Instron Corp., Canton, MA) was used to carry out the tensile tests on injection molded tensile bars and melt spun fibers at room temperature. The injection molded samples were clamped in the jaws of the testing machine and put under tension using a 10 kN load cell. In case of tensile testing of fibers, a single fiber was tested for every condition using a 100 N load cell. Tests were carried out according to ASTM D 638 test method using an extensometer at a cross head speed of 5 mm/min. A minimum of five samples were tested for both injection molded bars and melt spun fibers for each condition. The Young’s modulus, tensile strength and yield strain were measured. The average and standard deviation of obtained values were calculated.
The effect of ultrasonic wave on the state of dispersion of carbon nanofibers in a LCP matrix can be best visualized using microscopic studies. Scanning electron microscope (Hitachi S-2150 SEM at 20 kV) was used to study the surface morphology and state of dispersion of CNFs. For microscopic studies, cryofractured compression molded disc shape samples without any silver sputter coating were used.

6.3. Results and discussion

The results obtained after the characterization of the LCP/CNFs nanocomposites have been discussed in detail in this section.

6.3.1. Process characteristic

The entrance die pressure before the ultrasonic attachment zone of LCP/CNF nanocomposites at various loadings of CNFs as a function of ultrasonic amplitude during the extrusion of LCP/CNF nanocomposites is presented in Figure 6.1. The die pressure increases with increasing CNFs content, as expected, due to increase in viscosity caused by increase in CNFs content. A continuous decrease in die pressure with ultrasonic amplitude was observed. This decrease in die pressure becomes more efficient with an increase of concentration of CNF. This could be due to occurrence of acoustic cavitation phenomenon in the melt leading to the both permanent and thixotropic changes in the melt [200]. These effects of ultrasonic cavitation on the chain scission of the polymer matrix were not observed, as will be seen from the Figure 6.2 below, where no significant decrease in complex viscosity occurs upon application of ultrasound. However, degradation of matrix in the presence of CNFs cannot be ruled out, as the possibility of a
local energy density at the interfaces between polymer and CNFs may exist. The possible shear thinning behavior of the melt may get enhanced on application of ultrasonic waves leading to temporary decrease in melt viscosity that recovers after treatment. In addition to shear thinning and thixotropic changes, the reduction in die pressure is due to combination of heating from dissipated energy from ultrasound and reduction in friction at horn surfaces due to ultrasonic vibrations [200].

![Diagram showing die pressure versus amplitude at different CNFs loadings.](image)

Figure 6.1. Die pressure versus amplitude at different CNFs loadings.

6.3.2. Rheology

Figure 6.2 shows the complex viscosity of nanocomposites as a function of frequency at different CNF loadings for untreated and ultrasonically treated samples. It can be seen that there is continuous increase in the complex viscosity with the increase of CNFs loadings. The complex viscosity was increased by more than 2 orders of magnitude.
on an addition of 20 wt% of CNFs. Such a large increase in viscosity with CNF concentration does not conform with corresponding smaller increase of die pressure. This inconsistency on behavior of die pressure is apparently due to the presence of slip effects.

Figure 6.2. Complex viscosity as a function of frequency at different ultrasonic amplitudes and CNF loadings.
during flow throughout the die even in the absence of ultrasonic treatment. The decrease in viscosity with the increase of frequency indicates the non-Newtonian behavior of nanocomposites. A stronger shear thinning behavior was observed at higher CNFs loadings as compared to at low CNFs loadings. The orientation of the domains and rigid molecular chains in LCP on application of shear force results in increase of shear thinning behavior of nanocomposites. The behavior is in accordance with the earlier studies on PEI/CNF and PEI/CNT nanocomposites [227,228]. This increase in viscosity does not affect the processability of the melt as ultrasonic treatment helps in processability with decrease in die pressure as explained previously in process characteristic. By comparing die pressure and complex viscosity variations with amplitude one can see that the viscosity changes less with amplitude than the die pressure. This observation led us to believe that significant reduction of die pressure with ultrasonic amplitude in these LCP/CNF nanocomposites is due to thixotropic effects and a possible slippage on the horn surface.

The existence of rheological percolation threshold can be understood by plotting complex viscosity versus CNF concentration at low (0.03 rad/s) and high (75.35 rad/s) frequencies for untreated and ultrasonically treated samples at amplitude of 3.2 μm, as shown in Figure 6.3. A sudden increase in the complex viscosity is observed on an addition of 2 wt% of CNF indicating the possibility of occurrence of rheological percolation threshold at low concentration in comparison with the electrical percolation discussed later.
Figure 6.3. Complex viscosity versus CNF loadings at frequencies of 0.03 rad/s and 75.35 rad/s for untreated and ultrasonically treated nanocomposites at an amplitude of 3.2 μm.

Both the storage (G’) and loss (G”’) moduli of LCP and their nanocomposites increased with the increase of frequency (ω) (Figure 6.4). There was tremendous increase in the storage and loss modulus of nanocomposites with the increase of the CNF loadings. It was observed that as the CNF loadings increased the slope of the G’ and G” vs. ω curves keep changing and getting less steeper (approaching a plateau) at intermediate frequencies indicating the existence of interconnected structure of CNFs which are an anisotropic filler [76]. At low frequencies, similar to earlier observations on
Figure 6.4. Storage (a) and loss (b) modulii as a function of frequency at different ultrasonic amplitudes and CNF loadings.
PEI/MWNT nanocomposites [228], some drop in slope in $G'$ vs. $\omega$ was observed with frequency. The effect of ultrasound and CNFs loadings on the structural differences between the polymer and the nanocomposites can be seen from the logarithmic plot of $G'$ vs. $G''$ (Figure 6.5), which is similar to Cole-Cole plot. Curves without and with ultrasonic treatment at each concentration of CNF practically coincide indicating no significant changes in the molecular structure of LCP and nanocomposites due to ultrasonic treatment. It can also be seen that at a given $G''$ value, there is a significant increase in $G'$ value with the increase of CNFs loadings. This behavior is in accordance with earlier studies reported on PEI/CNF [227], PEI/MWNT [228], PC/MWNT [76] and HDPE/MWNT [80] nanocomposites where similar behavior was observed on addition of CNT and CNF to the polymer matrices.

The effect of ultrasound and CNF loading on the tan $\delta$ can be seen by plotting tan $\delta$ versus frequency at different CNF loadings for untreated and ultrasonically treated samples at 3.2 $\mu$m (Figure 6.6). It is observed that tan $\delta$ decreased with addition of CNF and the effect is more pronounced at higher frequency as compared to lower frequency, indicating that the relaxation behavior of polymer chains strongly get affected with CNF content. At low level of CNF loadings and high frequency the value of tan $\delta$ seems to be higher than that at the lower frequency. This is opposite to the behavior at high loading and at low frequency where tan $\delta$ value is higher. The ultrasonically treated samples do not show significant differences in value of tan $\delta$ as compared to the untreated samples at all CNF concentrations.

Ultrasound does help in the dispersion of the CNFs as seen from the morphological studies discussed in later part of this study. The increase in ultrasonic
Figure 6.5. $G'$ versus $G''$ for untreated and ultrasonically treated nanocomposites at an amplitude of 3.2 $\mu$m and at various CNF loadings.
Figure 6.6. Tan $\delta$ as a function of frequency for untreated and ultrasonically treated nanocomposites at an amplitude of 3.2 $\mu$m and at various CNF loadings.
amplitude does not significantly affect the complex viscosity of the LCP/CNF nanocomposites, as seen from Figures 6.2 and 6.3. However, the fibrillation structure of LCP apparently gets affected with increased dispersion. Therefore, this increased dispersion practically does not affect the rheological behavior of LCP/CNF nanocomposites, possibly, due to a reduction in fibrillation of LCP matrix in the presence of CNFs. In fact, in PEI/CNF [227] and PEI/MWNT [228] nanocomposites, where matrix does not fibrillate and dispersion of nanofillers was improved due to ultrasonic treatment, a significant increase of viscosity was observed resulting in permanent changes in rheological behavior.

6.3.3. Electrical resistivity

CNFs being highly electrically conductive fillers were added to the insulating LCP matrix to improve its electrical conductivity. A critical loading of CNFs are required where the interconnected network of CNFs formed resulting in creation of conductive path causing the material to behave like a conductor. This critical loading is termed as the percolation threshold, below which the conductivity of the nanocomposite is close to the conductivity of unfilled material. Above the percolation threshold a sharp reduction in resistivity occurred making it conductive and suitable for certain applications where electrical conductivity is required. Once the percolation threshold reached, there is not much decrease in the resistivity on a further addition of nanofibers and conductivity levels off and attains the value of conductive particles.

Figure 6.7 shows the volume resistivity of the nanocomposites as a function of CNFs loading at different ultrasonic amplitudes and at 1.0 volt (a) and 0.1 volt (b). The
Figure 6.7. Volume resistivity at 1.0 volt (a) and 0.1 volt (b) as a function of CNF concentration at various ultrasonic amplitudes.
volume resistivity decreased by over 3 and 4 orders of magnitude with 10 wt% CNFs loading without and with ultrasonic treatment at an amplitude of 3.2 $\mu$m (Figure 6.7 a). A sharp reduction in resistivity is observed between 5 and 10 wt% CNFs loading indicating the percolation threshold lies between 5 and 10 wt% loading. The resistivity further decreased by an order of magnitude on addition of 15 wt% of CNFs. Once the percolation threshold was achieved, a little drop in resistivity was observed on further increasing the CNFs content upto 20 wt%. For untreated nanocomposites at 0.1 volt, the volume resistivity dropped by about 2 orders of magnitude at 10 wt% CNFs loading, whereas, for the ultrasonically treated samples, this drop in volume resistivity was about 3 orders of magnitude at same CNFs loading, as can be seen from Figure 6.7 b. Therefore, an order of magnitude drop in volume resistivity of nanocomposites was observed due to ultrasonic treatment alone at same CNF loading and different voltages. Also, it should be noted that different voltages provide different conductivity values. Therefore, for comparison purpose measurements were done at low voltages, as it was difficult to take measurements at high voltages for the samples of high CNF loadings since the electrometer gets tripped off. Figure 6.7 indirectly indicates that high power ultrasonic treatment helps in improving the dispersion of CNFs in a polymer matrix and at the same time leading to the formation of better interconnected network of CNFs and, hence, resulting in improved electrical conductivity. The results are in accordance with the earlier study carried on PEI/CNFs nanocomposites [227], where the percolation threshold falls to 15 wt% of CNFs loadings for ultrasonically treated nanocomposites as compared to the 18 wt % of CNFs loadings for untreated nanocomposites. LCP nanocomposites reached percolation threshold at lower CNFs loadings as compared to other
thermoplastics. Lozano et al. [198] found the electrical percolation to be at 20 wt% of CNFs loading for PP/CNFs nanocomposites. A possible reason for lower values of percolation in LCP is the self aligning nature of their domains which get oriented under shear flow and tend to align nanofibers bringing them close to each other resulting in conductive material at much lower loading [223]. It was observed that both rheological and electrical percolation threshold values differ from each other as can be seen from Figure 6.3 and Figure 6.7, with rheological threshold values being lower than the electrical ones. This is in contrary to earlier study done on PEI/MWNT nanocomposite prepared by similar processing method where both rheological and electrical percolation threshold values lies in the same range. However, a number of other studies [113,115,211] also suggested the difference in value of rheological and electrical percolation threshold values.

Figure 6.8, shows the surface resistivity of LCP/CNF nanocomposites as a function of the CNF concentration. It can be seen that surface resistivity follows the same trend as that of the volume resistivity (Figure 6.7). A sharp decrease in surface resistivity was observed between 5 and 10 wt% of CNFs loading indicating percolation threshold lies between 5 and 10 wt% loading. The surface resistivity of nanocomposites decreased by more than two orders of magnitude on addition of 20 wt% of CNFs. It was also observed that decrease in surface resistivity was less as compared to the volume resistivity as can be seen from Figure 6.7 (a), where volume resistivity decreased by more than 4 orders of magnitude on addition of 20 wt% of CNFs. It can also be seen that ultrasonically treated samples shows lower surface resistivity as compared to the untreated samples. For the same CNFs loading level at 10 wt%, ultrasonically treated
samples at amplitude of 3.2 µm shows more than an order of magnitude decrease in surface resistivity as compared to the untreated ones. This indicates that high power ultrasonic treatment leads to better dispersed interconnected network of CNFs.

![Graph showing surface resistivity as a function of CNF concentration at various ultrasonic amplitudes and at 1.0 volt.](image)

Figure 6.8. Surface resistivity as a function of CNF concentration at various ultrasonic amplitudes and at 1.0 volt.

6.3.4. Mechanical properties

Figure 6.9 shows the typical stress-strain curves for untreated and ultrasonically treated LCP/CNF nanocomposites at 2.5 µm and at different CNFs loadings. In general, the composites are known to become brittle on an addition of fibers. However, in the present study it was observed that shape of the stress-strain curve did not change even on an addition of 20 wt% CNFs, as can be seen from Figure 6.8. On contrary the elongation
at break increases in the presence of high amount of CNFs as compared to the pure material.

The effect of ultrasonic treatment and CNFs loadings on the Young’s modulus, tensile strength and elongation at break of LCP/CNF nanocomposites is shown in Figure 6.10 and in Table 6.1. In general, no significant change in the Young’s modulus and tensile strength of the LCP/CNF nanocomposites were observed on an addition of CNFs and on application of ultrasound. However, a reduction in the tensile strength of the LCP/CNF

![Stress-strain curves for LCP and LCP/CNF nanocomposite moldings untreated and ultrasonically treated at an amplitude of 2.5 μm and at various CNF loadings.](image)

**Figure 6.9.** Stress-strain curves for LCP and LCP/CNF nanocomposite moldings untreated and ultrasonically treated at an amplitude of 2.5 μm and at various CNF loadings.
Figure 6.10. Tensile strength (a), Young’s modulus (b) and elongation at break (c) of moldings as a function of CNF concentration at various ultrasonic amplitudes.
Table 6.1. Mechanical properties of LCP and LCP/CNF nanocomposite moldings at different CNFs loadings and ultrasonic amplitudes.

<table>
<thead>
<tr>
<th>CNF (wt%)</th>
<th>Ultrasonic amplitude (µm)</th>
<th>Young's modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0</td>
<td>9.97 ± 0.41</td>
<td>135.7 ± 9.96</td>
<td>2.34 ± 0.42</td>
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<td></td>
<td>1</td>
<td>9.94 ± 0.09</td>
<td>142.0 ± 2.31</td>
<td>2.12 ± 0.55</td>
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<tr>
<td></td>
<td>2.5</td>
<td>9.54 ± 1.03</td>
<td>136.0 ± 13.8</td>
<td>2.65 ± 0.82</td>
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<td></td>
<td>3.2</td>
<td>10.06 ± 0.68</td>
<td>139.0 ± 9.09</td>
<td>2.51 ± 0.82</td>
</tr>
<tr>
<td>2%</td>
<td>0</td>
<td>9.66 ± 0.33</td>
<td>144.0 ± 14.0</td>
<td>3.12 ± 0.76</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>9.62 ± 0.6</td>
<td>143.7 ± 3.3</td>
<td>3.16 ± 0.74</td>
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<tr>
<td></td>
<td>2.5</td>
<td>9.29 ± 0.38</td>
<td>140.2 ± 6.3</td>
<td>2.99 ± 0.46</td>
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<tr>
<td></td>
<td>3.2</td>
<td>9.98 ± 0.81</td>
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<td>2.48 ± 1.16</td>
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<td>5%</td>
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<td>141.3 ± 18.5</td>
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<td>1</td>
<td>8.55 ± 0.64</td>
<td>151.7 ± 5.92</td>
<td>4.59 ± 0.77</td>
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<tr>
<td></td>
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<td>9.29 ± 0.94</td>
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<td></td>
<td>3.2</td>
<td>9.54 ± 0.86</td>
<td>130.4 ± 9.75</td>
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</tr>
<tr>
<td>10%</td>
<td>0</td>
<td>9.49 ± 0.4</td>
<td>150.4 ± 8.39</td>
<td>4.61 ± 0.84</td>
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<tr>
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<td>1</td>
<td>9.25 ± 0.42</td>
<td>146.8 ± 4.7</td>
<td>4.54 ± 0.97</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>8.96 ± 0.51</td>
<td>139.6 ± 12.5</td>
<td>4.22 ± 1.03</td>
</tr>
<tr>
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<td>3.2</td>
<td>8.92 ± 0.5</td>
<td>139.0 ± 13.3</td>
<td>4.22 ± 1.1</td>
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<tr>
<td>15%</td>
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<td>9.85 ± 0.66</td>
<td>144.1 ± 3.45</td>
<td>4.47 ± 0.6</td>
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<td>2.5</td>
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<td>139.0 ± 9.72</td>
<td>4.81 ± 1.01</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>9.89 ± 0.31</td>
<td>137.8 ± 6.6</td>
<td>4.05 ± 0.87</td>
</tr>
<tr>
<td>20%</td>
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<td>10.09 ± 0.45</td>
<td>111.3 ± 14.0</td>
<td>2.59 ± 1.02</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>10.05 ± 0.53</td>
<td>125.9 ± 12.7</td>
<td>3.6 ± 1.13</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>9.5 ± 0.75</td>
<td>122.2 ± 6.6</td>
<td>3.6 ± 1.23</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>9.9 ± 0.26</td>
<td>118.1 ± 11.3</td>
<td>2.75 ± 0.77</td>
</tr>
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</table>
nanocomposite was observed at 20 wt% of CNF loading. Surprisingly, the elongation at
break of the nanocomposites increased with the CNF loading in comparison with pure
LCP. Some reduction in the elongation at break was observed at 20 wt% of CNFs loading
but its value is still higher than that of pure LCP. LCPs are unique in their flow behavior,
as compared to conventional thermoplastics. LCPs form domains in the melt state which
get oriented and fibrillated in the elongational flow such as occurs in fiber spinning or
extrusion process. The latter leads to higher mechanical properties [222]. Hence, the
orientation of CNFs along with the orientation and fibrillation of LCP chains can
drastically improve the mechanical properties of the LCP/CNF nanocomposites.
However, CNFs on addition to the LCPs in melt state, may hinder the fibrillation process
or alignment of the LCP chains along the flow direction and, hence, no improvement in
mechanical properties was observed even on an addition of 20 wt% of CNFs. The same
behavior was also reported for LCP reinforced with carboxylated MWNTs [226]. On the
other hand, due to improved dispersion of the CNFs in a polymer matrix in the present
study, the mechanical properties also did not decrease even at such a high CNFs loading,
as compared to other study where even addition of even 5 wt% of CNFs showed
significant decrease in the mechanical properties [225]. To the best of our knowledge, this
is the first study showing no drop in the Young’s modulus and tensile strength along with
an increase in the elongation at break of LCP/CNF nanocomposite moldings in
comparison with those of pure LCP.

A significant improvement in the mechanical properties of CNFs based
nanocomposites can be achieved by providing orientation to the CNFs. As discussed
above LCPs domains also get oriented in the elongational flow giving rise to the very
high mechanical properties. LCP/CNFs nanocomposites were melt spun at different draw ratios to obtain oriented LCP domains and CNFs. The LCP/CNF nanocomposites were drawn only up to 5 wt% of CNFs; higher CNFs loading nanocomposites were difficult to draw due to high viscosity and melt fracture leading to breakup of spin line stream. Therefore, only rod-like strands were obtained. From the Figure 6.11 and Table 6.2, it can be seen that mechanical properties of fibers do get affected with the ultrasound, CNFs loading and with the draw down ratios (DDR).

It can be seen from the result in Table 6.2, that fiber spinning enhanced the mechanical properties of LCP/CNF nanocomposites by about 4 times at certain DDR in comparison with those of moldings. The Young’s modulus of pure LCP fibers at DDR of 75 increased by about 400 % in comparison with the moldings (from about 10 GPa to about 40 GPa). The tensile strength of pure LCP fibers at DDR of 75 was also increased in comparison to moldings by over 600% (from about 140 MPa to 865 MPa). It was observed that as the DDR increased the mechanical properties of nanocomposite fibers increased significantly indicating the alignment of the CNFs and LCP domains along the fiber axis. It was also observed that as the CNFs loading increased, the mechanical properties get decreased in the drawn fibers, which again indicates that these small nano scale fibers hinder the fibrillation process of the LCP domains and, hence, results in lower mechanical properties. The toughness of the LCP/CNF nanocomposite fibers also decreased as the CNF loadings increased. It is because of the increased brittleness of drawn fibers due to increased CNF loading.
Figure 6.11. Young’s modulus (a), tensile strength (b), elongation at break (c) and toughness (d) as a function of CNF concentration for melt spun fibers at DDR of 30 without and with ultrasonic treatment at an amplitude of 3.2 μm.
Table 6.2. Mechanical properties of LCP and LCP/CNF nanocomposite fibers without and with ultrasonic treatment at an amplitude of 3.2 μm and various draw down ratios.

<table>
<thead>
<tr>
<th>CNF, wt%/μm/DDR</th>
<th>Young's modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Toughness (MPa)</th>
</tr>
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<td>11.72 ± 2.84</td>
</tr>
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<td>845.2 ± 58.0</td>
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<td>10.52 ± 2.12</td>
</tr>
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<td>960.58 ± 43.0</td>
<td>2.61 ± 0.19</td>
<td>13.31 ± 1.38</td>
</tr>
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<td>4.20 ± 0.27</td>
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</tbody>
</table>
6.3.5. Thermal analysis

The thermal stability of the prepared nanocomposites was studied using thermal gravimetric analysis. The degradation curves for pure LCP and nanocomposites containing different loadings of carbon nanofibers have been presented in Figure 6.12 and 6.13. It can be seen from Figure 6.12 that at around 875°C the residual amount in all prepared nanocomposites is approximately 33% or more of the initial weight. There was not much improvement in the thermal stability of the prepared nanocomposites was observed on addition of the carbon nanofibers. It was observed that for nanocomposites with 20 wt% loading there was almost 54% residual weight in the temperature range studied, an almost 20% more than that for the neat LCP resin. It can be seen from Figure 6.13 that ultrasonic treatment does not have much effect on the thermal stability of the prepared nanocomposites.

Figure 6.12. TGA curves for LCP/CNF nanocomposites with various loadings of carbon nanofibers without ultrasonic treatment.
Figure 6.13. TGA curves for LCP/CNF nanocomposites with 20 wt% loading of carbon nanofibers without and with ultrasonic treatment.
6.3.6. Morphology

As received CNFs have large aspect ratio (>100) with diameters varying from 70 to 200 nm. Some catalyst impurity and amorphous carbon may also be present in these samples [198]. The SEM micrograph for as received CNFs reported in [227] indicated the presences of agglomerated nanofibers in the form of bundles of size ranging from 10 to 50 μm. The disc shape compression molded LCP/CNF nanocomposites for microscopic studies were used. Due to formation of the LCP fibril structure upon injection molding it was difficult to break the injection molded impact bars to get the leveled surface for SEM studies. Figure 6.14 shows the SEM micrographs of untreated (a) and ultrasonically treated (b) compression molded nanocomposites filled with 20 wt% CNFs. It is clearly seen from the micrographs that the fibrillation in LCPs is totally destroyed on addition of high loading of CNFs. It is very difficult to distinguish between LCP fibers and CNFs as both are looks to be of same structure. However, it can be clearly seen that samples ultrasonically treated at an amplitude of 3.2 μm (Figure 6.14 b) shows that the CNFs are more uniformly distributed across the whole matrix, whereas in case of untreated samples (Figure 6.14 a) LCP rich areas as big as 4 μm can be observed easily. SEM micrographs were taken at different magnifications and at different places. In case of the untreated samples LCP rich areas as big as 7 μm in size can be seen (Figure 6.14 c), whereas a uniform distribution of CNFs in the LCP matrix was observed in ultrasonically treated samples without an occurrence of LCP rich areas (Figure 6.14 d).
Figure 6.14. SEM micrographs of surface of cryofractured moldings at different locations of untreated (a,c) and ultrasonically treated (b,d) LCP/CNF nanocomposites of 20 wt% loading at an amplitude of 3.2µm.
6.4. Conclusions

Ultrasound assisted twin screw extrusion process with separate feeding of CNFs in the melt state was developed for manufacturing LCP/CNF nanocomposites. Ultrasonic treatment caused significant reduction in die pressure. The complex viscosity, storage and loss moduli of LCP/CNF nanocomposites significantly increased with increase of CNF loadings. However, no significant effect was observed upon ultrasonic treatment. Ultrasonically treated samples shows lower electrical percolation threshold values than the untreated ones, indicating the better dispersed but interconnected network of CNFs in a polymer matrix. An addition of CNFs in a LCP reduces the fibrillation of matrix. Hence, no significant improvement in the Young’s modulus and strength of moldings was observed on an addition of CNFs into the matrix. However, a significant improvement in the elongation at break of moldings was found upon an addition of CNFs to LCP. In comparison to moldings, melt spun fibers of LCP and nanocomposites shows tremendous increase in the Young’s modulus and tensile strength due to increased orientation of LCP domains and CNFs. In fibers a decrease in mechanical properties was observed on an increase of CNFs content. This indicates the destruction of fibrillar structure of LCP domains due to the presence of CNFs. Hence, this results in reduction in mechanical properties of LCP/CNF fibers. Microscopic studies show that ultrasound does help in improving the uniform dispersion of CNFs in a LCP matrix leading to the elimination of LCP rich areas. In comparison with existing literature available on LCP/CNF nanocomposites showing reduction of mechanical properties upon an addition of CNF or
CNT in comparison with those of pure LCP, the present study for the first time shows that mechanical properties can be preserved or improved along with significant improvement of the electrical conductivity.
CHAPTER VII

PROCESSING AND CHARACTERIZATION OF PEEK/MWNT NANOCOMPOSITES
PREPARED BY HIGH POWER ULTRASONIC WAVES

In the present work, PEEK/MWNT nanocomposites were prepared using ultrasound assisted single screw extruder. In comparison to the previous study in chapter IV, the screw designed was modified to reduce the breakage of the CNTs due to intensive shearing process. The melt star mixing element at the end of the screw, after the ultrasonic section, was replaced with the screw flights. The effect of ultrasonic treatment on the state of dispersion of CNTs was studied using rheological, morphological, mechanical, electrical and thermal characterizations.

7.1. Introduction

PEEK is a semi-crystalline high performance thermoplastic material having excellent chemical resistance and thermal stability. It has high mechanical properties with very good melt processability. Since PEEK has been around since the late 70’s significant research has been done on both the neat resin and its composites. In comparison to thermoset, PEEK based composite have shown interesting advantages and have found extensive applications in aerospace industry [229,230]. A number of studies have been done on PEEK composites containing carbon fibers, carbon nanofibers (CNFs) and carbon nanotubes (CNTs) [230,233,237].
In this study, PEEK has been reinforced with CNTs to prepare the advanced
generation materials.

The uses of CNTs as reinforcing agent in polymer matrix to fabricate high
performance polymer nanocomposites have gained considerable attention in recent years.
Due to excellent thermal, mechanical and electrical properties of nanotubes along with
their light weight, these polymer nanocomposites expected to have applications in many
fields. The performances of advanced polymer nanocomposites are greatly influenced by
the degree of dispersion of carbon nanotubes in a polymer matrix and an interaction
between the nanotubes and the matrix. Since in these nanocomposites, two chemically
dissimilar components are combined at the nanometer scale, they are too small to act as
stress concentrators. Even after almost two decades of discovery of CNTs their potential
as low loading filler has not been fully achieved and challenge still remains to utilize the
exceptional properties obtained at nanoscale level in macroscopic materials [43,231].

To our knowledge, there has been no work done to improve the dispersion of
carbon nanotubes in polyetheretherketone matrix with the help of ultrasound assisted
extrusion process.

This work presents a novel method for the continuous dispersion of carbon
nanotubes in a polymer matrix. Ultrasound assisted single screw extrusion of
PEEK/MWNT has been carried out. As compared to previous study in chapter IV, the
screw design was modified to prepare the PEEK/MWNT nanocomposites, as discussed in
section 3.3.1.1. In the new designed instead of mixing element after ultrasonic section, a
screw flights were introduced to reduce the breakage of the CNTs during intensive
shearing process. PEEK was chosen because of its extensive use in composites for
aerospace applications due to its desirable combination of mechanical and thermal properties. The effects of ultrasound on die pressure, electrical conductivity, rheological, morphological and mechanical properties were studied.

7.2. Experimental

In this section, ultrasonic extruder, experimental procedure to prepare polymer nanocomposites, processing conditions and characterization methods have been discussed.

7.2.1. Ultrasonic extruder

For melt processing, a single screw extruder equipped with high power ultrasonic attachment on barrel surface, having a diameter of 1 inch and L/D of 33, was used. Two mixing elements and ultrasonic treatment zone were made along the barrel. The details of the single screw extruder have been discussed in section 3.3.1.1. The schematic presentation of screw can be seen in Figure 3.3. As compared to the previous study, there were simple screw flights at the end of the extruder, after the ultrasonic treatment zone, instead of the melt star mixing element. This was done to reduce the intensive shearing action of the melt star mixing section and to avoid the excess breakage of the nanofiller. Two horns oscillating at a frequency of 20 kHz were mounted on the barrel and a constant gap thickness of 2.54 mm was maintained and molten compound was subjected to ultrasonic amplitudes of 0, 5.0, 7.5 and 10 μm. Ultrasonic horns were cooled using water at a constant temperature of 90°C. The screw speed was set up at 40 rpm to obtain a flow rate of 1 kg/hr.
7.2.2. Preparation of PEEK/MWNT nanocomposites

The PEEK pellets were mixed with 1, 2, 5, and 10 wt% MWNT loading in a plastic bag by hand mixing. The polymer and CNTs were dried for a minimum of 24 hrs at 110 °C in a vacuum oven prior to processing. The mixture was fed in the feed zone of the single screw extruder in a flood feeding manner. A pressure transducer was mounted on the barrel before the ultrasonic treatment zone. The temperature in the barrel section was set 300 °C in the feed zone and, 340 °C along the rest of the barrel and die section. The screw speed was adjusted at 40 rpm to obtain a flow rate of 1kg/hr. The residence time was 7s in the ultrasonic treatment zone. Extrudates were quenched in a water bath and were online pelletized using grinder.

7.2.3. Characterization

The rheological properties of the nanocomposites were studied using an ARES, TA Instruments. Prepared nanocomposites were compression molded into a disc of 25 mm diameter and 2.2 mm thickness at 365 °C using the compression molding press (CARVER 4122, Wabsah, IN). A 25 mm parallel plate geometry in oscillatory shear mode with dynamic frequency sweep test was used at 360 °C for a fixed strain amplitude of 2%. The studied frequency range was 0.03 rad/s to 100 rad/s. The complex viscosity, storage modulus, loss modulus and loss tangent were obtained as a function of the angular frequency. The disc shaped sample was placed between the heated parallel plates and squeezed and then excess material was removed from the sides to remove any boundary effects. Data acquisition was carried out with the aid of a microcomputer interfaced with the rheometer.
A Keithley electrometer (Model 6517A) equipped with an 8009 test fixtures was used to measure the volume and surface resistivity of the nanocomposites in accordance with the ASTM D257 method. Samples for electrical conductivity measurements were compression molded into disc of 90 mm diameter and 1 mm thickness using compression molding press. Alternating polarity method with ± 1V was used to improve repeatability [232]. Measurements were done 3 times for each specimen. The lower voltages was chosen as at higher voltages, electrometer get short circuited and was tripped for high loading CNTs. Hence it was very difficult to do any measurement at higher voltage for whole filler loading range.

Tensile bars according to ASTM D-638 were prepared using the HAAKE mini-jet piston injection molder at a temperature of 400 °C and mold temperature of 200 °C. The injection pressure was 640 bars in each case. High temperature mold release agent (Frekote HMT2) was sprayed before injecting the material. Tensile measurements on injection molded samples, without the use of the extensometer, were carried out using an Instron testing machine Model 4204; Instron Corp. Tests were carried out on minimum five samples at cross head speed of 5 mm/min using a 10 kN load cell. Samples were tested without the use of extensometer. The highest value of deviation for tensile strength and Young’s modulus was around 10%. Prepared nanocomposites were compression molded into discs of 25 mm diameter and 2.2 mm thickness at 365 °C using the Carver 4122 compression molding press, for the rheological measurements. The samples for electrical conductivity measurement were also compression molded into discs of 90 mm diameter and 1 mm thickness.
Microscopy study was carried out on PEEK/CNT nanocomposites to see the effect of ultrasonic waves on the state of dispersion of carbon nanotubes in a polymer matrix. Surface morphology and dispersion of CNTs was investigated using High resolution scanning electron microscopy and optical microscope. High resolution electron microscopy was performed on cryofractured injection molded tensile bar samples, without sputter coating, using field emission high resolution scanning electron microscope (HRSEM, Model JEOL JSM-7401 F, Tokyo, Japan). The optical microscope was used to study the macro size dispersion and distribution in a large scale at low magnification (x50-100). For optical microscopic study, specimens were prepared using a microtome (MS1B, microstar Technologies) at room temperature. Thin sections with a thickness of 0.5-1 μm were cut and collected on a glass slide to be analyzed under the optical microscope.

Thermal behavior was studied using a differential scanning calorimeter (DSC, Model Q200, TA instrument) and thermal gravimetric analyzer (Model HiRes TGA 2950, TA instruments). DSC was used to study the effect of CNTs loading on the crystallinity of the polymer matrix. The experiments were run at a heating rate of 10°C/min from room temperature to 370°C under N2 atmosphere. Between 5-7 mg of sample cramped in an aluminum hermetic pan was used in each run. Two consecutive heating runs were performed to eliminate any thermal history. Between the two heating runs, samples were cooled at controlled heating rate of 10°C/min.

Thermal gravimetric analysis (TGA) was performed on samples to study the effect of addition of CNTs on the thermal stability of the polymer matrix using (HiRes TGA 2950, TA instruments, New Castle, DE, US) at a heating rate of 20°C/min from
30°C to 900°C under nitrogen atmosphere. Each time about 12-20 mg of sample size was used.

7.3. Results and discussion

The results obtained after the characterization of the PEEK/MWNTs nanocomposites have been discussed in detail in this section.

7.3.1. Process characteristics

The entrances die pressure and power consumption for PEEK and nanocomposites as a function of ultrasonic amplitudes at various loadings of CNTs is shown in Figure 7.1 and 7.2, respectively. The measured pressure is before the ultrasonic treatment zone of PEEK/MWNT composites. There is a tremendous increase in die pressure with the increase of CNTs loading, as expected, due to increase in viscosity caused by increase of CNTs loading. It was observed that ultrasonic treatment causes the reduction of die pressure. A continuous decrease in die pressure was observed with the increase of ultrasonic amplitudes. This improves the processability of melt and provides a possibility in achieving faster extrusion rate. These effects are due to a combination of heating from dissipated energy from ultrasound, cavitation effect from ultrasonic waves leading to some thixotropic and permanent changes in polymer, reduction in friction at horn surfaces due to ultrasonic vibrations and possible shear thinning effect created by ultrasound waves.

The measured power consumption is the total power consumption during the treatment of nanocomposites, a part of which is dissipated as heat whereas the rest is
being utilized to disperse nanotubes in melt and increasing the polymer-nanotube interaction. Power consumption increased with the increase of CNTs loading. It is due to the fact that viscosity increased with CNTs loading which in turn required more energy to disperse the CNTs bundles. It was also observed that power consumption increased with the increase of ultrasound amplitude indicating more energy was transmitted from horns to polymer melt.

Figure 7.1. Die pressure versus ultrasonic amplitude at different MWNTs loadings.

Figure 7.2. Power consumption versus ultrasonic amplitude at different MWNTs loadings.
7.3.2. Rheology

The complex viscosity of PEEK/MWNT nanocomposites as a function of frequency for untreated and ultrasonically treated samples at various CNTs loading is shown in Figure 7.3. The complex viscosity increased by orders of magnitude with the increase of CNTs loading. A decrease in complex viscosity was observed for ultrasonically treated samples. The ultrasonic treatment does not have significant effect on the pure polymeric chains as not much reduction in viscosity was observed in treated samples. However, it seems that degradation of polymeric chains may become more pronounced in the presence of CNTs and the effect was more severe at high CNTs loadings. Possibly, there is a competition between the degradation of polymer chains and length of CNTs due to breakage and the increased dispersion of the CNTs due to ultrasonic cavitation phenomena. Ultrasonic treatment does break the bundles of CNTs and hence increased the dispersion, which can be seen from HRSEM micrographs (see Figure 7.10), which in turn should increase the complex viscosity by restricting the movement of molecular chains at local level due to increased surface area, as discussed in previous studies [227,228]. However, it seems that molecular chain scission and breakage of CNTs due to ultrasonic treatment overcomes the effect of improved dispersion and result in permanent reduction of viscosity. The existence of rheological percolation threshold can be understood by plotting complex viscosity versus MWNT concentration at low (0.03 rad/s) and high (75.35 rad/s) frequencies for untreated and ultrasonically treated samples at 10 μm, as shown in Figure 7.4. A sudden increase in the complex viscosity is observed on an addition of 2 wt% of MWNT indicating the
possibility of occurrence of rheological percolation threshold in the same range as of electrical percolation threshold discussed later.

![Complex viscosity as a function of frequency for untreated and ultrasonically treated PEEK/MWNT nanocomposites containing 0 to 10 wt% MWNT obtained at various ultrasonic amplitudes.](image)

Figure 7.3. Complex viscosity as a function of frequency for untreated and ultrasonically treated PEEK/MWNT nanocomposites containing 0 to 10 wt% MWNT obtained at various ultrasonic amplitudes.

The storage modulus, $G'$ (Figure 7.5) and loss modulus, $G''$ (Figure 7.6) of nanocomposites were increased by orders of magnitude with the increase in CNTs loading. A greater increase in $G'$ was observed as compared to $G''$ as CNTs loadings increased. It was observed that at higher loadings, $G'$ vs. frequency curve is almost reaching a plateau at low frequency indicating the existence of interconnected structure of anisotropic filler [76,227]. The storage modulus also increased with frequency, however the increase is more pronounced at low frequency rather at high frequency. The decrease in the storage modulus with ultrasonic treatment for all loadings was also observed and it further indicates the enhanced degradation of polymer chains and breakage of CNTs with
the application of ultrasonic waves. The same behavior was also observed for the loss modulus for all ultrasonic amplitudes.

Figure 7.4. Complex viscosity versus MWNT loading at frequencies of 0.03 rad/s and 75.34 rad/s for untreated and ultrasonically treated nanocomposites at an amplitude of 10 μm.

Figure 7.5. Storage (G’) modulus as a function of frequency for untreated and ultrasonically treated PEEK/MWNT nanocomposites containing 0 to 10 wt% MWNT obtained at various ultrasonic amplitudes.
Figure 7.6. Loss ($G''$) modulus as a function of frequency for untreated and ultrasonically treated PEEK/MWNT nanocomposites containing 0 to 10 wt% MWNT obtained at various ultrasonic amplitudes.

The effect of ultrasound and nanotubes loading on damping characteristics of the nanocomposites is shown in Figure 7.7. As the nanotube content increases the tan $\delta$ decreases and the curve becomes more flat in the low frequency region [80,227]. An increase in tan $\delta$ was observed on the ultrasonically treated nanocomposites indicating the competition between the chain degradation and increased nanotubes dispersion. This effect is in contrary with earlier study [227] on PEI/MWNT nanocomposites where reduction of tan $\delta$ was observed after ultrasonic treatment in twin screw extruder.
Figure 7.7. Tan δ as a function of frequency at various MWNT loadings for untreated and ultrasonically treated PEEK/MWNT nanocomposites at an ultrasonic amplitudes 10 μm.

7.3.3. Electrical resistivity

The volume resistivity results of nanocomposites as a function of CNTs loading are plotted in Figure 7.8. The volume resistivity decreased by $10^{10}$ times with 2 wt% loading. A sharp reduction in resistivity is observed between 1 and 2 wt% nanotubes content indicating the percolation threshold between 1 and 2 wt% nanotube loading which is in accordance with the percolation threshold reported for PEI/MWNT nanocomposites prepared by melt processing method [227]. In another study [238] on PEEK/SWNT nanocomposites, no percolation threshold was observed within the studied range of carbon nanotubes loading. It was suggested that studied carbon nanotube loading range was above the percolation threshold. No significant change in resistivity occurred with further increasing the nanotube loading up to 10 wt% and with ultrasonic treatment. It was observed that at 2 wt% loading of CNTs, an increase in volume resistivity was
observed upon ultrasonic treatment. This is possibly due to enhancement of dispersion and breakage of nanotubes in ultrasonically treated samples as these two effects lead to reduction of number of contacts between the nanotubes, therefore, causing an increase of the resistivity. No further decrease in volume resistivity of nanocomposites was observed with further increase of CNTs loadings. This is due to achievement of percolation threshold at lower loading. The measurement were done at low voltages for the comparison purpose as it was difficult to do measurements for high CNTs loadings due to tripping of electrometer at high voltages.

Figure 7.8. Volume resistivity as a function of MWNT loading for untreated and ultrasonically treated nanocomposites at various ultrasonic amplitudes.
Surface resistivity of nanocomposites as a function of MWNTs concentration is shown in Figure 7.9. It was observed that surface resistivity of nanocomposites decreased by more than 4 orders of magnitude on addition of 10 wt% of MWNTs. A sharp decrease in the surface resistivity for both untreated and ultrasonically treated samples was observed between 2 and 5 wt% of MWNTs loading. A further decrease in surface resistivity was observed with increasing MWNTs loading upto 10 wt%. It can be seen that at 2 wt% of MWNTs loading, untreated samples shows more decrease in resistivity as compared to the ultrasonically treated samples. This could be possibly due to the increase in dispersion of nanotubes and at the same time increased breakage of nanotubes with ultrasonic treatment. As these two effects leads to reduction in number ofcontacts between the nanotubes hence resulting in increase of resistivity. The same behavior was seen in volume resistivity measurement too as shown in Figure 7.8.

Figure 7.9. Surface resistivity as a function of MWNT loading for untreated and ultrasonically treated nanocomposites at various ultrasonic amplitudes.
7.3.4. Mechanical properties

The effect of CNTs loading and an ultrasonic treatment on mechanical properties of PEEK/MWNT nanocomposites have been presented in Figure 7.10. The results have been summarized in Table 7.1. In general, there is a tendency of an increase in the Young’s modulus on an increase of CNTs loadings. There is no significant change in the tensile strength of the nanocomposites was observed on addition of CNTs. At certain conditions of ultrasonic treatment the tensile strength of the nanocomposites is reduced. It could be due to the enhancement of degradation of polymeric chains in the presence of CNTs and a possible breakage of CNTs on application of ultrasonic waves. A similar linear increase was observed in case of PEEK/CNF nanocomposites where the tensile modulus was found to be increased from 4 GPa for pure PEEK matrix to 5.6 GPa for a CNF loading of 15 wt% [233]. In another study [234] for melt processed PEEK/MWNT nanocomposites, at 15wt% MWNT loadings, were tested for tensile properties above and below the glass transition temperature and 163% increase in the tensile modulus was observed for above glass transition temperature and 89% increase for below glass transition temperature. In study [235], sandwich like single walled carbon nanotubes (SWNT) paper/PEEK composites were prepared using hot compress method. It was observed that resulting composite with one layer of SWNT paper, exhibited about 40% increase in the Young’s modulus and 4% increase in the failure strength. However, as the number of SWNT layers increased the failure strength and the elongation at break decreased significantly. It was due to some air bubbles in the composites containing multi layer of SWNT paper which acts as defects and results in pre-fracture of the material.
Figure 7.10. Young’s modulus (a) and tensile strength (b) versus MWNTs loadings of nanocomposites at different ultrasonic amplitudes.
Table 7.1. Mechanical properties of PEEK/MWNT nanocomposites at different MWNT loadings and ultrasonic amplitudes.

<table>
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<th>MWNT (wt%)</th>
<th>Ultrasonic amplitude (mm)</th>
<th>Young's modulus (Gpa)</th>
<th>Tensile strength (MPa)</th>
<th>Yield strain (%)</th>
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<td>6.14 ± 0.81</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>1.801 ± 0.183</td>
<td>90.09 ± 4.04</td>
<td>7.58 ± 0.35</td>
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<tr>
<td></td>
<td>10</td>
<td>1.853 ± 0.14</td>
<td>87.29 ± 2.59</td>
<td>6.66 ± 0.43</td>
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7.3.5. Thermal studies

Thermal gravimetric analysis (TGA) was performed to study the effect of addition of carbon nanotubes on the thermal degradation behavior of the prepared nanocomposites. Results of the thermal gravimetric analysis of unfilled PEEK and CNT filled nanocomposites have been given in Figure 7.11 and 7.12. It can be seen from the results that there was not much change in thermal degradation temperature of the neat material on addition of the carbon nanotubes and on application of the ultrasonic amplitude.

Differential scanning calorimetric (DSC) analysis was performed to study the effect of addition of carbon nanotubes and ultrasonic amplitudes on the crystalline behavior of the filled and unfilled prepared nanocomposites. The degree of crystallinity was calculated using the following formula:

$$\Phi_c = \Delta H_{m, \text{PEEK}} / (\Delta H_{\text{PEEK}}^0) \times 100$$

where $\Delta H_m$ is the heat flux at melting of a given polymer and $\Delta H_{\text{PEEK}}^0$ is the heat flux at melting of the 100% crystalline polymer and the value was taken as 130 J/g [236]. Two runs on each samples were performed to eliminate the time - temperature thermal history. The second heating curve, run at the same rate, was taken as basis for all calculations. The DSC curves for second heating run have been shown in Figure 7.13. A slight shift in the second order transition region towards the higher temperature was observed with the increase of the MWNTs loading. There was no significant change in the glass transition temperature and melting temperature with addition of multiwalled carbon nanotubes and with ultrasonic treatment. The results have been summarized in the Table 7.2. It can be seen from the results there was a decrease in the degree of crystallinity as the CNTs
loadings increased. A significant decrease in crystallinity was observed at 10 wt% of CNTs loading. The similar results have also been reported in other studies [237,238]; however, no significant decrease in crystallinity was observed on addition of SWNTs upto 1 wt% of loadings.

Figure 7.11. TGA curves for PEEK/MWNT nanocomposites filled with various loading of MWNTs without ultrasonic treatment.
Figure 7.12. TGA curves for PEEK/MWNT nanocomposites filled with 10 wt% loading of MWNTs at various ultrasonic amplitudes.
Figure 7.13. DSC curves during the second heating for PEEK/MWNT nanocomposite for different nanotube loadings without and with ultrasonic treatment at amplitude of 10 μm.
Table 7.2. DSC crystallinity of PEEK/MWNT nanocomposites at different CNTs loadings and different ultrasonic amplitudes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT(wt%)</th>
<th>Amplitude (µm)</th>
<th>ΔH_m(J/g)</th>
<th>ϕ_c</th>
<th>T_g (°C)</th>
<th>T_m(°C)</th>
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<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>55.36</td>
<td>42.6</td>
<td>150.2</td>
<td>344.4</td>
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<td>2</td>
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<td>51.59</td>
<td>39.7</td>
<td>149.0</td>
<td>344.5</td>
</tr>
<tr>
<td>3</td>
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<td>42.3</td>
<td>150.3</td>
<td>344.2</td>
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<td>41.6</td>
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<td>51.01</td>
<td>39.2</td>
<td>150.6</td>
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</tr>
<tr>
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<td>49.91</td>
<td>38.4</td>
<td>150.3</td>
<td>345.1</td>
</tr>
<tr>
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<td>34.3</td>
<td>150.9</td>
<td>345.4</td>
</tr>
<tr>
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<td>45.88</td>
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</tr>
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<td>34.0</td>
<td>151.4</td>
<td>344.4</td>
</tr>
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<td>45.71</td>
<td>35.2</td>
<td>152.1</td>
<td>344.7</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>10</td>
<td>45.46</td>
<td>35.0</td>
<td>152.5</td>
<td>345.0</td>
</tr>
</tbody>
</table>
7.3.6. Morphology

The HRSEM micrographs sputter coated surfaces of treated and untreated nanocomposites filled with 5wt% CNTs, are presented in Figure 7.14. The bundles of CNT or agglomerates are clearly visible in the untreated sample, whereas there is no bundle of CNTs can be found in ultrasonically treated samples. CNTs seem to be uniformly distributed throughout the matrix in ultrasonically treated samples. The micrographs have taken at different locations and at different magnifications. Figure 7.15 shows the micrographs were also taken of surfaces without sputter coating. The bundles of CNTs can clearly be seen in ultrasonically treated samples (Figure 7.15a), however no bundles was found to be in ultrasonically treated samples and CNTs seems to be distribute uniformly throughout the polymer matrix. Micrographs were also taken for prepared nanocomposites with different CNTs loading. Figure 7.16 shows the micrographs of nanocomposites filled with 2wt% CNTs for untreated and ultrasonically treated samples. It was observed that the untreated sample shows the resin rich part along with a network of nanotubes (Figure 7.16 a), whereas the treated sample seems to indicate dispersed nanotubes forming the network all over the polymer matrix (Figure 7.16b). Another interesting observation can be made about the length of the carbon nanotubes. It can be seen that the ultrasonically treated sample shows reduced in length nanotubes as compared to the untreated ones. This fact also gets supported by other characterization techniques such as rheological and electrical conductivity where viscosity and volume resistivity was observed to be decreased with the ultrasonic treatment (see section 7.3.2 and 7.3.3).
Figure 7.14. HRSEM micrographs of sputter coated surface of cryofractured moldings of untreated nanocomposites (a) and ultrasonically treated nanocomposites (b) at 5wt% MWNT loading and an amplitude of 10 μm and at different magnifications.
Figure 7.15. HRSEM micrographs of without sputter coated surface of cryofractured moldings of untreated (a) and ultrasonically treated (b) nanocomposites at 5 wt% MWNT loading and an amplitude of 10 μm and at different magnifications.
Figure 7.16. HRSEM micrographs of sputter coated surface of cryofractured moldings of untreated nanocomposites (a) and ultrasonically treated nanocomposites (b) at 2wt% MWNT loading and an amplitude of 10 µm and at different magnifications.
Optical microscope was used further to investigate the state of dispersion and distribution of carbon nanotubes on a large scale at very low magnifications. Optical micrographs at x100 magnification have been presented in Figure 7.17. It can be seen from the micrographs that samples treated with ultrasound shows much more dispersion of nanotubes with very few bundles. However, it can be clearly seen that untreated samples shows a large number of carbon nanotubes agglomerates as compared to the treated ones suggesting that ultrasound does help in breaking the bundles of nanotubes and hence increasing its dispersion in polymer matrix.

Figure 7.17. Optical micrographs of microtomed samples of untreated (a) and ultrasonically treated (b) nanocomposites at 2 wt% MWNT loading and an amplitude of 10 μm and at x100 magnification.
7.4. Conclusions

PEEK/MWNT nanocomposites were melt processed using ultrasound assisted single screw extruder. The ultrasonically treated nanocomposites shows decrease in die pressure and tremendous changes in rheological behavior. The decrease in complex viscosity and storage modulus of ultrasonically treated samples indicates the competition between increased dispersion of nanotubes and the degradation of the polymeric chains and CNT length on application of high power ultrasonic waves. As a result of ultrasonic treatment the volume resistivity increased near the percolation threshold limit indicating the increased dispersion with reducing physical contacts between the nanotubes. The addition of nanotubes does not have any effect on the thermal degradation behavior of polymer matrix. A significant decrease in the crystallinity of the polymer matrix was observed on addition of 10 wt% of CNTs. It was observed that PEEK/MWNT nanocomposites have behaved differently with the ultrasonic treatment as compared to the studies discussed in previous chapters. It could be possibly due to the action of excessive shearing and ultrasonic treatment which possibly degraded the polymer chains and reduce the length of the carbon nanotubes. The degradation behavior seems to be enhanced in the presence of the MWNTs and with the ultrasonic treatment.
CHAPTER VIII
SUMMARY

A novel ultrasonic extrusion process was developed for manufacturing of high performance polymer nanocomposites containing carbon nanotubes and carbon nanofibers. The effectiveness of ultrasonic extrusion process to continuously disperse the nanofillers, within few seconds, in polymer matrix was demonstrated.

Three different types of thermoplastic high performance polymer matrices, both amorphous and semi-crystalline, were studied. The polymer matrices studied were polyetherimide (PEI), liquid crystalline polymer (LCP) (a copolymer of hydroxybenzoic acid and hydroxynapthoic acid) and polyetheretherketone (PEEK). The multi walled carbon nanotubes (MWNT) and carbon nanofibers (CNFs) were used as the reinforcing fillers. The effect of ultrasonic treatment was evaluated on PEI/CNF, PEI/MWNT, LCP/CNF and PEEK/MWNT nanocomposites. It was observed that ultrasonic treatment breaks the bundles of nanofillers in polymer matrices and improve their dispersion which in turn improve the mechanical and electrical properties of the prepared nanocomposites.

Effect of ultrasonic energy at a frequency of 20 kHz on the PEI and PEI/CNF nanocomposites with CNFs loadings upto 20 wt% was studied in a single screw extruder. The ultrasonic amplitude was varied from 0 to 10 μm. Process characteristics (die pressure and power consumption) were measured. The effect of CNFs loading and ultrasonic amplitude on the state of dispersion of nanofillers and resulting effect on rheological, mechanical, electrical, thermal and morphological properties of the
nanocomposites was studied. Morphological studies showed the presence of resin rich part and CNFs bundles in case of untreated samples whereas carbon nanofibers were fully dispersed in the ultrasonically treated samples. It was observed that improved dispersion of CNFs due to ultrasonic treatment results in increase of complex viscosity, storage modulus and reduced damping characteristics of prepared nanocomposites as compared to the untreated ones. The ultrasonically treated samples also showed lower electrical percolation threshold value and higher thermal conductivity as compared to the untreated ones indicating the better dispersed network of nanofillers in a polymer matrix. At certain conditions, ultrasonically treated nanocomposites showed improved mechanical properties as compared to untreated ones.

Effect of ultrasonic treatment at a frequency of 40 kHz on the PEI and PEI/MWNT nanocomposites with MWNT loadings upto 10 wt% was studied in a twin screw extruder. The ultrasonic amplitude was varied from 0 to 6.0 μm. Ultrasonic treatment reduced the die pressure enabling to run the high MWNTs loading. A significant increase in complex viscosity, storage modulus and damping characteristics was observed in ultrasonically treated samples as compared to the untreated ones indicating the improved dispersion of CNTs due to ultrasonic treatment. Both the rheological and electrical percolation threshold values lies between 1 and 2 wt% loading. At certain conditions, ultrasonically treated samples showed increase in mechanical properties. In particular, the Young’s modulus in treated nanocomposites show increase in value at 5 and 10 wt% loadings. At 10 wt% CNTs loading, the tensile strength was increased from 115 MPa to 123 MPa for treated samples at an amplitude of 2.5 and 4.0 μm. From high resolution SEM studies, it was observed that the PEI matrix getting
coated or wrapped around the MWNT showing the existence of interfacial interaction between filler and the matrix.

A separate feeder was used to add the CNFs in the LCP melt to reduce the breakage of CNFs in high stress feed zone of twin screw extruder. Ultrasonically treated samples at a frequency of 40 kHz showed a lower electrical percolation threshold value than the untreated ones indicating the better dispersed network of CNF in polymer melt. The addition of CNFs to the LCP interferes with the fibrillation process of the LCP matrix and hence no significant improvement in the Young’s modulus and tensile strength was observed. However, a significant improvement in the elongation at break of moldings on addition of CNFs to LCP was observed. It was observed that, as compared to the moldings, melt spun fibers of LCP and LCP/CNF nanocomposites showed tremendous increase in the Young’s modulus and tensile strength due to increased orientation of LCP domains and CNFs.

Effect of ultrasonic treatment at a frequency of 20 kHz on the PEEK and PEEK/MWNT nanocomposites with MWNT loadings upto 10 wt% was studied in a single screw extruder, with modified screw design without having mixing element after the treatment zone. The ultrasonically treated samples showed decrease in complex viscosity and storage modulus indicating the competition between increased dispersion of carbon nanotubes and degradation of polymeric chains on application of high power ultrasonic energy. Ultrasonically treated samples showed the increased volume resistivity near the percolation threshold value indicating the increased dispersion of nanotubes with reducing physical contacts between the nanotubes and also suggesting the possibility of the breakage of the nanotubes due to intensive shearing action in extrusion. No change in
thermal degradation behavior of PEEK was observed on addition of the nanotubes, however, a significant decrease in the crystallinity of the polymer matrix was observed with addition of 10 wt% of nanotubes.

In summary, a novel single screw and twin screw extrusion processes were developed for continuous dispersion of CNFs and CNTs in high performance polymer matrices.
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