A Dissertation
Entitled

Solid State Polymerization, Processing and Properties of PEN/PET Blends

by

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Blends of Poly (ethylene naphthalate) (PEN) and Poly (ethylene terephthalate) (PET) have attracted research interest because they combine the excellent properties of PEN with the economy of PET, and have commercial potential in the plastic packaging industry. The current work is a continuation of intensive research conducted on PEN/PET blends at the Polymer Institute at The University of Toledo. Acknowledging the effects of the transesterification levels and molecular weights of the blends, on the manufacturing of final products from PEN/PET blends, we brought solid state polymerization (SSP) into the PEN/PET blends processing cycle. After the blends were prepared using a twin screw extruder, they were subjected to SSP before the preform injection molding and bottle stretch blow molding processes. SSP has been proven to be a very effective method to
both enhance the miscibility of the two polymer phases and upgrade the molecular weights of the blends. The solid stated blends were used to produce bottles with a conventional PET injection molding and stretch blow molding process, without any changes in the machinery design. Blend bottles with optimal mechanical, optical, and barrier properties were obtained.

Systematic investigations were conducted on PEN/PET blends with PEN weight fractions of 5%, 10%, and 20%. Through approaches utilizing variation in IV and the end group concentrations, the kinetics and mechanisms of solid state polymerization reactions were investigated. Results have shown that the polymerization reactions were diffusion controlled rather than chemical reaction controlled. Important factors such as SSP temperatures, SSP times, blend compositions and initial precursor IV values of the precursor were investigated in terms of their effects on these reactions.

Results obtained with \(^1\)H NMR showed that transesterification reactions between PET and PEN occurred during SSP. The transesterification reactions were investigated in terms of SSP times, temperatures, blend compositions and initial IV of blend precursor. By assuming a second order transesterification reaction the reaction rate constant and activation energy were obtained for each blend.

Investigations were conducted on the blend samples to study the effects of SSP and transesterification reactions on several important thermal properties such as melting behavior, non-isothermal crystallization behavior, cold crystallization behavior and
thermal stability of the blends. It has been found that crystallization ability of the blends during non-isothermal and cold crystallization was reduced as a result of SSP and transesterification reactions. By conducting AA generation experiments, we found that blend thermal stability was improved by the SSP process.

Fabrication processes of injection molding and stretch blow molding of the blends were investigated. Minimum injection molding temperatures required to achieve optically clear preforms were shown to decrease for the solid stated blends as a result of enhanced miscibility between PET and PEN through the transesterification reaction during SSP. By monitoring the temperature profiles of the blend preforms, we found that the minimum stretching temperatures required to prevent stress whitening from occurring is about 22°C higher than T_g of each blend with different PEN weight fractions. An upper limit of stretching temperature was determined for each blend in order to obtain uniform thickness distributions in the bottle sidewalls. It has been found that the increased molecular weight of PEN/PET blends, as a result of SSP, is the key to producing good bottles from the PEN/PET blends. These bottles were characterized in terms of birefringence values, strain induced crystallinity levels, mechanical properties, and oxygen barrier properties.
DEDICATION

To my wife and my parents for their endless love and support.
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Chapter 1

Introduction

1.1 Introduction to PET and PEN

1.1.1 Properties and applications of Poly (ethylene terephthalate) (PET)

PET is a major member of the synthetic polyester family and of great importance in industrial applications. PET was first prepared in 1941 when J. R. Whinfield and J. T. Dickson, both working at Calico Printers Association in Accrington U.K. filed their patent application for this fiber-forming polymer. During the last five decades, PET has found itself in commercial markets for a variety of applications such as textiles and industrial fibers, films, foamed articles, containers for various beverage products such as carbonated soft drinks, water, tea, and fruit juices as well as thermoformed applications. Commodity fibers still remain the largest group among the three principal products, fibers, films and bottles, made of PET while films account for the smallest or about 10% of total PET consumption. Currently bottle grade PET is experiencing a rapid growth rate and has overtaken that of fiber grade PET in the United States and Western Europe. The annual growth rate of PET bottle resin is about 15% while it is less than 5% for fiber
resins. In 2000 the worldwide PET consumption in carbonated beverages and other foodstuff containers reached 12 billion pounds.

The big success of PET is a direct result of the combination of its low manufacturing cost and its excellent balance of properties, including ease of melt processing, high strength, high gaseous barrier, optical clarity, ability to strain induced crystallize, thermal resistance, high impact strength, good creep resistance, dyeability, environmental safety, and recyclability. All of these properties originate from the chemical structure of PET, which is shown in Figure 1.1.

![Chemical structure of PET](image)

Figure 1.1 Chemical structure of PET

PET is a semicrystalline aromatic polyester. Depending on the fabrication methods and conditions PET can be made into amorphous or crystalline forms. PET has a glass transition temperature (T_g) of around 80 °C and melting peak temperature (T_m) of around 255 °C.

There are two major approaches for production of PET differing in the starting raw materials used: the terephthalic acid (TPA) and ethylene glycol (EG) approach, and the
dimethyl terephthalate (DMT) and EG approach. In both methods, first, the diester bis (hydroxyl ethylene terephthalate) (BHET) is formed either by the direct esterification of purified TPA and EG or by the transesterification of DMT and EG, with water or EG as the byproducts. Secondly, BHET is polymerized by melt phase polycondensation reactions to produce PET, as shown in Fig.1.2. The catalysts used in melt phase polycondensation of PET include acetates of antimony (Sb), zinc (Zn) or lead (Pb), oxides of Sb, germanium (Ge), or Pb, Ti (OR)₄ and organotin compounds.
1st step:

\[
\text{TPA} + 2 \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{COOCH}_2\text{CH}_2\text{OH} + 2 \text{H}_2\text{O}
\]

2nd step:

\[
\text{DMT} + 2 \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{COOCH}_2\text{CH}_2\text{OH} + 2 \text{CH}_3\text{OH}
\]

Figure 1.2 Main reactions involved in PET polymerization.

Because of the difficulty in the purification of TPA the earlier PET plant production schemes were based on DMT technology. All the modern PET plants, however, follow the TPA route because of the increased availability of purified TPA as a result of technology advances in the TPA purifying processes. [2]
Depending upon the specific end-uses, different levels of molecular weight of PET should be selected. In industry, generally, the molecular weight of PET is reported as intrinsic viscosity (IV) or limiting viscosity number, \([\eta]\). The relationship between IV and molecular weight depends on the conditions of the measurements e.g. solvent system, and temperature. The typical IV ranges for different applications are listed in Table 1.1.\(^3\)

<table>
<thead>
<tr>
<th>Uses</th>
<th>IV (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textiles</td>
<td>0.55-0.65</td>
</tr>
<tr>
<td>Film &amp; Tape</td>
<td>0.65-0.75</td>
</tr>
<tr>
<td>Tire Cord</td>
<td>1.0</td>
</tr>
<tr>
<td>Bottles</td>
<td>0.70-1.00</td>
</tr>
</tbody>
</table>

The textile grade PET can be directly obtained through melt phase polymerization. In order to obtain high IV of bottle or tire cord grade PET, however, a separate process called solid state polymerization (SSP) should be applied to the PET pellets after the melt phase polymerization. The SSP process will be described in more details in section 1.3.
1.1.2 Properties and applications of Poly (ethylene 2, 6-naphthalene dicarboxylate) (PEN)

PEN, first synthesized in 1948 by ICI scientists [7], is a close cousin to PET in the polyester family. Its use has become more promising in various industrial applications during the last twenty years, due to its superior properties compared to those of PET and other polyesters. These properties result from the unique chemical structure of PEN as shown in Fig. 1.3.

![Chemical structure of PEN](image)

Figure 1.3 Chemical structure of PEN

In the position of the benzene ring on the PET main chain, PEN has a naphthalene repeat unit. The two condensed aromatic rings impart more stiffness in the PEN chain and account for the improvements in PEN’s physical and chemical properties, compared to those of PET. PEN has a higher glass transition temperature \((T_g)\) of about 122 °C as opposed to about 80 °C for PET. PEN offers four times higher oxygen barrier, five times better carbon dioxide barrier and 3.5 times better moisture barrier than PET. PEN also provides more UV light resistance and has better mechanical properties. Table 1.2 lists the comparative properties between PET and PEN. [1]
Table 1.2 Property comparison between PET and PEN

<table>
<thead>
<tr>
<th>Property</th>
<th>PET</th>
<th>PEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature $T_g$ (°C)</td>
<td>80</td>
<td>122</td>
</tr>
<tr>
<td>$O_2$ permeation (cm$^3$ mm/[m$^2$ day atm])</td>
<td>2.4</td>
<td>0.6</td>
</tr>
<tr>
<td>$CO_2$ permeation (cm$^3$ mm/[m$^2$ day atm])</td>
<td>12.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Water vapor transmission (g mm/[m$^2$ day atm])</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Hydrolysis resistance (h)</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>45</td>
<td>60</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>3900</td>
<td>5200</td>
</tr>
<tr>
<td>UV absorbance at 360 nm (%)</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>Radiation resistance (MGy)</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>Mechanical continuous use temperature (° C)</td>
<td>105</td>
<td>160</td>
</tr>
<tr>
<td>Wet shrinkage (% at 100 °C)</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Dry shrinkage (% at 150 °C)</td>
<td>1.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

PEN is also a crystallizable polyester, but with a reduced crystallization tendency\textsuperscript{[8]} and has a $T_m$ around 265 °C, which necessitates higher fabrication temperatures. Depending on the thermal history PEN’s crystalline phase can exist in two major crystalline modifications, an $\alpha$ form or $\beta$ form. Both forms are triclinic. When the crystallization temperatures are less than 200 °C the $\alpha$ crystalline form is obtained with the dimensions of $a = 0.651$ nm, $b = 0.575$ nm, and $c = 1.320$ nm, and angles of $\alpha = 81.33^\circ$, $\beta = 144^\circ$ and $\gamma = 100^\circ$, and a density of 1.407 g/ml. The crystal structure of the $\beta$ form, obtained at
crystallization temperature greater than 240 °C, has dimensions of a = 0.926 nm, b = 1.559 nm, and c = 1.273 nm, and angles of α = 121.6°, β = 95.57° and γ = 122.52°, with a density of 1.439 g/ml. [8]

The manufacturing methods of PEN are similar to those of PET and also follow two routes differing in the starting raw monomers used: dimethyl-2,6-naphthalenedicarboxylate (NDC) and EG, or 2, 6-naphthalenedicarboxylic acid (NDA) and EG. Currently the primary monomer used is NDC because of the very limited availability of high purity NDA, which is even more difficult to extract and purify than TPA, used for PET manufacturing. In addition to this, NDC was also in low productivity especially before the early 1990s when the method to produce it was extraction from petroleum, where NDC has low abundance. These difficulties faced by the PEN industry explain the fact that the commercial markets’ development of PEN is much more delayed than those of PET, although PEN is only seven years younger and offers much better properties by comparison. The situation has improved to some extent during 1995, when Amoco Chemical Company began to supply high purity NDC in amounts of up to 60 million pounds per year. Currently the resin cost is still too high for PEN to be able to take over PET’s leading position in polyesters. This is in spite of growing market pressures demanding products with levels of performance beyond the capabilities of current PET, such as high thermal stability, high mechanical properties, high O₂ barrier, and high UV resistance.
Nevertheless, the superior properties of PEN offer potential for polyesters to fill the commercial applications gap between PET and high performance plastics such as polyimides. With improvement in the economics of manufacturing, it is expected that PEN will replace polyimides or even glass in many applications. Various products made of PEN are already in commercial markets and in use worldwide, such as the PEN bottles and jars in Japan, [9] PEN returnable/ refillable beer bottles in Denmark, [10] and PEN cosmetic bottles in Japan. [10]

End-uses for PEN fall into the following four categories:

(1) Films applications, including magnetic storage, photographic media, electrical-electronic and light management applications, new applications such as flexible packaging, weatherable films and appliances. [11]

(2) Packaging applications, including returnable/ refillable beer and mineral water bottles, hot fill bottles for foods, juice, and sports drinks, sterilizable bottles, pharmaceutical/cosmetic applications, and industrial and specialty applications. [10]

(3) High performance fibers, including tire reinforcement, hosing, belting, sailcloth, engineered monofilament. [12]

(4) Engineering resins applications such as in the areas of automotive, electrical, food and medical uses. [13]
1.2 PEN/PET blends

1.2.1 Why blend?

Although PET is a very good packaging material used in a wide variety of applications, it has limitations in some areas. Because of their relatively high oxygen permeability monolayer PET bottles cannot be used for packing some oxygen sensitive beverages such as beer and orange juice. Without utilizing special technology such as heat setting or other kinds of heat treatment, PET bottles would have difficulty withstanding the conditions applied during hot fill of many foods and juices. In these areas an excellent alternative would be PEN, however, commercial applications of PEN are limited by its manufacturing costs. Combining the superior properties of PEN with the economy of PET through blending or copolymerization, therefore, is a practical way to achieve better performance materials, and has been attracting interest from both industrial and academic researchers.

Although copolymerization can give the needed intermediate material properties, blending is a better way to follow especially for bottle fabrication using stretch-blow molding process, where some extent of crystallinity is always required for the stretch blown products in order to have the desired mechanical and barrier properties. It has been reported that the PEN/PET blends have broader compositional range capable of being crystallized than the copolymers as illustrated in Fig. 1.4. [14] When the blend/copolymer composition is represented by the mole percent of monomer NDC used in the product,
the copolymer can only be crystallized readily when either PET or PEN constitutes the major phase. The blend, on the other hand, are crystallizable in the region from 15 NDC% to 85 NDC%. Thus blends are expected to have more commercial importance than copolymers.

Fig. 1.4 Thermal Properties of PET/PEN blends and copolymers \[^{14}\]

In order for PEN/PET blends to be put into practical use, especially for the stretch blow molded bottles, there are two major concerns.
1.2.2 Important concerns for PEN/PET blends

Miscibility

Miscibility between the polymer components is a concern during blending. Most polymer pairs are thermodynamically immiscible because of the positive free energy change ($\Delta G$) during mixing. This is true in the case of PEN/PET blends. The properties of the blends are to a large extent determined by the miscibility of the polymers. Poor adhesion at the interface will result in poor mechanical properties such as lower impact resistance and elongation at break. PEN/PET blends are inherently immiscible and opaque (milky-ivory) parts will generally result when insufficient miscibility between these two polymers is achieved. This is because the particle size of the dispersed phase is big enough to scatter the incident light. Only when the particle size is brought down as a result of sufficient miscibility between the two phases can a transparent polymer be obtained.

Various methods are available to promote the compatibility between components in polymer blends. Using block or random copolymers, possessing segments with chemical structures similar to those of polymers in the blend, is becoming increasingly important and it is the principle used in the reactive compatibilization of polymer blends. The copolymers can be added to the mixture of polymers or formed $in situ$ between the functional groups in the polymers.\[^{15}\] These copolymers act as compatibilizing agents to
decrease the surface energy thus inducing compatibilization in the system. More detailed discussion is presented in the literature review section.

In polyester blends, such as PEN/PET blends, the transesterification reaction between the two polyesters could produce the required copolymers to increase their compatibility. Most of the research on the transesterification reaction and its effect on miscibility in PEN/PET blends has focused on melt mixing or solution mixing of PET and PEN. [16-26] It was found that temperature and time are the main factors controlling the reactions in the melt phase. [17] In order to achieve sufficiently high levels of transesterification reactions in the blend, the melt mixing process would need to be operated either at relatively high temperatures or for longer residence times at moderate temperatures. This could cause undesired degradation reactions to the blends and deteriorate blends properties; therefore, a better process is thus desired to achieve the same compatibilization goal without negative effects on the blends.

Molecular weight

Another critical factor that needs to be taken into account for industrial applications, particularly packaging applications of PEN/PET blends, is the molecular weight. Using injection molding and stretch-blow molding to fabricate transparent bottles from polyesters is a very common practice in the packaging industry. The success of this injection-stretch-blow molding (ISBM) process depends heavily on three important properties of the polyester: the ability to crystallization, the slow crystallization kinetics
during cooling, and strain hardening ability of the polymer. The ability to crystallization is essential for the strain hardening to occur during the stretch blow molding process, and the slow crystallization rate will produce clear amorphous polymer preforms by injection molding. The polymer is drawn, at a temperature above $T_g$ during the preform blowing process. When the polymer is stretched beyond a value of stretch ratio called the natural draw ratio the strain hardening phenomena occurs together with the strain induced crystallization of the polymer chains. The occurrence of strain hardening helps the bottle maintain a uniform material distribution and an optimal orientation level of the bottle sidewall, and therefore optimal mechanical and barrier properties.

While a great deal of research has been done on the processes of manufacturing PET bottles, there is only a small amount of such work on PEN/PET blends. Tharmapuram and Jabarin [29] found that at the same molecular weight level PEN/PET blends have higher natural draw ratios than PET. They also found that this draw ratio is a function of blend composition. They concluded that PEN/PET blends of higher molecular weights than PET would be needed in order to produce optimal bottles using conventional ISBM machines without changing either preform or stretch blow mold design. One method to obtain higher molecular weight and transparent PEN/PET blends at the same time might be through directly melt blending high molecular weight PET and PEN by an extrusion process. This process has several disadvantages. Since melt-mixing often results in reducing IV we must begin with PET and PEN pellets with high enough molecular weights and consequently with high viscosities. These changes in turn will require higher operating temperatures resulting in higher degradation levels (i.e. high AA generation
and coloration). In addition, in order to obtain better mixed blends (i.e. achieving critical transesterification levels) we would have to use higher temperatures or longer residence times that also can cause undesired material degradation as discussed.

These two crucial concerns for PEN/PET blends cause us to ask if there is a better process, which can be applied to the blends so that they will possess both sufficient miscibility (transesterification reaction level) and high enough IV, without the disadvantages experienced in the melt mixing process. Solid state polymerization (SSP) is the required process.

1.3 Apply SSP to PEN/PET blends

A method widely used for increasing the relatively low molecular weight melt polymerized PET to a higher value required for bottle-grade PET resin is SSP. This reaction is carried out at a temperature below the melting temperature of PET, but above its glass-transition temperature. The temperature range (200-230 °C) is much lower than that of melt polymerization (250-300 °C); therefore, the thermal degradation can be significantly reduced and the cost of this operation is also lower than that of melt polymerization. Another advantage of SSP is that the byproduct of water or EG in the solid state polymer pellets is more easily removed by the inert gas purging or vacuum applied during the process compared to removal from the highly viscous polymer mixture in melt phase polymerization.
Because SSP is conducted at temperatures above $T_g$, the polymer pellets have great potential to be agglomerated together. An important step in SSP is to precrystallize the polymer pellets to a certain degree of crystallinity prior to the actual polymerization in order to prevent them from sticking to each other during the reaction. With the necessary ability to crystallize, PEN/PET blends are readily processable by SSP. In addition, it has been shown\textsuperscript{[30-32]} that the transesterification reaction can occur in the solid state of the blend at temperatures higher than $T_g$ and lower than the melting temperature of the blend. The SSP process therefore, is promising for PEN/PET blends in terms of both taking advantage of SSP to increase the molecular weight and for improving the miscibility between these two polymers simultaneously.

Our research has been designed to concentrate on applying SSP to the PEN/PET blends to obtain blends with both higher molecular weights and improved miscibility between these two polymers. See Fig.1.5 for the schematic diagram applying SSP to blends.
1.4 Objectives

PEN/PET blends have been attracting research interest since Shepherd et al. [33] introduced tri-component polymer blends of PET, PEN and a copolyester in 1991.

Beginning in 1994 the Polymer Institute at The University of Toledo has been pursuing a systematic study of PEN/PET blends. Shi and Jabarin [21-24] studied the transesterification reaction between PET and PEN during the melt blending process in an extruder. They found that the reactions were controlled by many factors such as blending temperature, blending time, blending compositions, and the different sources and viscosity matches of the two homopolymers. More importantly their work has shown that after passing some critical level of transesterification, the blend’s properties become constant in terms of the reaction and only vary with blend composition. Patcheak and Jabarin [34, 35] studied the structure and morphology of PET/PEN blends. Their results showed that quiescent crystallization of blends led to independent crystallization of the major component while the minor component was rejected into the amorphous phase. When the two components have similar fractions (such as 40% PEN/PET blends), both phases crystallize independently. They also showed that PET and PEN co-crystallized in the case of strain induced crystallization of blends. Jiang and Jabarin [36] studied the photo degradation of PEN/PET blends in terms of different weathering factors such as UV irradiation time and condensation. They found that blending PEN with PET improved the UV barrier properties of PET significantly.
It was believed that in order to produce containers from PEN/PET blends, either the design in preform produced from injection molding or the mold in blow molding needed to be specially adjusted for the blends.\(^1\),\(^9\) Obviously this will bring undesired cost increases in fabrication processes of the blends. The situation could be even worse when considering that different blend compositions would demand further modification on the machinery design. Therefore a better route would be to optimize the nature of the material to make it compatible with existing machine design. Encouragement to pursue change in this direction is offered by the work done by Tharmapuram and Jabarin\(^{29}\). They have predicted that conventional PET blow molding machines can be used for PEN/PET blends, without changing the preform or the mold design, provided the blends have higher molecular weights than usually required for PET resin.

Research in this area would not be complete without the successful preparation of PEN/PET blend products. As a continuation of work in the area of PEN/PET blends, the current project was designed to achieve the goal of producing PEN/PET blend containers with optimal properties. The key in fulfilling this goal is to bring the SSP process into the whole cycle of the PEN/PET blend fabrication process. By doing so we hope that better PEN/PET blends with improved miscibility and increased molecular weight can be used directly on the conventional injection molding and stretch blow molding equipment, without any changes in the machinery design. Therefore the following issues have been recognized to be the specific objectives of the current research:
a) Investigate the effects of important factors involved in the SSP process such as SSP time, SSP temperature, PEN concentration in the blends, and initial IV of blends precursors on the SSP reaction and transesterification reaction. Develop an understanding of the kinetics and mechanism of the polycondensation and transesterification reactions of the PEN/PET blends during the SSP process.

b) Establish the relationship between the thermal properties of the solid state polymerized PEN/PET blends and the SSP processing conditions. Important properties include the melting behavior, the dynamic crystallization behavior, the cold crystallization behavior, and the thermal stability (AA generation).

c) Utilize the conventional fabricating process (i.e. injection molding and stretch-blow molding) to manufacture clear bottle containers with optimum properties from the PEN/PET blends. Establish the relationship between the important processing parameters such as injection molding temperature, stretch blow molding temperature and the properties of the solid stated PEN/PET blends such as transesterification reaction level and molecular weight.
Chapter 2

Literature Review

2.1 Transesterification reactions: Effects on miscibility properties of PEN/PET blends

2.1.1 Compatibilization of polymer blends

The history of polymer blends can be traced back to more than a century ago when the first blends of trans- and cis- 1, 4-polyisoprene (i.e. the natural rubber with gutta-percha) were prepared in 1846. \[^{37}\] The modern era of polymer blending started with the commercial blends of polyphenyleneether (PPE) and styrenics in 1965. \[^{37}\] Since then polymer blends have become of tremendous commercial importance. This is due to the advantages of polymer blending being a very versatile and economic method to tailor-make polymer materials with the desired performances by combining the unique properties of available polymers. At present polymer blends consume over 80 wt % of all plastics and constitute about 20 – 40 % of the polymer market, according to different estimations. \[^{38,39}\] The polymer blends segment of the plastic industry grows at a pace of three times faster than that of the whole plastic industry. \[^{37}\]
The first challenge faced in the development of polymer blends is always to make the polymer components in the blends compatible with each other through the compatibilization process. Otherwise, the properties of the immiscible blends would be very poor, because of the poor interfacial adhesion, large domain size, and unstable morphologies.

A strict definition of “compatibility” in a thermodynamic sense would mean that the polymer blends are miscible on a molecular scale. Unfortunately, only very few polymers can meet the criteria and form truly miscible blends, homogenous down to the molecular level. The majority of the polymer pairs are immiscible.

From the second law of thermodynamics, two components will only mix when the following condition is met: \[^{[40]}\]

\[ \Delta G^M = \Delta H^M - T \Delta S^M < 0 \]

Furthermore, thermodynamic stability of a one phase mixture exists only when: \[^{[40]}\]

\[ \left( \partial^2 \Delta G^M / \partial \phi^2 \right)_{T,P} > 0 \]

where, \( \Delta G^M \) is the Gibbs free energy of mixing,
\( \Delta H^M \) is the enthalpy of mixing,
\( \Delta S^M \) is the entropy of mixing,
T, P is temperature and pressure of mixing,
\(\Phi\) is blend composition (volume fraction)

In the case of a polymer-polymer blend, the entropy term \(\Delta S^M\) is very small due to the small number of moles of each polymer in the blend as a result of their larger molecular weights. So the contribution to \(\Delta G^M\) from the term of \(T\Delta S^M\) will be small. Therefore miscibility can only occur for an exothermic polymer-polymer mixture, that is if the heat of mixing \(\Delta H^M\) is negative. For endothermic mixtures (\(\Delta H^M > 0\)) miscibility can only occur at very high temperatures. In general, \(\Delta H^M\) for nonpolar polymer systems is positive. So only when very similar structures or precisely matched solubility values exist for these nonpolar polymers, can they form miscible blends at normal temperatures. There are only very rare cases for such a condition to be satisfied. \(\Delta H^M\) can become negative for mixture of polymers, when specific interactions exist among these polymers. Examples of these interactions include hydrogen bonding, acid-base, charge-transfer, ion-dipole, donor-acceptor interactions. \[^{[38]}\] This shows that compatibility, defined as miscibility of polymers down to the molecular level, can only exist for a small group of polymers either having precisely matched solubility values or certain specific interactions.

Another definition for compatibility is "technological compatibility", which means the blend does not separate into its individual components and possess a desirable set of properties. \[^{[41, 42]}\] As shown in Fig. 2.1 the immiscible blends have separated macroscopic phases with minimal interfacial adhesion and unstable morphologies. The compatibilized blends although also macroscopic phase separated, have increased interfacial adhesion,
more finely dispersed phase, and satisfactory physical and mechanical properties as a result of added interfacial agents or chemical bonds formed at the inter phase.\cite{43}

Fig. 2.1 Difference between miscible, immiscible, and compatibilized blends\cite{43}

There are many methods we can choose in order to achieve the compatibilization of the phases. Among them, reactive compatibilization is becoming increasingly common. This method can be categorized into the following groups as suggested by Xanthos and Dagli.\cite{44}
1) Utilize reactions of functionalized blend components to produce *in situ* compatibilizing and interchain block or graft copolymers, such as the transesterification reactions in PEN/PET blends.

2) Add a polymeric compatibilizer, which can be a reactive copolymer or functionalized polymer, in the form of A-C, where A is one homopolymer component in the blend of polymers A and B, and C has the ability to chemically react with another homopolymer component B.

3) Add low molecular weight components, such as catalyst or curing agent, to promote copolymer formation and/or cross linking reactions.

The strategy of utilizing *in situ* copolymer formation is more preferred than the others. It is a more economic choice. In addition, the reactions occur directly at the interface and the copolymer formed can act more effectively as a compatibilizer to promote interface adhesion and morphology stabilization, compared to the case of adding separated species which must diffuse to the interface with difficulty. \[^{41}\] The classic view of how such copolymers are located at the interface is shown in Fig. 2.2. \[^{42}\]
The copolymers concentrated at the interface between two originally immiscible polymer phases act as the polymeric surfactant or emulsifiers to lower the surface tension and promote interfacial adhesions between the dispersed and matrix polymer phases. \[^{[41]}\]

Wu \[^{[45]}\] studied the formation of dispersed phase of incompatible polymer blends during melt extrusion in a twin screw extruder. He found a master curve exists for the relationships among the dispersed-drop size, shear rate, interfacial tension, and viscosities of matrix and dispersed phases. The equation for the master curve is shown below:

\[
\frac{G \eta_m a}{\gamma} = 4 p^{0.84}
\]

Where, \(G\) is the shear rate,

\(\eta_m\) is the viscosity of continuous phase,

\(a\) is the particle diameter,
\( \gamma \) is the interfacial tension,

\( p \) is defined as the ratio of the viscosity of dispersed phase \( (\eta_d) \) over that of continuous phase \( (\eta_m) \), \( p = \frac{\eta_d}{\eta_m} \).

We can see that the dispersed particle size is proportional to the interfacial tension between the two phases. Reduced interfacial tension will decrease the dispersed particle size. Therefore, copolymers formed as a result of reactive compatibilization will make the dispersed particle size smaller.

Milner and Xi \cite{46} recently proposed that rather than reducing the interfacial tension, the formed copolymers induce repulsive interactions between droplets and prevent them from collision-induced coalescence in the mixing flow.

We can see that the effects of copolymers on the compatibilization of two polymers in the blend are complex. Nevertheless, these copolymers are critical in the compatibilization process by reducing the dispersed particle size in the resultant blend.

2.1.2 Studies of interchange reactions in polycondensation polymers

Among all the polymer blends, the blends between polycondensation polymers such as polyesters, polyamides, and polycarbonates are widely studied for the copolymer forming interchange reactions, because of the numerous reactive groups (such as \(-\text{COO}^–\), \(-\text{CONH}^–\), \(-\text{OH}^–\), \(-\text{COOH}^–\), \(-\text{NH}_2^–\)) that exist in their polymer chains or at their chain ends.
Examples of such blend systems include (bisphenol A polycarbonate) PC/poly(butylene terephthalate) PBT, \textsuperscript{[47-56]} PC/PET \textsuperscript{[57-81]}, PET/PBT, \textsuperscript{[82-85]} PET/PEN, \textsuperscript{[16-27]}, PET/ polyarylate (PAR), \textsuperscript{[63, 64, 95, 96]} PET/liquid crystalline polymer (LCP), \textsuperscript{[97]} PBT/LCP, \textsuperscript{[98, 99]} PC/LCP, \textsuperscript{[100-105]} nylon 6/nylon 6,6, \textsuperscript{[103]} PET/nylon 6, \textsuperscript{[104-108]} PET/nylon 6,6, \textsuperscript{[109-111]} PC/nylon 6. \textsuperscript{[112-115]}

Several techniques have been used to study the interchange reactions in terms of the copolymer formation, miscibility, and the physical properties of the blend systems. Infrared spectroscopy (IR), which reflects the molecular vibrations that causes changes in the dipole moment and polarize ability of the molecular chains, is a very useful tool to detect new components or products formed as the result of interchange reactions. NMR is an even more powerful method in the study of polymer microstructure, miscibility and the chemical changes in polymer pairs, as well as the kinetics of the interchange reactions (i.e, the reaction rate and the extent of the reaction). NMR may, however, become less sensitive or inaccurate at very low or very high levels of the interchange reactions. \textsuperscript{[116]}

The thermodynamics of interactions between blend components can be changed from the beginning of the reaction. Therefore, methods such as DSC, DTA, and DMA, which detects the thermal or thermomechanical behaviors, have also been of primary use in the study. Morphological changes resulting from the interchange reactions can be followed by X-ray diffraction, scanning electron microscopy (SEM) or transmission electron microscopy (TEM). As a consequences of the interchange reactions the skeletal structure, the molecular weigh and the molecular weight distribution of the polymers will also change simultaneously. Some chromatography techniques sensitive to these kinds of
changes can also be used to follow the reactions. Examples are thin-layer chromatography (TLC) and size exclusion chromatography (SEC).

The mechanism of the interchange reactions in polycondensation of polymer blends, particularly of the transesterification reactions in polyesters blends, has been extensively studied. There is, however, no final agreement on the matter. As has been reviewed by Kotliar [117] the transesterification reaction is a collective term that encompasses three main reactions:

**Intermolecular alcoholysis:**
\[
-\text{O} - \text{CO} - + -\text{OH} \rightleftharpoons -\text{OH} + \text{CO} - \text{C}
\]

**Intermolecular acidolysis:**
\[
-\text{O} - \text{CO} - + -\text{COOH} \rightleftharpoons -\text{COOH} + \text{CO} - \text{C}
\]

**Ester-ester interchange (or transesterification):**
\[
-\text{O} - \text{CO} - + -\text{CO} - \text{O} - \rightleftharpoons -\text{O} - \text{CO} - + \text{CO} - \text{C}
\]

Devaux et al. [48-51] used the method of model compounds and NMR to investigate the transesterification reaction mechanism between PC and PBT. Model studies were conducted between polymer (PC or PBT) and small molecules, which were different case by case, corresponding to the specific reaction (i.e. alcoholysis, acidolysis, or ester-ester interchange) being studied. From the results they concluded that the direct ester-ester interchange reaction is the most likely mechanism for PC and PBT. This reaction is second-order reversible reaction.
The direct ester-ester interchange reaction is still the most widely agreed upon mechanism for the transesterification reactions between polyesters. This mechanism has; however, been challenged by other studies. Kenwright et al. [18] studied PEN/PET blends prepared by solution blending in different solvents, such that in one blend the hydroxyl end groups were capped. They provided clear evidence that hydroxyl end groups play a major role in the transesterification between PET and PEN. Study results from Collins et al. [19-20] also proved the significant effect of hydroxyl end groups on transesterification. A recent study from Alexandrova, [118] however, supports the ester-ester interchange mechanism. They conducted the kinetics study on the transesterification between PET and PEN using model compounds of ethylene dibenzoate (BEB) and ethylene dinaphthoate (NEN) and concluded that the ester-ester interchange is the prevailing mechanism and the overall reaction is second order reversible.

By taking into account the end-groups of the polymers and the reactive sites where reactions occur between different polymer chains, Montaudo et al. [119] proposed the inner-inner and outer-inner mechanism for the exchange reaction mechanisms as illustrated in Fig. 2.3.
Fig. 2.3 Schematic representation of the exchange reaction mechanism which can occur in polymers containing reactive function groups\textsuperscript{[119]}

By using polymers with different treatment (i.e. end group trapped or with active chain end groups) they investigated several polymer blends systems, such as PBT/PC, PET/PC, and nylon 6/PC, to determine the specific mechanisms involved.
2.1.3 Miscibility and properties of PEN/PET blends

Since Shepherd et al. [33] introduced the tri-component polymer blends of PET, PEN and a copolyester in 1991, the studies of mechanisms and kinetics of this transesterification reaction and its relationship to the blend properties have been attracting both academic and industrial interest.

Stewart et al. [17] studied PET/PEN blends with high PEN content melt-mixed through a single-screw extruder. They have observed that transesterification between PET and PEN was a strong function of blending time and temperature and a minor function of blend composition and catalyst system. The transesterification level was found to have a linear relationship to blending time. They also reported that about 10% transesterification level was required to produce a transparent product.

Andresen and Zachmann [86] studied PET/PEN blends coprecipitated from solution followed by different times of melt pressing and subsequently quenched in iced water. They found when the melt pressing time was short (0.2 and 0.5 min) there were two \( T_g \) values detected by DMA and two crystallization and two melting peaks from DSC, indicating separate PET and PEN phases. When the melt pressing time was longer than 2 min only one \( T_g \) and no crystallization and melting peaks indicating copolymers of PET and PEN were formed by transesterification during melt pressing.

Ihm et al. [87] also investigated the miscibility of solution coprecipitated PET/PEN blends. The blends were annealed for different times at different temperatures after solution
preparation. The properties of the blends were analyzed by WAXS, DSC, and NMR. These results showed that the physical blends of PET and PEN were immiscible in terms of two T_g values of the blends that were the same as those of pure PET and PEN. When the reaction reached 50% of the completely random state, the blends became non-crystallizable and showed only one T_g value as the results of transesterification reaction, which was influenced by both annealing time and temperature. The T_g value obeyed the Fox equation.

In a U.S. patent, Hoffman [31] discussed a method to increase the transesterification reaction level of PET/PEN blends in a solid state polymerization process. He showed that the molecular weight of the blend was also increased and the transesterification level was more easily controlled than in the case of melt extrusion.

Lee et al. [88] did research using solution coprecipitated PET/PEN blends. The blends were heat treated by DSC to 280 °C and annealed for different times. The ^1H NMR results showed copolymer formation by transesterification between the two polymers during annealing. Also the number average sequence lengths of the two polymers decreased with the increase of randomness. Originally separated T_g values approached each other as reaction times increased. By measuring heat capacity changes, at the T_g of the blends and homopolymers, the weight fractions of the two coexisting phases and the interfacial zone were calculated. This showed that the composition difference between phases decreases as the transesterification reaction proceeded.
Time resolved light scattering and 1H NMR were employed by Okamoto and Kotaka to study melt extruded PET/PEN blends. They found that at the early stage of annealing of the blends, phase separation occurred due to spinodal decomposition. After the formation of a sharp interface during the intermediate stage of annealing, the blends began a homogenization process as a result of transesterification at the interface. The addition of copolymer to the system was found to accelerate the homogenization process.

By using temperature modulated DSC (TMDSC) Kampert et al. showed essentially complete incompatibility between PET and PEN during the early stage of mechanical melt-mixing. Later blocky crystallizable copolymer was formed as a result of transesterification reaction.

Jun et al. studied the relationship between sequence distribution and transesterification of PEN/PET copolymer produced in a reaction tube. Their results showed that at a similar composition ratio, the degree of transesterification increased and the block length decreased with increased blending time. The melting peak was depressed with the increase of the minor component and disappeared at similar composition ratio. A critical chain length of three repeat units is needed for a component to be crystallized.

Bang et al. investigated phase behavior and structure development in melt extruded PET/PEN blends. Their results agreed with the results from Okamoto and Kotaka that the phase separation at the initial stage was due to spinodal decomposition and at later
stages the blends were homogenized by transesterification. Crystallization rate depended on the sequence distribution as the result of transesterification reaction.

PET/PEN blends with different compositions and transesterification levels were studied by Becker et al. \cite{Becker92} for their phase behavior, thermal transitions and melt rheological properties. The intrinsic viscosity results showed some significant deviation from the rule of mixing, which was caused mainly by the thermal degradation and also molecular weight reduction by transesterification reaction. It was also found that all the thermal transitions were strongly influenced by the transesterification level and a master curve was found for the melting temperature and relative degree of transesterification reaction.

PET and PEN oligomer blends were investigated by James et al. \cite{James93} in terms of their simultaneous solid state polymerization and transesterification. 1H NMR results showed that transesterification reactions were active during early stage of SSP. X-ray and DSC studied showed that SSP and transesterification occurred only in the amorphous phase. The increases in transesterification levels and increased melt viscosity made crystallization of the blends more and more difficult.

Yang et al. \cite{Yang94} studied the kinetics of transesterification in PET/PEN blends with and without a chain extender of 2, 2 – bis (1, 3- oxazolin) BOZ and confirmed the second-order reversible kinetics. The addition of BOZ was found to promote the transesterification by lowering the activation energy of reaction.
Shi and Jabarin [21-24] showed that the transesterification reaction between PET and PEN during the melting process is complicated and controlled by many factors such as blending temperature, blending time, blending compositions, as well as the different types and viscosity matches of the two homopolymers. Their work also showed that after passing some critical level of transesterification reaction, the blends’ properties became constant with the transesterification reaction level and only varied with blend composition. This is important since it means that in industrial applications, we can ignore the transesterification effects on the properties of these blends once the critical RD has been achieved. Also their study results showed the $T_g$ values of the blends increase almost linearly with blend composition, indicating copolymer-like behavior of the blend systems.

Patcheak and Jabarin [34, 35] studied the structure and morphology of PET/PEN blends. Their results showed that quiescent crystallization of blends led to independent crystallization of the major component while the minor component was rejected into the amorphous phase. When the two components have similar fractions (such as 40% PEN/PET blends), both phases crystallize independently. They also showed that PET and PEN co-crystallized in the case of strain induced crystallization of blends.

Tharmapuram and Jabarin [26-29] predicted the critical transesterification temperature during processing through the application of reaction kinetics, and investigated the influence of the equilibrium melting point of the miscible blends on the critical transesterification temperature. They also studied both the rheology and degradation
kinetics of the blends as a function of material composition. They have predicted that conventional PET blow molding machines can be used for PEN/PET blends, without changing the preform or the mold design, provided the blends have higher molecular weights than usually required for PET resin.

By the study of dynamic mechanical properties of PEN/PET blends, prepared by melt-mixing in a mixer, Aoki et al. [14] have observed that all the blends having a transesterification level of above 10% were in the one-phase state. They concluded this because the blends showed a single $T_g$ and the $T_g$ was independent of blending time, which in agreement with the observation of Shi and Jabarin. [21, 23] They also showed that the cold-crystallization of blends remained for the samples having number-average chain length PET or PEN blocks ($L_{\text{PET}}$ or $L_{\text{PEN}}$) larger than 5 repeat units. The cold-crystallization of the blends disappeared when $L_{\text{PET}}$ or $L_{\text{PEN}}$ were less than 5.

Po. et al. [32] found that the level of transesterification of PEN/PET blends increased during the SSP process and that a limiting value of randomness degree, attainable during SSP, seems to exist.

### 2.2 SSP of PET

Very little work [30-32] has been done on SSP of PEN/PET blends but there are many studies on SSP of PET. We can thus utilize those studies as references for our study of solid state polymerization of blends.
The temperature of SSP is kept below $T_m$ to prevent particle agglomeration and above $T_g$ to provide enough mobility for the polymer end groups to react. In practice, the process is usually carried out just below $T_m$ to take the advantage of the higher reaction rate at higher temperature. \textsuperscript{[120]} At higher temperatures, however, another problem arises which is sticking between particles. Since the precursor (the relative low molecular weight polymer before SSP) is usually amorphous and heated up to a temperature above 80 °C the pellets will stick together. For this reason before SSP the precursor is usually preheated to increase its crystallinity and prevent it from sticking.

It is generally accepted that the chemical reactions that occur in solid state during SSP are the same as those in the melt state and that the reaction occurs only in the amorphous phase or at the surface of the crystalline phase. One very important distinction between SSP and melt polymerization, however, lies in the mobility of the polymer chain ends. Before reactions can occur, the end groups of different polymer chains must diffuse to and collide with each other. In the solid state this required mobility is significantly restricted compared to the situation in the melt phase. In addition, the crystalline phase of the polymer would be expected to introduce restrictions to the polymer chain movement. Thus more complicated reaction kinetics is expected for SSP.

The two main reactions accounting for molecular weight increases during SSP of polyesters are the ester-interchange reaction and the esterification reaction as shown below:
The step-growth polymerization reactions in SSP are reversible equilibrium reactions. The removal of byproducts is favored to drive the reactions forward. This is accomplished by applying vacuum or flushing the reactor with inert gas (e.g. \( \text{N}_2 \)). The reaction rate is not only dependent on chemical, but also on physical processes, in terms of four possible steps. The overall polymerization rate will be controlled by one or more of these steps, depending on the operating and processing variables.

- Chemical reaction in pellets.
- Byproduct diffusion within pellets.
- Byproduct diffusion from pellets surface to gas stream.
- Polymer chain diffusion in the amorphous region.

Many factors influence the SSP process including:
• Reaction temperature
• Reaction time
• Particle size
• Crystallinity of precursors
• Initial IV of the precursors
• Carboxyl and hydroxyl end group concentration
• Inert gas flow rate
• Inert gas purity

A detailed review of studies concerning these factors can be found in articles written by Culbert and Christel, [121] and Goltner. [122]

In order to get a better understanding of SSP of PET various models have been developed by different researchers:

• A byproduct diffusion controlled model by Chang (1970). [123]

Chang established a diffusion model to study the kinetics of SSP of PET. He found that diffusion through the polymer is a controlling step, when temperature is higher than 210 °C and particle size is no smaller that 100 mesh. He also observed that the diffusivity is influenced by crystallinity and it is linearly proportional to the mass fraction of the amorphous phase in the PET polymer.
• An improved diffusion controlled model by Chen et al. (1987). [124]

In addition to the diffusion of byproducts, in this model they took into account the end group diffusion in the polymer. They also studied the esterification reaction that occurred during SSP. They found that at temperatures from 170 ºC to 200 ºC and particle size of 80-100 mesh the SSP is end group diffusion limiting. At temperatures from 210 ºC to 240 ºC and particle sizes of 14-16 mesh the ester interchange reaction is ethylene glycol (EG) diffusion limiting and the esterification reaction is end group diffusion limiting.

• A reaction-limited model by Ravindranath and Mashelkar (1990). [125]

In this model they assumed that ethylene glycol (EG) is the predominant byproduct and its removal will favor the forward reaction of the equilibrium main polycondensation reaction. By taking into account the contribution of EG formed, as a result of the polycondensation reaction, some fundamental errors imbedded in previous models have been corrected. The esterification and the degradation reactions of PET, during SSP, have been neglected in this model.

• A comprehensive model considering end groups diffusion limitation by D.Wu et al. (1997). [126]
This model was developed based on analyzing the similarities and differences between solid state polymerization and melt polymerization of PET. The end groups’ diffusion limitation and the modification of concentrations of end groups and byproducts in the amorphous phase have been considered. The degradation and other side reactions neglected in the earlier models were also included in this model.


This model was developed by the polymer segment approach, where the polymerization reactions are regarded as reactions between two functional groups. The effects of temperature and chain entanglement on chain mobility were considered to estimate the rate constants of chemical reactions. The diffusivities of volatile byproducts were determined using the free volume theory.

### 2.3 Injection molding and stretch blow molding

In the practice of making PET containers for carbonated soft drinks, water, and beer, injection-stretch blow-molding is widely used. There are two possible routes to follow for injection-stretch blow-molding. One is the single stage molding process, where the injection molded PET performs are cooled to a temperature greater than $T_g$ (called the orientation temperature) and directly transferred to a blow station to finish the process. Another process is called the reheat and blow process. In this process, the preform is
cooled in the injection mold to a temperature below $T_g$ and ejected out of the mold. Then the preform can be stored for a short period of time. Before the blowing process, the preform is reheated by IR radiation to the orientation temperature and then stretch blow molded into a bottle. Currently, the reheat and blow process is the one primarily used industrially. $[3, 26]$

### 2.3.1 Injection molding

During the injection molding process, the polymer is melted in the extruder and then injected into a mold cavity over a chilled core pin. The polymer melt is then solidified in the mold until its temperature is lower than $T_g$. Finally the mold opens and the preform is ejected, before the mold is closed for the next cycle.

The properties of the preform are determined by both processing conditions and the nature of the material. Minimizing IV drop, AA generation, and ensuring optically clear preform are of great importance.

Barnscome $^{[128]}$ studied the processing factors affecting preform properties and found that the injection molding temperature is the most significant factor for AA generation, while other minor factors include screw speed, back pressure, injection rate, and gate temperature. The injection temperature, hold pressure, injection rate and cooling temperature will influence the haze of the preform.
Schaul \cite{129} found that the hydrolytic degradation is the principle cause for the IV drop, so the resin needs to be dried to less than 50 ppm moisture content before undergoing the injection molding process. AA generation is a function of residence time, melt temperature and thermal history.

Stefandl \cite{130} pointed out that in order to get good clarity and minimize thermal degradation screw speed, cycle time, back pressure and injection pressure should be reduced.

Shukla and Jabarin \cite{131} investigated the effects of processing parameters on AA generation during injection molding of PET performs using gas chromatography (GC). Their results showed that the injection temperature is a more important factor than back pressure and shear rate to increase the AA generation rate. Increases in both back pressure and shear rate will cause increases in the melt temperature and AA generation.

Jabarin’s \cite{132} results showed that the haziness of a PET preform dramatically increases even at a very low level of crystallinity. The key to achieve clear preforms is to quickly quench the preform to the amorphous phase and prevent spherulites formation. For this reason material with low crystallization rate is preferred.

In other studies Jabarin \cite{133-135} has investigated the effects of molecular weight, crystallization temperature, moisture and catalysts used in resin preparation on the crystallization process of PET.
Results from Shi and Jabarin \cite{21, 22} on the isothermal crystallization of PEN/PET blends showed that the crystallization rate is slower for blend systems than for pure PET and reaches the lowest point when the two blended polymers have similar fractions.

For blends of PET and PEN the clarity of the preform will also be a function of the miscibility of the two components in the blends, since the large dispersed phase in the blends without enough compatibilization will impose haziness in the final product. Tharmapuram \cite{26, 29} conducted experiments to determine the critical injection molding temperature required to achieve optically clear PEN/PET blend preforms. Depending on the initial polymers used and PEN composition in the blends, this critical temperature could be as high as 310 °C.

2.3.2 Stretch blow molding

During stretch blow molding a PET preform is softened at a temperature greater than $T_g$ but lower than the cold crystallization temperature ($T_c$) of PET. The hot preform is then transferred to and enclosed in a bottle-shaped mold. A stretch rod is inserted into the preform through the preform mouth and rapidly stretches it to the bottom of the mold. At the same time high pressure air is introduced and blows the preform into a balloon-like shape. When the expanded PET bubble touches the cold metal surface of the mold it hardens and transforms into a rigid bottle. The simultaneous stretching and blowing process result in the biaxial orientation of PET polymer chains. As a result of this
orientation, strain induced crystallization occurs and causes strain hardening of the stretched polymer.

If the preform is heated to a temperature higher than $T_c$ the PET will crystallize, and cause haziness in the bottle sidewall. Lowering the temperature too close to or below $T_g$ will cause the appearance of pearlescence in the bottle sidewall. This is called stress whitening. A study by Kim [136] showed that this phenomenon is caused by microvoid formed in the cooler inner bottle sidewall during stretching.

The success of stretch blow molding in the production of PET bottles is largely due to PET’s ability of strain hardening. During deformation of PET, when it is stretched at a temperature higher than $T_g$ the strain hardening will occur when the stretch ratio is higher than a critical value called the natural draw ratio. This is the point at which the amount of stress needed for further elongation increases. Thinner sections of the PET preform will reach the natural draw ratio earlier than thicker sections, making it difficult for them to achieve further extension. Thicker sections, however, continue to be stretched at a higher rate that the thinner parts. Eventually, all sections deform at the same rate and thickness will become uniform in the bottle sidewall. The natural draw ratio is a function of both molecular weight and the stretching temperature. [2] Keeping other conditions constant, the lower the molecular weight or the higher the stretching temperature the higher the natural draw ratio.
Strain induced crystallization is different from thermal crystallization. Strain induced crystallization has a very fast crystallization rate and results in smaller crystallites than those resulting from thermal crystallization. An explanation for the difference has been given by Varma and Jabarin.\cite{137, 138} They have shown that as a result of the reduction in the conformational entropy change by chain extension, the melting point is increased and thus the degree of undercooling increases. As a result the nucleation rate and nuclei density increases dramatically.

Bonnebat et al.\cite{139} studied the uni- and biaxial stretching of PET specimens and showed that the natural draw ratio in both the uni- and biaxial mode decreases with the increasing molecular weight and these two parameters obey a linear relationship.

Jabarin\cite{5} investigated the relationships among physical properties, degree of orientation and molecular weight of PET films, as well as their dependence on orientation variables such as stretch ratio, and strain rate. The degree of orientation was represented by birefringence values. The results showed that the degree of orientation is a function of many variables including stretch ratio, strain rate, molecular weight, and orientation temperature. The mechanical and transport properties are dependent on degree of orientation. At the same degree of orientation the mechanical properties increase with increased molecular weight. The transport properties such as O\textsubscript{2} and CO\textsubscript{2} permeation are independent of molecular weight and are only a function of degree of orientation.
There is little research on the stretch blow molding of PEN/PET blends. By conducting free blow experiments on the blend performs Tharmapuram and Jabarin [26, 29] developed relationships among the natural draw ratio and molecular weight, PEN composition, and transesterification level of the PEN/PET blends. Results showed that the natural draw ratio increases linearly with decreasing molecular weight and increasing PEN composition. Once the transesterification level is beyond a critical value, the natural draw ratio will be independent of transesterification level.
Chapter 3

Polycondensation and transesterification reactions during SSP: kinetics and mechanism

3.1 Introduction

As a result of the limitations of melt polymerization and the advantages of solid state polymerization, SSP is a widely used process in the molecular weight upgrading of polyesters including PET, PEN, PBT, and Poly (trimethylene terephthalate) (PTT). PEN/PET blends are obtained from two polyesters (i.e. PET and PEN). They possess the required reactive groups (e.g. –OH and –COOH end groups) for the polycondensation reactions, as well as the necessary ability to crystallization. They can therefore be subject to SSP to increase their molecular weight, just as the pure polyesters are. In addition, the transesterification reactions have been found to create enhanced compatibility between the two polymers components. This is brought about by the copolymers produced as a result of the reactions that proceed simultaneously in the PEN/PET blends during the SSP process. [31, 32, 93]
The first publication on SSP of PET/PEN blends is from Po. et al. [32]. In 1996 they showed that the level of transesterification of the blends increased during SSP, and a limiting transesterification level seems to exist for long time SSP process.

In a 1997 U.S. patent, Hoffman [31] discussed the method of using SSP to increase the transesterification reaction level of PET/PEN blends. The patent shows that the molecular weight of the blends was also increased and the transesterification level was more easily controlled than during melt extrusion.

Recently James et al. [93] investigated the simultaneous solid state polymerization and transesterification for PET and PEN oligomer blends. The $^1$H NMR analysis of the blends revealed that the transesterification reactions occurred during early stage of SSP. X-ray and DSC results showed that SSP and transesterification occurred only in the amorphous phase.

Among the currently available literature on SSP of PEN/PET blends, none of the researchers has systematically investigated the kinetics and mechanism of the polycondensation and transesterification reactions. These SSP investigations have not included effects of important processing factors (such as reaction time and temperature) or the nature of blends (such as the PEN composition and initial IV) on these reactions. Most of the work done on these subjects has been for the PEN/PET blends in the liquid phase, either in melt or in solution.
In this project we recognized that the SSP process is an integrated and essential part of the whole processing cycle of the PEN/PET blends from the blends preparation to the final product manufacturing. SSP is the key for the success of utilizing conventional injection and stretch blow molding without any change in the preform or mold design to obtain containers from the blends with desired properties. A detailed understanding of the reactions occurring during SSP is thus very important.

In this part of our research we investigated the effects of several important factors on the polycondensation and transesterification reactions during SSP of PEN/PET blends. These factors include the SSP temperature, SSP time, PEN concentration, and the initial IV of the blends precursors. By using techniques such as melt rheometry, FT-IR, and NMR the kinetics and mechanisms of the polycondensation and transesterification reactions were studied. We also established some important relationships, such as those between the number average chain length and SSP time, and between molecular weight and the level of transesterification of the blends.

3.2 Experimental

3.2.1 Materials

Due to the limitation of material availability, two sets of commercial PET and PEN pellets were used to make the blends. The first set of materials was for the first part of the kinetics and mechanism study as listed in Table 3.1.
Table 3.1 Material information for PET A and PEN A

<table>
<thead>
<tr>
<th>Pure polymer resin</th>
<th>Manufacturer</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET A</td>
<td>PET copolymer</td>
<td>Eastman 9921</td>
</tr>
<tr>
<td>PEN A</td>
<td>PEN homopolymer</td>
<td>Amoco</td>
</tr>
</tbody>
</table>

The second set of PET B and PEN B was used for investigations of the effects of initial IV of blends precursors. Information about these materials is listed in Table 3.2.

Table 3.2 Material information for PET B and PEN B

<table>
<thead>
<tr>
<th>Pure polymer resin</th>
<th>Manufacturer</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET B</td>
<td>PET copolymer</td>
<td>Voridian</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aqua WA314</td>
</tr>
<tr>
<td>PEN B</td>
<td>PEN homopolymer</td>
<td>M &amp; G Polymers</td>
</tr>
</tbody>
</table>

Because of material availability restrictions, we obtained the PEN/PET blends with different IV through the degradation of the above commercial PET B as shown in Table 3.2 and subsequent blending with PEN B. A Werner & Pfleiderer (ZSK-30) self-wiping co-rotating twin-screw extruder was used to degrade the PET and to make the PET/PEN blends as discussed in 3.2.2.
The original PET B underwent different levels of degradation as a result of being passed through the twin screw extruder one time or two times. The IV of PET B was decreased to 0.67 and 0.63 respectively after the first and second pass. Together with the original PET B three different IV levels of PET were obtained, 0.75, 0.67, and 0.63. Each PET with different IV level was then blended with three different weight fraction of PEN B through the twin screw to obtain the following PEN/PET blend samples for conducting SSP experiments to study the effect of initial IV of the blend.

Table 3.3 Material information for PEN/PET blend for investigation of initial IV effects on SSP

<table>
<thead>
<tr>
<th>PEN composition (wt% PEN)</th>
<th>IV of PEN</th>
<th>Apparent IV of PET</th>
<th>Apparent IV of blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>0.64</td>
<td>0.63</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.75</td>
<td>0.71</td>
</tr>
<tr>
<td>10%</td>
<td>0.64</td>
<td>0.63</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.75</td>
<td>0.71</td>
</tr>
<tr>
<td>20%</td>
<td>0.64</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.75</td>
<td>0.70</td>
</tr>
</tbody>
</table>

3.2.2 Blend preparation

A Werner& Pfleiderer (ZSK-30) self-wiping co-rotating twin-screw extruder was used to make the 5 wt%, 10 wt% and 20 wt% PEN/PET blends from pure PET and PEN resin pellets. A uniform temperature profile of 280 °C and screw speed of 200 rpm were used for the extrusion. A Nitrogen purge was used to protect material from oxidative
degradation. Prior to extrusion, blend materials were dried using an Aircon hopper/drier for 12 hrs at 140°C. The extrudate was pulled through a cool water bath and a pelletizer to obtain the blend pellets. The average dimension of the PEN/PET blend pellets is shown below in Fig.3.2.1.

![Fig.3.2.1 Average dimension of PEN/PET blend pellets](image)

### 3.2.3 Solid State Polymerization

Before solid-state polymerization the blend samples were first vacuum-dried overnight at 150 °C in a vacuum oven. The drying process not only decreased the water concentration in the blend pellets to avoid the hydrolytic degradation at the initial stage of SSP, but also increased the crystallinity of the precursors, which was beneficial to prevent the pellets from sticking at the subsequent solid-state polymerization temperatures.

A SSP laboratory reactor (LOKTN, OVLA) made by Buhler Company was used to conduct the solid state polymerization of PET/PEN blends. A schematic diagram of the SSP reactor is shown in Fig. 3.2.2.
The reactor with an inner diameter of 90 mm and a height of 250 mm is within a heating chamber with air circulation and independent temperature regulation. Nitrogen gas (with a controlled flow rate) is heated by the electrical heater before entering the temperature-controlled reactor. Three thermocouples are used to monitor the product temperature at the top, middle and bottom of the reactor.

Prior to being filled with resin, the reactor is heated by the heating chamber to the desired reaction temperature with nitrogen gas flowing through the reactor at the same temperature. For each solid state polymerization experiment, 1 kg of the blend is charged into the reactor. The reaction times are counted only after the temperature in the middle of the reactor had reached 5°C lower than the desired reaction temperature. During the SSP process the samples are taken out of the reactor at specified time intervals for further analysis.

In our experiments, the SSP temperature range is from 200 ºC to 230 ºC. The SSP time for each run is 12 hours. The nitrogen flow rate was 2.5 L/hr. Samples were taken from the reactor for subsequent analysis every 2 hours.
3.2.4 Measurement of the equivalent number average molecular weight

For the convenience of analysis, the number average molecular weight of PET during SSP can be quickly obtained from the PET equivalent intrinsic viscosity (IV) values of the sample using the relationship between number average molecular weight and IV, the Mark-Houwink equation:

\[
I.V. = 7.5 \times 10^{-4} (M_n)^{0.68}
\]

or
\[ M_n = 3.92 \times 10^4 \text{ (I.V.)}^{1.47} \]  

The equivalent (or apparent) number average molecular weights of PEN/PET blend samples can also be calculated in a similar way.

Melt viscosities of blend samples were measured using a plate-plate type rheometrics tester, RDA III made by Rheometric Scientific, at a temperature of 280 °C, strain rate of 10 rad/sec and under a nitrogen gas purge. The apparent IV values were estimated from the calibration curve of IV and \( \ln (\eta) \) obtained from the pure PET standard samples. Finally the apparent number average molecular weight was evaluated from the Mark-Houwink equation, equation 3.2.1.

The calibration curve (in Fig.3.2.3) of IV vs. \( \ln (\eta) \) of the standard PET samples was obtained from the correlation between the solution IV values measured by the dilute solution method with 60/40 phenol/tetrachloroethane as solvent and the melt viscosities measured at strain rate of 10 rad/s and 280 °C by RDA III. All samples were dried overnight in a vacuum oven at 120°C before melt viscosity measurements.
It must be noted that the calibration and the Mark-Houwink equation used for the calculations of number average molecular weight of the blend samples are all based on pure PET, so the results obtained for the blend samples are really equivalent (or apparent) values with respect to pure PET rather than the actual values of the blends.

3.2.5 **Number average molecular weight calculation from end group analysis**

As mentioned above, from melt viscosity measurements we can only obtain the apparent IV and number average molecular weights of the blends, which are not the true values of the blends. A more accurate way to study the kinetics of the SSP reactions would be by utilizing the values of actual number average molecular weight of the blends, calculated from the hydroxyl and carboxyl end groups concentrations.
The hydroxyl and carboxyl end groups in the blend precursors and solid stated samples were analyzed using FT-IR. This method was used in work of Ward et al. \cite{140} Later, Al-AbdulRazzak and Jabarin \cite{141} utilized this technique in their investigation on the hydrolytic and thermal degradation of PET. Kim and Jabarin \cite{142,143} further modified the method and utilized it for the end group analysis of solid stated PET samples. They used flattened PET pellets samples and the measured intensities of IR peaks corresponding to carboxyl and hydroxyl end groups for concentration calculations. In the current work we followed the method of Kim and Jabarin. \cite{142,143} Below is a discussion of the procedure for the measurement and calculation.

**Sample preparation**

1. The pellet samples of the blends were first dried in vacuum oven at 120°C for 12 hrs before FT-IR experiments.

2. The flattened film like pellet samples, which are suitable for FT-IR measurements, were obtained by either squeezing between two bolts in a potassium bromide pellet mini press (blends made from PET A and PEN A), or between two circular stainless steel plates (blends made from PET B and PEN B) using a electrical controlled hydraulic press.

3. Flattened samples are measured by FT-IR to obtain the hydroxyl and carboxyl peak intensities at 3545 cm\(^{-1}\) and 3268 cm\(^{-1}\) respectively, as shown in Fig.3.2.4.
Fig. 3.2.4 FT-IR spectra for solid-state polymerized sample and deuterated sample
Calculation

1. Zero point was made at 3714 cm\(^{-1}\).

2. Normalized intensity values were calculated based on the intensity at 3995 cm\(^{-1}\) according to the following equations:

\[
I_{OH} = \frac{I_{3545\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}{I_{3995\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}
\]

\[
I_{COOH} = \frac{I_{3268\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}{I_{3995\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}
\]

In order for the calculation to be made independently of sample thickness the intensities of hydroxyl and carboxyl peaks were normalized according to the method of Kim and Jabarin. \[142, 143\]

3. Normalized intensity differences of hydroxyl and carboxyl end group peaks were calculated with respect to the deuterated sample according to the following equations. Sample deuteration was performed according to the method described by Al-AbdulRazzak.\[57\]

\[
\Delta I_{OH} = \frac{I_{3545\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}{I_{3995\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}_{\text{sample}} - \frac{I_{3545\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}{I_{3995\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}_{\text{deuterated sample}}
\]

\[
\Delta I_{COOH} = \frac{I_{3268\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}{I_{3995\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}_{\text{sample}} - \frac{I_{3268\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}{I_{3995\text{ cm}^{-1}} - I_{3714\text{ cm}^{-1}}}_{\text{deuterated sample}}
\]
4. End group concentrations were then calculated using the calibration curves relating end group concentrations obtained by titration to normalized intensity difference calculated from FT-IR spectra.

The calibration curves for carboxyl and hydroxyl concentrations were determined in the following way:

- Concentrations of carboxyl end groups of PET samples with known molecular weight, which was determined from melt viscosity, were measured by the titration method as described by Jabarin and Lofgren \[146].

- The same samples were also measured for normalized IR intensity differences of carboxyl and hydroxyl end groups (\(\Delta N_{OH}\) and \(\Delta N_{COOH}\)) by the procedure described above.

- The calibration was then made between \(\Delta N_{COOH}\) and concentrations of carboxyl end groups obtained by the titration method, as shown in Fig. 3.2.5.

- Assume there are only carboxyl and hydroxyl end groups in PET samples, since concentrations of other end groups are very small. The concentrations of hydroxyl were calculated using the following equation:

\[
M_n = \frac{2 \times 10^6}{[OH] + [COOH]} \quad (3.2.2)
\]
• The calibration curve was then made between $\Delta N_{\text{OH}}$ and concentrations of hydroxyl end groups, as shown in Fig. 3.2.6.

**Fig. 3.2.5** Calibration between carboxyl end group concentrations obtained from titration and normalized intensity differences of carboxyl end groups obtained from FT-IR
Fig.3.2.6 Calibration between hydroxyl end group concentrations calculated from relationship of [COOH] to $M_n$ using equation (3.2.2) and normalized intensity differences of hydroxyl end groups from FT-IR

3.2.6 Transesterification analysis by $^1$H NMR

There are many analytical methods employed by researchers to study the transesterification reactions. These include DSC, FT-IR, NMR, solubility methods and chromatography methods. Among them NMR is popularly favored because of its ability to study microstructure (i.e. copolymer formation and composition) resulting from the transesterification reaction. Thus $^1$H NMR became our primary method for analyzing the transesterification reaction.
The successful characterization by $^1$H NMR of copolymers formed between PEN and PET is based on the fact that the chemical shifts of the ethylene moiety (-CH$_2$-CH$_2$-) in a polymer chain are different when it is under different chemical environment (i.e., TET, NEN, or NET as shown in Fig. 3.2.7) in NMR spectra. The intensity of each peak can help us calculate the transesterification level between PET and PEN.

We can see clearly in Fig. 3.2.7 the different chemical environment that is encountered by the ethylene moiety and the positions of corresponding peaks.
Fig. 3.2.7  NMR spectra of PET/PEN blend
The extent of the transesterification reaction can be represented by a parameter called degree of randomness (RD), which is defined below:

\[ \text{RD} = P_{nt} + P_{tn} \]

Where, \( P_{nt} \) (\( P_{tn} \)) is the probability of finding a T (N) unit next to a N (T) unit along the PET/PEN copolymer chain from one end to the other.

From the areas under the different peaks in an NMR spectrum (i.e., \( A_{TET} \), \( A_{NEN} \), or \( A_{NET} \)) RD can be calculated as follows: \(^{[21, 23]}\)

\[ A = A_{NEN} + A_{NET} + A_{TET} \]

\[ P_{NEN} = A_{NEN} / A \]
\[ P_{NET} = A_{NET} / A \]
\[ P_{TET} = A_{TET} / A \]

\[ P_n = P_{NET} / 2 + P_{NEN} \]
\[ P_t = P_{NET} / 2 + P_{TET} \]

\[ P_{tn} = P_{NET} / 2P_t \]
\[ \text{P}_{nt} = \frac{\text{PNET}}{2\text{P}_n} \]

\[ \text{RD} = \text{P}_{nt} + \text{P}_{tn} \]

An RD value of 1 (or 100%) represents a totally random copolymer, values of RD < 1 indicates a block copolymer and value of RD = 2 is for the alternative copolymer.

The number average sequence lengths (L) of T and N units in the polymer are given by

\[ L(T) = \frac{1}{\text{P}_{tn}} \quad (3.2.3) \]
\[ L(N) = \frac{1}{\text{P}_{nt}} \quad (3.2.4) \]

The transesterification reaction between PET and PEN was studied by proton nuclear magnetic resonance (\(^1\text{H NMR}\)) with a Varian VXR-400 spectrometer made by Varian Association Inc.

### 3.2.7 Additional analyses

#### 3.2.7.1 Density measurement

The densities of the blends samples were measured at 25°C using a density gradient column made of calcium nitrate solutions and calibrated by suspending glass beads of known densities.
3.2.7.2. Melting behavior

The melting behaviors of blends samples were monitored with a Perkin-Elmer differential scanning calorimetry (DSC-7) in unsealed aluminum pans in a dry nitrogen atmosphere with an empty aluminum pan as reference at preset heating rates of 10°C/min.
3.3 Results and Discussion

3.3.1 Effects of temperature and time on the SSP reaction

A series of SSP reactions were conducted for the 5 wt%, 10 wt% and 20 wt% PEN/PET blends. The SSP temperatures used for each blend were from 200 °C to 230 °C. SSP time was 12 hours. Every two hours, a 50 gram sample of each blend was removed from the reactor for subsequent characterization.

Before being subjected to SSP in the reactor the blends were first dried and precrystallized at 160 °C in a vacuum drier for 12 hrs. The process not only dried the material to prevent hydrolytic decomposition, but also transformed the blend from an amorphous form to a semi-crystalline form and thus reduced the risk of sticking between pellets in the reactor. The chosen precrystallization (drying) temperature of 160 °C is within the temperature range at which the studied PEN/PET blends have the fastest crystallization rate, as shown in the research. [21, 22] The precrystallized blends had volume fraction crystallinity values of about 30%. This value is lower than that which a typical PET sample would have at the same condition, because of the reduced crystallization ability of the blends caused by the interruption of the PET chains with PEN. We found that this crystallinity level is sufficient to prevent the blend pellets from sticking together; therefore, all the blend samples were precrystallized at 160 °C.
3.3.1.1 SSP temperature

Temperature is an important parameter in the SSP process. Although in principle, the SSP reaction can take place when the temperature is higher than the $T_g$ of the material, the preferred temperature is usually chosen to be as close as possible to the melting point ($T_m$). This is done in order to give the polymer chains and end groups sufficient mobility for reaction and thus shorten the reaction time. Empirically it has been found that the SSP reaction rate doubles with a 12-13°C increase of SSP temperature. \[121\]

The temperature dependence data obtained for PEN/PET blend SSP experiments are shown in Figures 3.3.1 - 3.3.3 for the blends with PEN weight fractions of 5%, 10%, and 20%. From these figures we can clearly see that with the increasing SSP temperatures the rates of increase of apparent number average molecular weights (calculated from melt viscosity values) also increases. For example, in order to have an apparent number average molecular weight of 32,000 for the 5% PEN/PET blends the SSP time required is only about 4 hours at 230 °C in comparison to about 10 hours at 210 °C. The temperature effects can be better understood in terms of an Arrhenius analysis, as will be discussed in section 3.3.2.
3.3.1.2 SSP time

Time is another important variable in the SSP process. The relationship between molecular weight and SSP time will help us to control the reaction, according to the desired molecular weight of the polymer.

Fig.3.3.1. Apparent $M_n$ as a function of time at various SSP temperatures for 5% PEN/PET blends
Fig. 3.3.2  Apparent $M_n$ as a function of time at various SSP temperatures for 10% PEN/PET blends
Fig. 3.3.3 Apparent $M_n$ as a function of time at various SSP temperatures for 20% PEN/PET blends
The results shown in Figures 3.3.1 through 3.3.3 confirmed that indeed SSP helped the molecular weight of the PEN/PET blends increase. Longer SSP time will result in higher molecular weight. This trend may not be true, however, for a very long SSP time, since we can also see that the molecular weight of the blends tended to level off with longer SSP time, and a non-linear relationship is shown between $M_n$ and SSP time. Investigations concerning the mechanism of SSP of the PEN/PET blends will help us to understand the non-linearity between number average molecular weight and SSP time.

It is generally accepted that the chemistry that occurs in the solid state during SSP is the same as that in the melt state and that the reaction occurs only in the amorphous phase or at the surface of the crystalline phase. The very important distinction between SSP and melt polymerization, however, lies in the mobility of the polymer chain ends. Before reactions can occur, the end groups of different polymer chains must diffuse to and collide with each other. In the solid state the required mobility is significantly restricted compared to in the melt phase. In addition, the crystalline phase of the polymer would introduce more restrictions to the polymer chain movement. Thus more complicated reaction mechanisms are expected for SSP than for melt phase polymerization.

As was discussed in Chapter 2, the main reactions accounting for molecular weight increases during SSP of polyesters are the ester-interchange reaction and the esterification reaction. These are both reversible equilibrium reactions. The removal of byproducts is favored to drive the reactions forward. This is accomplished by either applying vacuum or flushing the reactor with inert gas such as nitrogen. The reaction rate
is not only dependent on chemical, but also on physical processes, in terms of the following three possible steps: polymer chain diffusion in the amorphous region, byproduct diffusion within pellets, and byproduct diffusion from pellet surfaces to the gas stream. The overall polymerization rate will be controlled by one or more of these steps, depending on the operating and processing variables.

If the reaction rate is limited only by the chemical reaction itself, as in case when the SSP temperature is very low or the precursor pellets size is very small, the molecular weight will increase linearly with SSP time. The non-linear behavior always means that the polymerization rate is not controlled only by the chemical reaction, but that some diffusion processes (e.g. the byproduct diffusion and/or polymer chain diffusion) are the limiting steps in the whole SSP process.

Since the sizes of our PEN/PET blend pellet samples are fairly large, as can be seen in Fig. 3.2.1 on page 53, and the temperatures of our SSP experiments are within the high temperature range of typical SSP process, it is reasonable to propose that the SSP reactions of our blend samples are diffusion controlled and not chemical reaction controlled.

Study of the reaction kinetics can help us identify the specific SSP controlling mechanisms and confirm our speculations.
3.3.2 SSP reaction kinetics (Apparent IV approach)

For the diffusion controlled SSP reactions, results from researchers like Lofgren and Jabarin [146] and Dröschel et al. [149] have shown that there is good linear correlation between the number average molecular weight and the square root of SSP time. This relationship can also be found from the theory of Flory [150], which shows that the degree of polymerization is approximately proportional to the square root of time for third-order condensation reactions, except during the early stages of the reaction.

In accordance with the proposed diffusion controlled SSP mechanism of PEN/PET blends we examined the number average molecular weight in terms of the square root of SSP time. The results can be seen in Figures 3.3.4 - 3.3.6.
Fig. 3.3.4 Apparent $M_n$ as a function of the square root of time at various SSP temperatures for 5% PEN/PET blends
Fig. 3.3.5 Apparent $M_n$ as a function of the square root of time at various SSP temperatures for 10% PEN/PET blends
Fig. 3.3.6  Apparent $M_n$ as a function of the square root of time at various SSP temperatures for 20% PEN/PET blends
All the data show very good linear relationships between these two variables. This indicated the validation of the proposed diffusion controlled SSP mechanism.

The slope of each straight line can be used to calculate the average apparent rate constant \( k \) and each line can be described by the following empirical equations:

\[
M_n = M_{n0} + k \sqrt{t}
\]  

(3.3.1)

where, \( M_n \) is the number average molecular weight at time \( t \)

\( M_{n0} \) is the initial number average molecular weight

\( t \) is the SSP time (min)

The results of the calculated apparent rate constant \( k \) for each blend sample are tabulated in Table 3.3.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>5 % blend (g/mol min^{1/2})</th>
<th>10 % blend (g/mol min^{1/2})</th>
<th>20 % blend (g/mol min^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>211</td>
<td>206</td>
<td>208</td>
</tr>
<tr>
<td>210</td>
<td>318</td>
<td>304</td>
<td>289</td>
</tr>
<tr>
<td>220</td>
<td>439</td>
<td>453</td>
<td>438</td>
</tr>
<tr>
<td>230</td>
<td>584</td>
<td>591</td>
<td>585</td>
</tr>
</tbody>
</table>

Table 3.3.1. Apparent rate constant of SSP for each blend sample at different SSP temperatures (Calculation based on apparent \( M_n \))
We can see from the above table that the rate constants for the same blend samples increase with increasing SSP temperature, but at the same temperature the rate constants show very little difference among the blends with different PEN compositions. We can thus say that the blend composition has very little influence on the SSP reaction, within our investigation range. This conclusion, however, should be confirmed by analysis using molecular weight values calculated from end groups, because calculations based on the apparent IV approach will bring some errors with the reasons we discussed in section 3.2.4 and 3.2.5. These analyses will be discussed in section 3.3.3.

The Arrhenius equation \[^{[151]}\] is used to describe the temperature effects on the rate constant \(k\). The equation is written as:

\[
k = A e^{-\frac{E_a}{RT}} \tag{3.3.2}
\]

where 

\(E_a\) = activation energy for rate constant (cal/mol)

\(A\) = frequency factor

\(R\) = gas constant (1.987 cal/mol K)

\(T\) = temperature (K)

The natural logarithms of the rate constant \([\ln (k)]\) can be plotted against \(1/T\) to obtain an Arrhenius plot as shown in Fig. 3.3.7. The values for \(E_a\) and \(A\) can be calculated from the slope and intercept of each line in the figure to give the values shown in Table 3.3.2.
Fig. 3.3.7. Arrhenius plot of rate constant for apparent molecular weight increases at various SSP temperatures for different blend samples.
The activation energy values obtained for PEN/PET blends here are very similar to the values obtained by Kim and Jabarin \cite{142,143} for SSP of PET. They proposed a method distinguishing the activation energy values for different reaction controlling steps, to determine the mechanism of SSP. They found that the activation energies for byproduct diffusion from within the polymer pellets and for polymer chains diffusion are around 4 and 13 kcal/mol respectively. An activation energy of about 17 kcal/mol was determined as an indication that the SSP reaction is controlled by both byproduct diffusion from within the polymer pellets and polymer chains diffusion.

In our experiments of SSP of PEN/PET blends, the SSP conditions were very similar to those in the studies of Kim and Jabarin \cite{142,143} in terms of the temperatures, pellets dimensions and inert gas purge rates. The blend activation energies of about 17 kcal/mol imply that the same mechanisms of SSP control current blend SSP. These mechanisms include the combination of byproduct diffusion from within blend pellets and the diffusion of polymer chains.

<table>
<thead>
<tr>
<th>Blend composition (wt% PEN)</th>
<th>Activation energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>16.0</td>
</tr>
<tr>
<td>10%</td>
<td>16.9</td>
</tr>
<tr>
<td>20%</td>
<td>16.6</td>
</tr>
</tbody>
</table>
Combining equations (3.3.1) and (3.3.2), we obtain for the apparent $M_n$

$$M_n = M_{n0} + Ae^{-E_a/RT} \sqrt{t} \quad (3.3.3)$$

This kinetic rate equation describes the empirical relationship of SSP time, temperature and polymer molecular weight. By substituting the corresponding values for $E_a$ and $A$ the following equations were obtained for blend sample with different PEN composition.

5% PEN/PET blend:

$$M_n = 2.38 \times 10^4 + 0.53 \times 10^{10} e^{-16000/RT} \times t^{1/2} \quad (3.3.4)$$

10% PEN/PET blend:

$$M_n = 2.38 \times 10^4 + 1.33 \times 10^{10} e^{-16900/RT} \times t^{1/2} \quad (3.3.5)$$

20% PEN/PET blend:

$$M_n = 2.38 \times 10^4 + 1.00 \times 10^{10} e^{-16600/RT} \times t^{1/2} \quad (3.3.6)$$
3.3.3 SSP reaction kinetics (End group concentrations approach)

Utilizing apparent IV of the PEN/PET blend samples to investigate SSP kinetics is convenient. A more accurate approach is to study the kinetics of SSP of PEN/PET blends using molecular weight values that have been calculated from carboxyl and hydroxyl end groups concentrations. These values can be measured by FT-IR, using the method described in section 3.2.4. Figures 3.3.8-3.3.13 show the results of hydroxyl and carboxyl end group concentration changes for 5%, 10%, and 20% PEN/PET blends during SSP.

From Figures 3.3.8 and 3.3.9 we can see that both carboxyl and hydroxyl end group concentrations decrease with increased SSP time and with increased SSP temperatures. This is can be easily understood, since the polycondensation reactions responsible for the molecular weight increases consume end groups as a result of ester interchange and/or direct esterification reactions. It can also be seen that with increasing temperature the rates of decreasing of end group concentrations are faster. This is in agreement with the effects of SSP temperatures on the apparent molecular weights of the blends.

By knowing the hydroxyl and carboxyl end group concentrations the number average molecular weight can be calculated using equation 3.2.2:

\[
M_n = \frac{2 \times 10^6}{[OH] + [COOH]} \quad (3.2.2)
\]
Fig. 3.3.8 Hydroxyl end group concentration as a function of SSP time at various SSP temperatures for 5% PEN/PET blends.
Fig. 3.3.9  Carboxyl end group concentration as a function of SSP time at various SSP temperatures for 5% PEN/PET blends
Fig. 3.3.10 Hydroxyl end group concentration as a function of SSP time at various SSP temperatures for 10% PEN/PET blends
Fig. 3.3.11 Carboxyl end group concentration as a function of SSP time 

at various SSP temperatures for 10% PEN/PET blends
Fig. 3.3.12 Hydroxyl end group concentration as a function of SSP time at various SSP temperatures for 20% PEN/PET blends
Fig. 3.3.13  Carboxyl end group concentration as a function of SSP time at various SSP temperatures for 20% PEN/PET blends
In order to obtain the apparent rate constants of the solid state polymerization reactions, the molecular weights can be plotted versus the square root of SSP times as was previously done with PET equivalent molecular weight data. The results are shown in Fig. 3.3.14 - 3.3.16 for the 5%, 10%, and 20% PEN/PET blends respectively. The apparent rate constant results are given in Table 3.3.2.

Fig. 3.3.14 $M_n$ as a function of the square root of time at various SSP temperatures for 5% PEN/PET blends (calculation based on FT-IR)
Fig. 3.3.15  $M_n$ as a function of the square root of time at various SSP temperatures for 10% PEN/PET blends (calculation based on FT-IR)
Fig. 3.3.16 $M_n$ as a function of the square root of time at various SSP temperatures for 20% PEN/PET blends (calculation based on FT-IR)
Table 3.3.3  Apparent rate constant of SSP for each blend sample at different SSP temperatures (Calculation based on Mn from hydroxyl and carboxyl end groups concentrations)

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Apparent rate constant (k) (g/mol min$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 % blend</td>
</tr>
<tr>
<td>200</td>
<td>551</td>
</tr>
<tr>
<td>210</td>
<td>764</td>
</tr>
<tr>
<td>220</td>
<td>1026</td>
</tr>
<tr>
<td>230</td>
<td>1617</td>
</tr>
</tbody>
</table>

The good fit of the linear relationship between number average molecular weight and the square root of SSP time confirms the proposed diffusion controlled mechanism, which will be further proven by the activation energy values as discussed later.

By comparing the molecular weight results, calculated from both the apparent IV and end groups concentration approach, as shown in Table 3.3.4 - 3.3.6, we can see that values obtained utilizing end group concentrations were higher than those obtained as a result of the apparent IV method. One of the reasons for this difference is that the melt viscosity of the blends (when the composition is below 20 wt% of PEN) is lower than that of PET as has been reported by Tharmapuram and Jabarin. [26, 28] They attributed this to the dilution effect of mixing low amounts of PEN into PET. Another reason is that when calculating the apparent molecular weight from the IV values we were using the Mark-Houwink equation for PET, which inevitably would bring errors in the calculation. The end group concentration approach is thus more accurate. From Table 3.3.3 we see no major
differences among the SSP rate constant values for blends with different PEN compositions. As a result we conclude that the PEN composition in the PEN/PET blends has no major effects on the polycondensation reaction rates.

Table 3.3.4 Comparison between $M_n$ values calculated from apparent IV approach and end group concentration approach for 5% PEN/PET blends

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Time (hr)</th>
<th>Number average molecular weight ($M_n$) From apparent IV approach</th>
<th>From end group concentration approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0</td>
<td>$2.38 \times 10^4$</td>
<td>$2.94 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$2.51 \times 10^4$</td>
<td>$3.34 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>$2.63 \times 10^4$</td>
<td>$3.52 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>$2.72 \times 10^4$</td>
<td>$3.92 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$2.79 \times 10^4$</td>
<td>$4.12 \times 10^4$</td>
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<tr>
<td></td>
<td>10</td>
<td>$2.86 \times 10^4$</td>
<td>$4.32 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$2.95 \times 10^4$</td>
<td>$4.46 \times 10^4$</td>
</tr>
<tr>
<td>210</td>
<td>0</td>
<td>$2.38 \times 10^4$</td>
<td>$2.94 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$2.59 \times 10^4$</td>
<td>$3.53 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>$2.73 \times 10^4$</td>
<td>$3.88 \times 10^4$</td>
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<tr>
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<td>6</td>
<td>$2.88 \times 10^4$</td>
<td>$4.23 \times 10^4$</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>10</td>
<td>$3.14 \times 10^4$</td>
<td>$4.93 \times 10^4$</td>
</tr>
<tr>
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<td>12</td>
<td>$3.23 \times 10^4$</td>
<td>$5.05 \times 10^4$</td>
</tr>
<tr>
<td>220</td>
<td>0</td>
<td>$2.38 \times 10^4$</td>
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<td>$2.70 \times 10^4$</td>
<td>$3.97 \times 10^4$</td>
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<tr>
<td></td>
<td>4</td>
<td>$2.94 \times 10^4$</td>
<td>$4.33 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>$3.13 \times 10^4$</td>
<td>$4.73 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$3.28 \times 10^4$</td>
<td>$5.19 \times 10^4$</td>
</tr>
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<td></td>
<td>10</td>
<td>$3.42 \times 10^4$</td>
<td>$5.63 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$3.56 \times 10^4$</td>
<td>$6.33 \times 10^4$</td>
</tr>
<tr>
<td>230</td>
<td>0</td>
<td>$2.38 \times 10^4$</td>
<td>$2.94 \times 10^4$</td>
</tr>
<tr>
<td></td>
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Table 3.3.5  Comparison between $M_n$ values calculated from apparent IV approach and end group concentration approach for 10% PEN/PET blends

<table>
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<th>Temperature (°C)</th>
<th>Time (hr)</th>
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<th>From end group concentration approach</th>
</tr>
</thead>
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<td>$4.67 \times 10^4$</td>
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<tr>
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<tr>
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<td>4</td>
<td>$2.98 \times 10^4$</td>
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<tr>
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<tr>
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<td>$2.74 \times 10^4$</td>
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<td>$2.98 \times 10^4$</td>
<td>$4.36 \times 10^4$</td>
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<td>6</td>
<td>$3.11 \times 10^4$</td>
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<td>8</td>
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<tr>
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<td>10</td>
<td>$3.51 \times 10^4$</td>
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<td></td>
<td>12</td>
<td>$3.57 \times 10^4$</td>
<td>$6.18 \times 10^4$</td>
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<tr>
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<td>12</td>
<td>$3.94 \times 10^4$</td>
<td>$7.74 \times 10^4$</td>
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</tbody>
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Table 3.3.6 Comparison between $M_n$ values calculated from apparent IV approach and end group concentration approach for 20% PEN/PET blends

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>Number average molecular weight ($M_n$)</th>
<th>From apparent IV approach</th>
<th>From end group concentration approach</th>
</tr>
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<tbody>
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<td>3.07 × 10⁴</td>
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<tr>
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<td>2</td>
<td>2.56 × 10⁴</td>
<td>3.94 × 10⁴</td>
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</tr>
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<td>2.84 × 10⁴</td>
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<td>12</td>
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<td>4.64 × 10⁴</td>
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</tr>
<tr>
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<td>2.73 × 10⁴</td>
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<td>6.10 × 10⁴</td>
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<tr>
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<td>0</td>
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<td></td>
<td>10</td>
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<td>7.53 × 10⁴</td>
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<tr>
<td></td>
<td>12</td>
<td>3.97 × 10⁴</td>
<td>8.02 × 10⁴</td>
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The activation energies ($E_a$) of the SSP reactions can be obtained by the method described earlier. Activation energy results are shown in Fig. 3.3.17. We can see the values of activation energy (i.e. around 17 kcal/mol) obtained from end group analyses are very close to those we calculated from the apparent molecular weights of the samples, as shown in Table 3.3.7. It is thus confirmed that the SSP reaction of the PEN/PET blends is controlled by the polymer chain and end group diffusion as well as byproduct diffusion from within blend pellets.

![Arrhenius plot of SSP rate constant for Mn increase at various temperatures for different blend samples](image)

Fig. 3.3.17 Arrhenius plot of SSP rate constant for $M_n$ increase at various temperatures for different blend samples
Table 3.3.7 Comparison of activation energy values of SSP of PEN/PET blend samples using apparent IV approach and end group concentration approach

<table>
<thead>
<tr>
<th>Blend composition (wt% PEN)</th>
<th>Activation energy (kcal/mol)</th>
<th>From apparent IV approach</th>
<th>From end group concentration approach</th>
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</tr>
<tr>
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<td>16.0</td>
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</tr>
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<td>10%</td>
<td>16.9</td>
<td>17.3</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>16.6</td>
<td>16.9</td>
<td></td>
</tr>
</tbody>
</table>

3.3.4 Transesterification reaction

When two polyesters which have similar chemical structures are blended at elevated temperatures, a transesterification reaction occurs. Transesterification is a collective term that encompasses three main reactions:

Alcoholysis:

\[
\text{R}_1\text{C}-\text{O}-\text{OH} + \text{R}_2\text{C}-\text{O}-\text{R}_3 \rightleftharpoons \text{R}_1\text{C}-\text{O}-\text{R}_3 + \text{R}_2\text{C}-\text{O}-\text{OH}
\]

Acidolysis:

\[
\text{HOOC-}\text{C}-\text{O}-\text{R}_1 + \text{R}_2\text{C}-\text{O}-\text{R}_3 \rightleftharpoons \text{R}_1\text{C}-\text{O}-\text{R}_3 + \text{R}_2\text{C}-\text{O}-\text{COOH}
\]

Ester interchange:

\[
\text{R}_1\text{C}-\text{O}-\text{R}_2 + \text{R}_3\text{C}-\text{O}-\text{R}_4 \rightleftharpoons \text{R}_1\text{C}-\text{O}-\text{R}_3 + \text{R}_2\text{C}-\text{O}-\text{R}_4
\]
The microstructure of the blend is strongly dependent on the transesterification reaction level. It is thus important to find out whether or not copolymers have formed as a result of the reaction, to determine the sequence length distributions, to study the kinetics of the reactions, and the properties of the resultant blends. Previous research [16-27, 30-32, 86-94] has been focused on the miscibility of PEN/PET blends, due to the transesterification reaction, as been discussed in chapter 2. According to the diagram given in Figure 3.3.18, a block copolymer is initially formed. As this reaction proceeds further, a random copolymer is formed and the miscibility of the blend is enhanced.

Fig.3.3.18 Formation of block and random copolymers during blending of PET and PEN.

(T represents ethylene terephthalate unit; N represents ethylene naphthalate unit) [32]
The transesterification reaction can be analyzed by $^1$H NMR as discussed in section 3.2.5. The typical changes of different peaks in the NMR spectra of the PEN/PET blends undergoing SSP are shown in Figure 3.3.19. (The peaks for samples of solid stated for 6 hrs and 12 hrs have been offset to the left so it is easier to compare the results)

Fig. 3.3.19  Expansion of $^1$H MMR spectra for 20% PEN/PET blends

SSP for 0 hr, 6 hrs and 12 hrs at 230 ºC
Figure 3.3.19 shows how the peaks corresponding to the ethylene moiety (CH₂), present in different chemical environments, change in relative intensity during the SSP process. At the beginning of SSP only a very weak peak of NET is observed, which results from the copolymer formed during melt blending. As the SSP proceeds the NET peak intensity grows and the TET and NEN peaks becomes smaller. This implies that the transesterification reaction proceeds in the solid state of the blend just as in the melt phase, although the rate is slower. Further, SSP leads to more and more of the homopolymers (PET and PEN) being converted to copolymers as indicated by the continuously decreasing intensities of TET and NEN peaks and the simultaneous increasing of the NET peak intensity.

### 3.3.4.1 Change of degree of randomness during SSP

Using the method described in section 3.2.5 we calculated transesterification level (i.e. the degree of randomness RD) as a function of SSP time at various SSP temperatures for each blend sample. The results are shown in Figures 3.3.20 - 3.3.22.

Clearly the transesterification levels increase with increasing SSP time. This is in agreement with results obtained by other researchers [31, 32, and 93] and satisfies one of our initial goals for this project. The SSP temperature has a similar effect on the transesterification reaction. With increasing SSP temperature, the transesterification reaction rates increase as shown by the fact that at the same SSP times, blends solid stated at higher temperatures have higher levels of degree of randomness.
Fig. 3.3.20  Degree of randomness as a function of SSP time at various SSP temperatures for 5% PEN/PET blends
Fig. 3.3.21  Degree of randomness as a function of SSP time at various SSP temperatures for 10% PEN/PET blends
Fig. 3.3.22  Degree of randomness as a function of SSP time at various SSP temperatures for 20% PEN/PET blends
The effects of SSP time on the transesterification levels (RD values) for the SSP conditions applied in our experiments indicated that with increased SSP time the RD value increases. Since these SSP times are relatively short (12 hours), we could not determine whether or not the RD values would continue to increase to higher values, without leveling off as the molecular weight did, for very long SSP time. Investigations of the effects of long SSP time on transesterification level will be presented in section 3.3.4.4, where the relationship between transesterification levels and molecular weights is discussed.

3.3.4.2 Transesterification reaction kinetics

Despite previous work on the transesterification reaction of PEN/PET blends there still is no agreement on the mechanism of the reaction. There exists proposed first-order (with respect to one component) reaction between PET and PEN by Stewart et al. [17]. Similarly Kenwright et al. [18] suggested that the transesterification reaction between PET and PEN is through alcoholysis mechanism by the reaction of hydroxyl end groups. However, some other authors believed [48-51, 21, 23, 26, 27, and 118] that the reaction is second-order (first order to each component) reversible direct ester-ester interchange reaction. Recent work from Alexandrova et al. [118] introduced some new evidence for the second-order mechanism. In our study, we have therefore based our method of kinetic analysis on the assumption that the transesterification reactions are second-order reversible ester-ester interchange reactions.
Devaux et al. [51] have done extensive work on PC/PBT and PC/PET blends with the assumption of second-order reversible direct ester-ester interchange reactions. By applying their method to the PEN/PET blends, the following equation can be obtained:

$$\ln\frac{b}{b-r} = kt$$

Where $r$, the transesterification ratio, is $x/a$

$x$ is the mole fraction of TEN sequence in the blend

$a$ is the initial mole fraction of TET sequence

$b$ is the initial mole fraction of NEN sequence

$k$ is the rate constant

$t$ is reaction time

Since at the beginning of SSP the blends samples already have some degree of randomness, which is a result of the transesterification reactions occurred during melt phase blending of PEN and PET in the twin screw extruder, the above equation can be modified as the following equation to account for this fact.

$$\ln\frac{b}{b-r} = kt + y_0 \quad (3.3.5)$$

The additional term $y_0$ is to account for the degree of randomness of the blends at the beginning of SSP as a result of melt phase blending.
Using equation (3.3.5) we can obtain plot of $\ln[b/(b-r)]$ as a function of SSP reaction time ($t$). The slope of the plot of $\ln[b/(b-r)]$ versus $t$ will give us the reaction rate constant $k$. The plots are shown in Figures 3.3.23-3.3.25 for the blend samples with 5%, 10%, and 20% PEN respectively and the calculated rate constant values are listed in Table 3.3.7.

![Graph](image)

**Fig. 3.3.23** $\ln[b/(b-r)]$ vs. SSP time at various SSP temperatures for 5% PEN/PET blends
Fig. 3.3.24  $\ln\left[\frac{b}{(b-r)}\right]$ vs. SSP time at various SSP temperatures for 10% PEN/PET blends
Fig. 3.3.25  \(\ln\left[\frac{b}{(b-r)}\right]\) vs. SSP time at various SSP temperatures for 20% PEN/PET blends
Table 3.3.8 Transesterification rate constant for each blend sample at different SSP temperatures

<table>
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<tr>
<th>Temperature (°C)</th>
<th>rate constant k (min⁻¹)</th>
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<tbody>
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<td>5 % blend</td>
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<td>0.05 × 10⁻²</td>
</tr>
<tr>
<td>210</td>
<td>0.07 × 10⁻²</td>
</tr>
<tr>
<td>220</td>
<td>0.19 × 10⁻²</td>
</tr>
<tr>
<td>230</td>
<td>0.27 × 10⁻²</td>
</tr>
</tbody>
</table>

The linear relationship between ln[b/(b-r)] and SSP time indicates the validation of the assumed ester-ester interchange mechanism.

When we compare the transesterification reaction rate constant values shown in Table 3.3.8 and obtained for blends with different PEN compositions, we cannot find any significant differences among them. This means that the blend composition has little effect on the transesterification reaction.

The natural logarithms of the rate constant [ln (k)] can be plotted against 1/T to obtain an Arrhenius plot as shown in Fig. 3.3.26. The values for E_a can be calculated from the slope of each line in the figure to give the values shown in Table 3.3.9.
Fig. 3.3.26  Arrhenius plot of rate constant for transesterification level increases at various SSP temperature for different blend samples.
Table 3.3.9 Activation energy of the transesterification reaction for each blend sample

<table>
<thead>
<tr>
<th>Blend composition (wt% PEN)</th>
<th>Activation energy</th>
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<th></th>
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</thead>
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<td>kJ/mol</td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>10%</td>
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<td>117.2</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>27.9</td>
<td>116.8</td>
<td></td>
</tr>
</tbody>
</table>

The activation energy values we obtained are in the same range as those reported by other authors \[21, 23\] for PEN/PET blend systems and some other polyester blend systems. These are typical values for the ester exchange reaction. The assumed transesterification reaction mechanism is thus again found to be that of second-order reversible ester-ester interchange reactions.

Another proof for the assumed ester-ester interchange mechanism can be found from the entropy term in the reaction rate constant $k$. According to collision theory \[151\], $k$ contains two terms, entropy and enthalpy and can be written as follows:

$$k = \frac{k_B T}{h} \gamma_A \gamma_B e^{\Delta S / R} e^{-\Delta H / RT}$$

Where, $k_B$ is Boltzmann’s constant, $1.38 \times 10^{-16}$ erg/K

$h$ is Plank’s constant, $6.024 \times 10^{-27}$ ergs

$\gamma_A, \gamma_B$ are the activity coefficients
R is gas constant \((8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1})\)

\(\Delta S\) is the entropy term \((\text{J/mol } 0\text{K})\)

\(\Delta H\) is the enthalpy term (related to activation energy) \((\text{J/mol})\)

Comparing this equation with the Arrhenius equation (3.3.2) shows that the frequency factor can be expressed as:

\[
A = \frac{k_B T}{h} \gamma_A \gamma_B e^{\Delta S/R}
\]

If we neglect the activity coefficient term, then \(\Delta S\) can be calculated from \(A\) (the intercept of the straight line in the Arrhenius plot) by

\[
\Delta S = 2.303R \log \left( \frac{Ah}{k_B T} \right)
\]

(3.3.6)

The average \(\Delta S\) values for each blend are listed in Table 3.3.10.

<table>
<thead>
<tr>
<th>Blend composition (wt% PEN)</th>
<th>(\Delta S) (J/mol 0K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>-59</td>
</tr>
<tr>
<td>10%</td>
<td>-65</td>
</tr>
<tr>
<td>20%</td>
<td>-67</td>
</tr>
</tbody>
</table>
According to collision theory\textsuperscript{[151]}, the large negative $\Delta S$ values indicate that there is an intermediate phase during the transesterification reaction, where an intermediate active complex is formed. This intermediate complex has a more regular structure compared to the final random copolymer-like product. This is in agreement with the traditional belief that the ester-ester exchange reaction occurs by substitution at carbonyl carbon atoms through addition-elimination mechanisms\textsuperscript{[119]} as shown in equation 3.3.7. During the reaction, addition intermediates (a) or (b) with more regular structures are formed.

\[ \begin{align*}
\text{(a)} & \quad \text{or} \quad \text{(b)} \\
R-C-X + Y & \rightleftharpoons [R-C\overset{\delta^+}{\|}X] \quad & \rightleftharpoons & \quad [R-C\overset{\delta^-}{\|}X] \rightleftharpoons R-C-Y + X \\
\end{align*} \]  

\( (3.3.7) \)

X can be OH, OR, OCOR and Cl, Y can be a neutral or negatively charged nucleophilic agent (ROH and RO or RCOO, respectively), and R is alkyl or aryl group. For ester-ester interchange reaction X is OR and Y is R’COOR’’.

3.3.4.3 Number-average sequence chain length change

Additional information obtained from NMR analysis is the number-average sequence chain length of each component [repeat unit L (T) or L (N)], which decreases as a result of the transesterification reaction. If the length of the minor component is 1 then a
strictly alternating copolymer is indicated. A length of 2 is characteristic of a random distribution of the minor component repeat units over all molecules in the system. \cite{21,23}

The number-average sequence chain length can be calculated using equation (3.2.3) and (3.2.4). The results for 5%, 10%, and 20% PEN/PET blend samples are illustrated in Figures 3.3.27-3.3.32. We can see from these graphs that $L(T)$ and $L(N)$ decrease faster in the early stage of the SSP process, then the rate of decrease becomes slower.

![Average chain length (T) vs. SSP time](image)

Fig. 3.3.27 Number-average sequence chain length of T units vs. SSP time at various SSP temperatures for 5% blend samples
Fig. 3.3.28  Number-average sequence chain length of N units vs. SSP time at various SSP temperatures for 5% blend samples
Fig. 3.3.29 Number-average sequence chain length of T units vs. SSP time at various SSP temperatures for 10% blend samples
Fig. 3.3.30  Number-average sequence chain length of N units vs. SSP time at various SSP temperatures for 10 % blend samples
Fig. 3.3.31  Number-average sequence chain length of T units vs. SSP time at various SSP temperatures for 20% blend samples
Fig. 3.3.32 Number-average sequence chain length of N units vs. SSP time at various SSP temperatures for 20 % blend samples
The sequence length for PEN/PET blends with different PEN compositions shows different behavior in terms of decreasing length, particularly for PET sequences. We can see by comparing Figure 3.3.28 with Figure 3.3.32 that the sequence lengths of PET units decreased more rapidly for the blends having higher PEN composition. This is because the higher the PEN composition the more PEN units would be brought into the chains of PET units through the transesterification reaction. Thus we should expect different levels of the effects of the transesterification reaction on the properties of the blends. One example will be the crystallization ability, since shorter PET unit lengths will make the crystallization process more difficult. This effect will be discussed in chapter four.

3.3.4.4 Relationship between RD and molecular weight

We have seen that both the number-average molecular weights and transesterification reaction levels of blend samples increase, through the SSP process. This could have some practical benefits for industrial applications in the sense that while building up the molecular weights of blends samples we can also homogenize the blends. We already know that the transesterification levels of the blends have some effects on the properties of the polymer. For example, in order to have injection molding preforms with good clarity the blend samples must achieve a critical transesterification level during the extrusion process, [26, 27] This, however, may cause undesired degradation reactions of the sample. The SSP process could be a better way to improve the homogeneity of the blend system.
The relationship between $M_n$ and RD can be demonstrated through plots of these two values. Figures 3.3.33-3.3.35 show RD values plotted versus number average molecular weights ($M_n$), calculated from end groups concentrations.

![Transesterification level vs. Molecular weight](image)

Fig. 3.3.33  RD value versus number average molecular weight of 5% blends
Fig. 3.3.34 RD value versus number average molecular weight of 10% blends
Fig. 3.3.35  RD value versus number average molecular weight of 20% blends.
From these figures we find that a linear relationship exists between RD and \( M_n \) when the molecular weight is lower than 50000-60000 g/mol. After that, the RD value starts to level off. That means a limiting value seems to exist for the RD value. To investigate what the limiting value would be we conducted an experiment with very long SSP time. The blend used contained 20% PEN/PET and the reaction was carried out at 230°C for 44 hours. As before, the number average molecular weights were obtained from the end groups concentrations by the FT-IR method, and RD values were measured by NMR analysis. The results are shown in Fig.3.3.36.

Fig. 3.3.36  RD value versus number average molecular weight of 20% blends SSP for 44 hours
From these results we can see that beyond the molecular weight level of about 60000 g/mol the rate of RD increase begins to slow down and further SSP leads to even slower rate of increase. The RD reached a limiting value of about 70% after SSP for 44 hours. The same phenomenon has also been found by other authors. [32] The reason for this is not clear. It is proposed [39] that at this stage the crystallization induced sequential reordering acts as the driving force that counteracts the entropy driving randomization process. Fakirov and Denchev [39] gave a very detailed review of sequential reordering. This process occurs when the material is annealed at a temperature very close to its melting point and for a very long time. Since the copolymer average sequence length is a distribution of broad block length, some blocks with repeat unit numbers of crystallizable component greater than 5 will crystallize at this condition. As a consequence, their concentration in the amorphous phase is reduced. Transesterification reactions will restore this concentration by converting the random copolymers to block copolymers. As a result RD values will no longer increase. A schematic diagram of crystallization induced sequence reordering is shown in Fig. 3.3.37.

Fig. 3.3.37 Schematic diagram of crystallization induced sequence reordering [39, 77]
3.3.5 Effect of initial IV of blends precursors on polycondensation and transesterification reactions

As previous research [126, 152, and 153] has shown, the initial IV of the precursor will affect the kinetics of the SSP reactions. The recent work from Kim and Jabarin [142-145] investigated in detail this effect on the PET SSP process. In order to determine if the same effect would be found in the case of PEN/PET blends, a series of samples with different initial IV values were prepared. This section describes investigations of the effects of initial IV of the PEN/PET precursors on the polycondensation (SSP) and transesterification reactions, specifically on the SSP reaction rate and transesterification reaction rate.

3.3.5.1 Effects on SSP reaction rate (Apparent IV approach)

As in section 3.2 the apparent IV values of the blends samples were first measured by the melt viscosity method and apparent SSP rate constants were obtained by plotting the apparent number average molecular weights against the square root of SSP time as indicated in Figures A1- A9 in Appendix A.

Apparent SSP rate constants, calculated for all the blends samples are listed in Table 3.3.11.
Table 3.3.11  Apparent rate constant for each blend sample at different SSP temperatures

<table>
<thead>
<tr>
<th>PEN composition (wt% PEN)</th>
<th>Apparent Initial IV (from melt viscosity)</th>
<th>Apparent rate constant (k) (g/mol min$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>210°C</td>
</tr>
<tr>
<td>5%</td>
<td>0.60</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>283</td>
</tr>
<tr>
<td>10%</td>
<td>0.60</td>
<td>305</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>311</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>294</td>
</tr>
<tr>
<td>20%</td>
<td>0.61</td>
<td>595</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>578</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>508</td>
</tr>
</tbody>
</table>

From the results in the above table we cannot see a clear trend of how the initial IV of the blends affects the SSP reaction rate. The reason for this comes from the method of measuring molecular weight in terms of the melt viscosity. Since the rheological properties of the blends are very complicated function of factors such as morphology, miscibility, and blend composition, the molecular weights calculated from the melt viscosity will cause ambiguity in the results. Additionally, as mentioned before, all the calculations involving the melt viscosity of the blends are based on equations developed for PET, therefore we can only obtain the apparent IV and molecular weight of a blend, which is not its true value. In order to obtain unbiased results and make accurate
comparison to determine the initial IV effects on SSP reaction rates, an end group concentration approach is more appropriate.

3.3.5.2 Effects on SSP reaction rate (end group concentrations approach)

Using the FT-IR method described in section 3.2.2 the number average molecular weights ($M_n$) were obtained for all the blends samples. Plots of $M_n$ calculated using end group concentrations against the square root of SSP time are shown in Figures B1 – B9 in Appendix B. From the slopes of the straight lines of the plots of number average molecular weight versus square root of SSP time, the apparent SSP rate constants were obtained for each blend as shown in Table 3.3.12.

Table 3.3.12 Apparent SSP rate constant for each blend sample at different SSP temperatures (Calculated from the end group concentrations)

<table>
<thead>
<tr>
<th>PEN composition (wt% PEN)</th>
<th>Apparent Initial IV</th>
<th>[COOH]/[OH]</th>
<th>Apparent rate constant (k) (g/mol min$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>210°C</td>
</tr>
<tr>
<td>5%</td>
<td>0.60</td>
<td>0.343</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>0.338</td>
<td>481</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>0.183</td>
<td>452</td>
</tr>
<tr>
<td>10%</td>
<td>0.60</td>
<td>0.336</td>
<td>309</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>0.340</td>
<td>459</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>0.196</td>
<td>437</td>
</tr>
<tr>
<td>20%</td>
<td>0.61</td>
<td>0.270</td>
<td>376</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>0.283</td>
<td>427</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.144</td>
<td>487</td>
</tr>
</tbody>
</table>
From Table 3.3.12 it can be seen that the initial IV of the blend did have an effect on the SSP reaction rate, especially between the samples with initial IV of 0.60 and 0.65. Higher initial IV favors faster IV increases during SSP. The same phenomenon is well known for the PET SSP process. Explanations have been made by several researchers. Wu [126] and Buxbaum [152] attributed it to the negative crystallinity effects by saying that the diffusion rate of the byproducts decreased as the crystallinity increased for the lower IV precursor. Duh [153] explained it in terms of the crystalline structure and chain mobility. We think the crystalline structure and chain mobility are the main reasons as discussed below.

Since all the reactions during SSP occur in the amorphous region and the end groups of the polymer chains must come together for the reaction to occur. Kang [127] took into account the chain diffusion in the amorphous phase as a rate-controlling factor and introduced the activation energy of the chain diffusion into the whole activation energy of the SSP reaction. Kim and Jabarin [142, 143] confirmed that the activation energy included two terms from end group diffusion and chemical reactions. No doubt the chain mobility has a great effect on the reactions. Duh [153] stated that it is easier for the shorter polymer chains to fit into the crystal lattice and they tend to form more regular and rigid crystals and have higher crystallinity. The molecular chains of higher IV precursor on average have a higher mobility. We believe this is the case in our study, as can be seen from the volume crystallinity results measured from density for the 5% blends SSP at 230 °C shown in Fig. 3.3.38. We can see that samples with lower initial IV had higher crystallinity, although the difference between the crystallinity was not big.
Fig. 3.3.38 Volume crystallinity as a function of SSP time for 5% PEN/PET blends with different Initial I.V. SSP@ 230°C

Another reason for the effect of initial IV can be found from the crystalline structures by studying the melting behaviors of blend samples with different initial IV. It has been found through our investigations that the blend samples with higher initial IV tended to have a greater portion of crystals formed during secondary crystallization therefore less perfect crystals. On the contrary, lower IV of the precursor allowed the formation of more perfect crystal and reduced the chain mobility in the amorphous region. This made the diffusion of the chain ends toward each other more difficult, resulting in lower SSP reaction rates. Detailed discussions of the effects of initial blend IV on melting behaviors is presented in Section 4.3.1.2.
The effect of initial IV on SSP of the blends samples with initial IV values of about 0.65 and 0.71 is not very clear. For example, the apparent rate constant (k) values of SSP for 5% PEN/PET blend with an initial IV of 0.71 are lower than those of 5% PEN/PET blend with initial IV of 0.65 at all three SSP temperatures. The k values of SSP for the 10% PEN/PET blend with an initial IV of 0.71 are lower than those of the 10% PEN/PET blend with an initial IV of 0.67 at SSP temperatures of 210 °C and 220 °C. We believe this is due to the ratio of carboxyl and hydroxyl end groups. Kim and Jabarin [142-144] discussed the effect of the molar ratio of the end groups ([-COOH] / [-OH]) on the SSP reaction rate. There are two kinds of reactions that occur during SSP. One type is the ester-interchange reaction, which is between two hydroxyl end groups and give EG as a by product. Another one is the esterification reaction, where one hydroxyl and one carboxyl end groups react and give water as the byproduct. Since water has a higher diffusion rate in the solid polymer, the esterification reaction proceeds more favorably than the ester-interchange reaction when the overall SSP reaction is diffusion controlled, which is always the case for pellets. There is an optimum ratio of [-COOH] over [-OH] for obtaining a maximum SSP reaction rate. Wu [126] reported a 0.5-0.8 value for the optimum ratio, while Duh [153] found this value was to be 0.33-0.67. As it can be seen in Table 3.3.11 the value of [-COOH] / [-OH] for our blends with lower initial IV (0.60 and 0.65) was around 0.34, while the values for the blends with initial IV values of 0.71, were around 0.18. In terms of this ratio, a slower SSP reaction rate would be expected for a blend with higher initial IV. This counteracts the effects of molecular weight. As a result, no obvious increases in the SSP reaction rate constants were found for the blends with the highest initial IVs.
3.3.5.3 Initial IV effects on transesterification reaction

By assuming the mechanism of second-order reversible direct ester-ester interchange reactions, the rate constants for transesterification reactions of PEN/PET blends with different initial IV were calculated. This was done by plotting $\ln \left( \frac{b}{b-r} \right)$ against reaction time as described in section 3.3.4. Plots of $\ln \left( \frac{b}{b-r} \right)$ versus time for the blend samples are shown in Figures C1 – C9 in Appendix C. The rate constant values calculated for transesterification reactions of every sample are listed in Table 3.3.13.

<table>
<thead>
<tr>
<th>PEN composition (wt% PEN)</th>
<th>Apparent Initial IV (from melt viscosity)</th>
<th>[COOH]/[OH]</th>
<th>Rate constant (k) (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>210°C</td>
</tr>
<tr>
<td>5%</td>
<td>0.60</td>
<td>0.343</td>
<td>0.07 $\times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>0.338</td>
<td>0.14 $\times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>0.183</td>
<td>0.23 $\times 10^{-2}$</td>
</tr>
<tr>
<td>10%</td>
<td>0.60</td>
<td>0.336</td>
<td>0.09 $\times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>0.340</td>
<td>0.12 $\times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>0.196</td>
<td>0.18 $\times 10^{-2}$</td>
</tr>
<tr>
<td>20%</td>
<td>0.61</td>
<td>0.270</td>
<td>0.05 $\times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>0.283</td>
<td>0.07 $\times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.144</td>
<td>0.12 $\times 10^{-2}$</td>
</tr>
</tbody>
</table>
It is clear from the above results that the initial IV of the blends also has the same effect on the transesterification reaction as on the SSP reaction. This can be easily understood by the fact that the transesterification reaction also is a reaction between the polymer chains and/or end groups. The factors that influence the chain mobility will also have an effect on the transesterification reaction. Blends with lower initial IV have higher crystallinity and lower chain mobility, and therefore decreased transesterification reaction rates. In this case, however, we do not see any effect coming from the molar ratio of [-COOH] over [-OH] as before for the SSP reaction. This could be understood from the fact that the transesterification reactions are not necessarily reactions only between end groups and produce EG or water as byproducts, as required for the SSP reactions to increase molecular weight. The transesterification reactions can happen between the reactive sites in the polymer chains. Thus the diffusion of byproducts such as water and EG will not be a rate limiting factor in this case.
3.4 Conclusions

The SSP reactions of PET/PEN blends with three different PEN weight fractions (5%, 10%, and 20% respectively) were found to be diffusion controlled rather than chemical reaction controlled, under our experimental conditions. The kinetics of these SSP polymerization reactions were studied in terms of the apparent IV as well as end group concentration approaches. The values of activation energy, calculated using both methods, were very close to each other. These activation energy values, of about 17 kcal/mol, confirmed that the SSP process is controlled by the combination of byproduct diffusion and the polymer chain diffusion in the pellets. Within the range investigated, no major effects on SSP kinetics were found to result from differences in PEN blend composition.

The apparent rate constants of the SSP reactions were calculated using both the apparent IV and end group concentration approaches. The approach using end groups is a more reliable way to obtain accurate SSP apparent rate constants, as is indicated by the higher rate constant values obtained when using the end group concentration approach.

During SSP, the transesterification reaction occurred in the blends. The transesterification levels (RD %) increased with increasing SSP temperatures and times. Higher SSP temperatures favor higher transesterification reaction rates. The compositions of PEN in the different blends have little effect on the transesterification kinetics.
By assuming the second order transesterification reaction, a reaction rate constant and an activation energy value were obtained for each blend. The values of activation energy and the entropy term in the activation energy, confirmed the proposed reaction mechanism.

The number-average sequence chain lengths of the components in the blends were shortened as a result of transesterification reaction during SSP. The higher the PEN compositions in the blends, the more rapid the decreases of PET unit sequence lengths.

The advantages of SSP were shown by the simultaneous increases of the transesterification reaction levels (RD %) and the molecular weights of the blends during SSP. Long SSP times at higher temperatures resulted in leveling off of the transesterification reactions. This phenomenon was explained in terms of crystallization induced sequential reordering.

The effect of the initial IV of the blend precursor on the SSP reaction was illustrated by changes in the molecular weight, calculated from the end group concentrations. Samples with higher initial IV tend to have higher SSP reaction rates than those with lower initial IV values. The is because higher initial IV blends have lower overall levels of crystallinity, and greater portion of their crystalline structure results from secondary crystallization than in the case the blends with lower initial IV. Blend samples with higher initial IV tend to have greater chain mobility and thus higher SSP reaction rates. However, for the blend samples with the highest initial IV in our investigation, the effect
of [COOH] / [OH] counteracted with the crystallinity effect mentioned above. As a result, the initial IV effect on SSP rate is not clear for these blend samples.

Higher initial IV of the blend precursor favors a higher transesterification reaction rate, because of the higher chain mobility as a result of a lower level of crystallinity. The ratio of [COOH] / [OH] has no apparent effect on the transesterification reaction.
Chapter 4

Thermal properties of solid state polymerized PEN/PET blends

4.1 Introduction

Solid state polymerization has been adapted for use with PEN/PET blends as a critical process for both increasing the molecular weight and improving the miscibility of the blends. In addition to these modifications of the characteristics of the blends, the thermal properties will also be altered as a result of the SSP process. In this chapter several important thermal properties of the solid stated PEN/PET blends will be related to their effects on subsequent fabrication process, such as injection molding and stretch blow molding. Specific properties include melting behavior, dynamic crystallization behavior, cold crystallization behavior and AA generation kinetics.

These thermal properties are very important for processing PEN/PET blends. When blends are subjected to injection molding, it is important to understand their melting behavior. During the cooling cycle of the injection molding process, the polymer melt is cooled in the mold to the glassy state. Dynamic crystallization is carried out under different cooling rates from the melt state. It is therefore a better method to use for
simulating the crystallization of blend preforms during cooling in an injection molding process than an isothermal crystallization method. Another important factor to be considered in the injection molding process is the AA generation rate. For less influence on taste of the beverage in the polymer container, less AA generated is better during injection molding. SSP is known to improve the thermal stability of the polymer in terms of AA generation; therefore, we expect the thermal stability of PEN/PET blends will also be improved by SSP. AA generation tests were thus employed to study blend thermal stability. During stretch blow molding the polymer preform is heated to temperatures above $T_g$. The polymer is desired to have low crystallization rate in order to prevent crystallization from occurring during this heating process. Studies of the cold crystallization behavior of the PEN/PET blends are helpful for the understanding of the crystallization ability of the blends during the stretch blow molding process.

4.2 Experimental

4.2.1 Material

Because of the material availability limitations, the PEN/PET blends made from PET A and PEN A were used for the study of melting behavior, dynamic crystallization behavior, and AA generation kinetics. The PEN/PET blends made from PET B and PEN B were used for the study of melting behavior and cold crystallization behavior.
4.2.2 Method

4.2.2.1 Melting and crystallization analysis

The melting and crystallization behaviors of blends samples were monitored with a Perkin-Elmer differential scanning calorimetry (DSC-7). Samples were placed in unsealed aluminum pans in a dry nitrogen atmosphere with an empty aluminum pan as reference at preset heating/cooling rate. For melting behavior 10°C/min was used. For dynamic crystallization studies the heating/cooling rates are specified in section 4.3.2. For cold crystallization behavior studies the samples were ground to powders with the size of less than 40 mesh before the DSC measurements and dried at 100°C for at least 12 hrs.

4.2.2.2 Thermal stability analysis

An AA generation test was employed to study the changes in thermal stability of blend samples, after exposure to various solid-state polymerization conditions. A Perkin Elmer Gas Chromatograph was used for these experiments. The system consists of two instruments: the Auto Thermal Desorption (ATD) unit and the GC unit as seen in the schematic diagram in Fig. 4.2.1.
The function of the ATD unit is to extract the volatile compounds such as AA from the samples contained in the small sample tube and transfer the compounds to the GC for analysis. To accomplish this goal the ATD unit performs two-step desorption. In the first step, the heating oven heats the samples to the preset temperature for a preset period of time, the compounds generated during heating are carried by the inert gas (He) stream to the cold/heat trap where the AA is captured by the electrically cooled trap (its temperature is kept at -30 °C at this step). In the next step the trap is heated rapidly at a rate of 40 °C/s, so that the desorbed AA is transferred quickly to the GC unit where it will give a high-resolution peak.

Fig. 4.2.1  Schematic diagram of Pelkin Elmer GC system
4.3 Results and discussion

4.3.1 Melting behavior of solid stated PEN/PET blends

4.3.1.1 Multiple melting endotherms

Melting behavior is a very important characteristic of the solid stated samples. It can help us in the determination of the operation conditions during processing, e.g. the injection molding process.

The Perkin-Elmer DSC-7 was used to perform the experiment and analyze the data. Results for the 5% PEN/PET blends are shown in Fig.4.3.1 to Fig.4.3.3. The 10% and 20% blend samples show similar trends.
Fig. 4.3.1 Melting endotherms of 5% blend samples (Initial I.V. = 0.60) SSP at 210°C for different times
Fig. 4.3.2 Melting endotherms of 5% blend samples (Initial I.V. =0.60) SSP at 220 °C for different times
Fig. 4.3.3  Melting endotherms of 5% blend samples (Initial I.V. =0.60) SSP at 230 °C for different times
The well documented multiple melting peaks of polyesters are clearly shown for these blend samples. For the precursor, there is a lower melting peak at about 160 °C. For the solid stated samples there are one or two melting peaks, depending on the SSP temperature and time. As the SSP time (or temperature) increases, the first peak (for the double peak case) moves toward the higher temperature with the intensity increasing, while the second peak moves to the lower temperature with decreasing amplitude, until one single peak is formed and moves to higher temperature.

4.3.1.2 Initial IV effect on multiple melting endotherms

Another interesting study is to examine at the timing of the formation of the single peak in terms of the initial IV of the blend samples. Results obtained after 2 hours of exposure to 220 °C SSP are shown in figures 4.3.4 - 4.3.6 for the 5, 10, and 20% PEN/PET blends. We can see that for all blend compositions the single peak always occurs earlier for the blends with the higher initial IV for all the blend compositions.

Many explanations have been given concerning the multiple melting peaks. The most common mechanisms are the dual morphology model \cite{154-159} and the melting-recrystallization-remelting model \cite{160-163}. The dual morphology model claims that two types of spherulites are responsible for the two melting peaks in polymers. The melting-recrystallization-remelting model indicates that crystals obtained at low crystallization temperatures have a low degree of perfection and can partially melt and recrystallize during the course of thermal analysis scans to yield thicker and/or more perfect crystals.
Recently a different model proposed by Medellin-Rodriguez et al. [164, 165] has helped to explain the molecular weight effects on the multiple melting peak behavior, which is very similar to the results obtained for our blend samples. They suggested that the first melting peak was related to the last step of secondary crystallization involving the melting of the small branches of metastable crystalline material. The second peak came from the melting of the main metastable secondary branches formed during the secondary crystallization. The third melting peak is from the isothermal crystals, which will undergo recrystallization under linear heating.

Here we used the Medellin-Rodriguez’s model to explain the effect of initial IV on the melting behavior of the blends. According to this model, as the molecular weight of the polymer increases the mobility of the polymer chains are reduced by the entanglements, therefore there will be a greater portion of the chain section to be rejected out of the primary lamellae and participating in the secondary crystallization resulting in a stronger second melting peak and forming the single peak earlier. As shown in Figures 4.3.4 – 4.3.6, although they were crystallized at same SSP temperature and for same period of time, the blends with higher initial IV showed greater portions of the second melting peaks. This is what Medellin-Rodriguez’s model predicts. Therefore, their model can be used to explain our results.
Fig. 4.3.4 Melting endotherms of 5% blend samples with different initial I.V., SSP at 220°C for 2 hrs
Fig. 4.3.5 Melting endotherms of 10% blend samples with different initial I.V., SSP at 220 °C for 2 hrs
Fig. 4.3.6 Melting endotherms of 20% blend samples with different initial I.V., SSP at 220°C for 2 hrs
4.3.2 Dynamic crystallization behavior of solid stated PEN/PET Blends

4.3.2.1 Effect of cooling rate on crystallization peak temperature and crystallinity

The physical and mechanical properties of semi-crystalline polymers are highly dependent on the crystallinity and the morphology of the crystalline phase. This is why crystallization behavior is a very important research topic in the field of polymer science. Traditional studies of crystallization kinetics are often conducted under idealized conditions, for example isothermal crystallization is done by keeping the temperature constant. In real situations the external conditions change continuously. The dynamic (non-isothermal) crystallization analysis, which is carried out under changing conditions, therefore is a better choice for understanding real situations. In 1999 a review of the non-isothermal crystallization of polymers was published. It provides us with an overview of the theoretical approaches in this analysis.\textsuperscript{[166]}

In our studies the dynamic crystallization analysis is conducted by cooling the polymer sample from the melt state to the glassy state at a constant cooling rate. It can give a close simulation to the fabrication process.\textsuperscript{[134]} In the injection molding process the molten polymer is introduced into a mold and then cooled by the coolant to room temperature. This is similar to the dynamic crystallization process, although it is not necessarily at a constant cooling rate.
In making polymer parts we generally want them to be clear. This means we should make the degree of crystallinity in the final part as low as possible. The dynamic crystallization experiment can help us to predict the cooling rate required to have undetectable crystallization in the polymer. This work was first conducted by Dr. Jabarin in 1987 [134]. He successfully predicted the minimum cooling rate required to produce PET without detectable crystallinity, as a result of non-isothermal crystallization studies. In this work we will follow the same procedures to study our blend samples.

A Perkin-Elmer DSC-7 was used to perform the crystallization experiments and analyze the data. The samples used are listed in Table 4.3.1. Prior to the experiment the samples were dried in a vacuum oven to remove the moisture. The samples were heated from 40°C to 300°C at 80°C/min and held at that temperature for 5 minutes to erase the thermal history from the samples. The dynamic crystallization was achieved by cooling the sample to 40°C at different cooling rates. For the 5% PEN/PET blends we chose the cooling rates of 5°C, 6°C, 7°C, 8.5°C and 10°C/min. For the 10% PET/PET blends and the PET the cooling rates were 3°C, 3.5°C, 4°C, 4.5°C and 5°C/min. The 20% blends even the non-solid-stated samples (I.V. =0.7) did not show any crystallization exothermal peak during the DSC measurement even at the very slow cooling rate of 1°C/min. For this reason only crystallization behaviors of 5% and 10% PEN/PET blends were investigated.
Table 4.3.1 The selected samples for crystallization behavior study

<table>
<thead>
<tr>
<th>5% PET/PEN Blend</th>
<th>10% PET/PEN Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP condition</td>
<td>Apparent I.V.</td>
</tr>
<tr>
<td>No SSP</td>
<td>0.70</td>
</tr>
<tr>
<td>200°C, 10hrs</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The typical DSC curves for the dynamic crystallization are shown in Fig.4.3.7.

Fig.4.3.7 Crystallization exotherms of 5% blend samples (SSP@200°C for 10 hrs) at different cooling rates
The general trend for each sample is that the onset and the peak temperature of crystallization shifted to a lower temperature with increasing cooling rate. This is because there is sufficient time to activate nuclei at higher temperature when the cooling rate is lower; while insufficient time will cause the activation of nuclei occur at lower temperature as a result of faster cooling rate. The crystallization peak temperatures recorded for different samples at different cooling rates are shown in Fig.4.3.8.

![Crystallization peak temperature vs. cooling rate](image)

Fig.4.3.8 Crystallization peak temperatures at various cooling rates for different samples
From the above figure we can also see that the crystallization temperatures vary for these samples with respect to a certain cooling rate. The fact that the blend samples have different molecular weights, PEN compositions as well as various average chain lengths resulted from the transesterification reaction, can contribute to this phenomenon. We will discuss this in more detail in the kinetics study.

**Crystallinity vs. cooling rate**

It has been shown by the work in the Polymer Institute \cite{34, 35} that the thermal crystallization of blend with PEN fraction less than 40% is not co-crystallization. Only the major component (PET in our case) will crystallize while the minor component (PEN) is rejected into the amorphous phase. Also considering the PET compositions in blend samples, the degree of crystallinity of the blend sample can be calculated based on the heat of crystallization of completely crystalline PET:\cite{168}

\[
X_c = \frac{\Delta H_c}{\Delta H} \cdot \frac{1}{W_{PET}}
\]  
(4.3.1)

Where $\Delta H_c$ is the measured heat of crystallization, which is the area under the crystallization peak.

$\Delta H$ is the heat of crystallization of completely crystalline PET (84.6 J/g).\cite{168}

$W_{PET}$ is the weight fraction of the PET in blend sample
The results of calculated percent crystallinity of the PEN fraction of each blend are shown in Fig. 4.3.9. Using the method introduced by Jabarin [134] we plotted the percent crystallinity as a function of the reciprocal of cooling rate. A good linear relationship was obtained between these two variables for each sample. If we extrapolate the trend line to 0% crystallinity we can obtain the cooling rates required to produce clear parts. The results are listed in Table 4.3.2.

Fig. 4.3.9  The percent crystallinity as a function of the reciprocal of cooling rate for all the samples
Table 4.3.2. Estimated cooling rates required in order to achieve 0% crystallinity for each blend sample

<table>
<thead>
<tr>
<th>Cooling rate needed for zero Crystallinity (°C/min)</th>
<th>5% PEN/PET blend</th>
<th>10% PEN/PET blend</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IV = 0.70</td>
<td>IV = 0.81</td>
</tr>
<tr>
<td></td>
<td>~ 800</td>
<td>~ 30</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7</td>
</tr>
</tbody>
</table>

We see that for the same crystallization conditions the non-solid stated 5% blend with apparent IV of 0.70 and the solid stated 10% blend with apparent IV of 0.81 have the highest and lowest crystallization ability respectively. To produce clear parts we need the cooling to be around 800 °C/min for the non-solid-stated 5% blend sample (I.V. =0.7), while for the solid-stated same composition blend only 30 °C/min is needed. For 10% blend samples these values are 10 °C/min and 7 °C/min. Therefore by conducting SSP we not only increased the blends’ molecular weight but also made it less difficult to produce clear parts. The study of the non-isothermal crystallization kinetics of the blend samples will provide us with more information in order to have a better understanding of these results.
4.3.2.2 Non-isothermal crystallization kinetics

Many theoretical approaches have been used to study the kinetics of non-isothermal crystallization. \[^{166}\] The Ozawa model is commonly used for crystallization under constant cooling rate. It is a modified form of the Avrami equation, which is given by:

\[1 - \alpha_v = e^{[-k(T)/R]^n}\]  

(4.3.2)

Where, \(\alpha_v\) is the volume fraction of transformed material at temperature \(T\),

\(k(T)\) is the cooling crystallization function

\(R\) is the cooling rate

\(n\) is the Avrami exponent

We can obtain the kinetic parameters using this equation by rewriting it in the following form:

\[
\log[-\ln(1 - \alpha_v)] = n \log k - n \log R
\]  

(4.3.3)

If we plot \(\log[-\ln(1 - \alpha_v)]\) against \(\log R\) at a given temperature we obtain a straight line.

The slope of this straight line is (-n) and the intercept is (n log k).

The weight fraction of the crystallized material \(\alpha_w\) at any time \(t\) can be obtained as
\[
\alpha_w = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^\infty \frac{dH}{dt} dt}
\] (4.3.4)

where, \(\frac{dH}{dt}\) is the rate of evolution of heat.

Therefore \(\alpha_w\) is the ratio of the area under the crystallization exotherm at any time (t) to the area under the exotherm when the crystallization is complete. This weight fraction must be transformed into volume fraction since the Ozawa model is expressed in terms of volume fraction. This can be done by using the following relation: \(^{[168]}\)

\[
\alpha_v = \frac{\rho_a \alpha_w}{\rho_c} \frac{1}{1 - (1 - \frac{\rho_a}{\rho_c}) \alpha_w}
\] (4.3.5)

where, \(\rho_a\) and \(\rho_c\) are the density of the complete amorphous and crystalline sample.

For PET these values are 1.335 and 1.455 g/cm\(^3\) respectively. For blend samples, since only PET is in the crystalline phase and the amorphous phase contain both PET and PEN, the value for amorphous density is calculated as follows:
where, $X_{am\ PET}$ and $X_{am\ PEN}$ are the weight fractions of PET and PEN in the amorphous phase respectively,

$\rho_{am\ PET}$ and $\rho_{am\ PEN}$ are the density of pure PET and PEN respectively.

Using equations (4.3.4), (4.3.5), and (4.3.6) the volume fractions ($\alpha_v$) for different samples at different cooling rates were calculated, the results are illustrated in Fig.4.3.10.

Fig. 4.3.10 $\alpha_v$ vs. crystallization time at various cooling rates (10% PET/PEN blend SSP@200°C for 10 hrs)
Another calculation was done before using equation (4.3.3) to obtain the Avrami exponents and cooling functions \( k \). Since in the Ozawa model the secondary crystallization is neglected and only the primary crystallization regime is concerned \(^{168}\), we need to find the primary crystallization region in which to carry out this analysis for our samples. Another modified Avrami equation was used for this purpose. At a constant cooling rate there is a simple relation between temperature and time at a certain cooling rate, which is expressed in equation (4.3.7):

\[
t = \frac{T_0 - T}{R} \tag{4.3.7}
\]

where, \( T_0 \) is onset temperature of crystallization, and \( R \) is the cooling rate.

We can then substitute the calculated time \( t \) from equation (4.3.7) at a cooling rate into the Avrami equation (4.3.8):

\[
1 - \alpha_v = e^{[-kt]^n} \tag{4.3.8}
\]

and change it to the double-logarithmic form:

\[
\log[-\ln(1 - \alpha_v)] = n \log k - n \log t \tag{4.3.9}
\]
The plots of $\log [-\ln(1 - \alpha_v)]$ versus $\log t$ of 5% blend samples solid stated at 200 $^\circ$C for 10 hours are shown in Fig.4.3.11.

Fig.4.3.11 $\log [-\ln(1 - \alpha_v)]$ versus $\log t$ for 5% blend SSP @200 $^\circ$C for 10hrs
We can see that the linear variation between $\log[-\ln(1-\alpha_v)]$ and $\log t$ show different slopes at the later stage of crystallization than those shown at the early stage, especially at lower cooling rates, which is similar to the two-regime behavior in isothermal crystallization. This second regime behavior might be due to the secondary crystallization. Therefore using this method we could obtain the temperature range of the primary crystallization for each sample, which will be used in our non-isothermal crystallization kinetics analysis.

The Ozawa plots for each sample are presented from Figures 4.3.12 - 4.3.15.

Fig. 4.3.12 Ozawa plot of dynamic crystallization of non-solid stated 5% PET/PEN blends
Fig. 4.3.13 Ozawa plot of dynamic crystallization of solid stated 5% PET/PEN blends
Fig. 4.3.14 Ozawa plot of dynamic crystallization of non-solid stated 10% PET/PEN blends
Avrami plot of dynamic crystallization at various crystallization temperatures
(10% PET/PEN blend SSP @ 200 °C for 10 hrs)

Fig. 4.3.15  Ozawa plot of dynamic crystallization of solid stated 10% PET/PEN blends
The calculated n and k values are listed in Table 4.3.3.

Table 4.3.3  Values of n and k of dynamic crystallization by Ozawa analysis for each sample

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>5% PET/PEN blends</th>
<th>10% PET/PEN blends</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I.V.=0.7</td>
<td>I.V.=0.81</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>k</td>
</tr>
<tr>
<td></td>
<td>(°C/min)</td>
<td>(°C/min)</td>
</tr>
<tr>
<td>179</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>175</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>171</td>
<td>3.1</td>
<td>3.8</td>
</tr>
<tr>
<td>167</td>
<td>2.8</td>
<td>4.4</td>
</tr>
<tr>
<td>163</td>
<td>2.5</td>
<td>5.2</td>
</tr>
<tr>
<td>159</td>
<td>2.2</td>
<td>6.0</td>
</tr>
<tr>
<td>155</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>151</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The results in the above table show that for every sample, the n values decrease with decreasing temperature, from about 3 to about 2, indicating a transition in the crystallization mechanism, which is probably due to the change in the crystal dimension. This kind of behavior has also been observed by Jabarin [133]. The rate constant of crystallization (value k) increases with decreasing temperature. This is because the degree of undercooling, the driving force for crystallization, increased with decreasing temperature.

We see that for each composition, the non-solid-stated blend samples always have higher crystallization rate constants than the solid-stated samples. The reason is that the solid-
stated samples have higher molecular weight, which increases the viscosity of the polymer and decreases the rate at which a crystallizing segment can diffuse across the liquid-crystal interface.\[134] This will be understood better by the activation energy difference discussed in the next section.

It is clear that with increasing PEN composition, the tendency of the blend to crystallize decreases as illustrated by the decreasing crystallization rate. There are two possible reasons that contribute to this. First, as we discussed before, there are transesterification reactions between the PET and PEN components, as we have investigated using NMR. The degree of randomness increases and the number average chain length of each component decreases during the SSP process. Table 4.3.4 shows results obtained for selected samples.

Table 4.3.4 The RD, L_T and L_N values for selected blend samples

<table>
<thead>
<tr>
<th>SSP condition (Temperature and time)</th>
<th>5% PET/PEN blend</th>
<th>10% PET/PEN blend</th>
<th>20% PET/PEN blend</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RD</td>
<td>L_T</td>
<td>L_N</td>
</tr>
<tr>
<td>No SSP</td>
<td>3.9</td>
<td>520</td>
<td>27</td>
</tr>
<tr>
<td>200ºC, 10 hrs</td>
<td>15.1</td>
<td>133</td>
<td>7</td>
</tr>
</tbody>
</table>

We can see from the above table that there are no big differences between the RD values obtained for each solid-stated sample. With the increase of PEN composition, the number average chain length of PET units or PEN units in the blends decreases. This means that the PET chains become less and less regular from the 5% blend to the 20% blend. This irregularity of polymer chains makes the crystallization more difficult. Zheng and Qi et.
al \[^{169}\] studied the dynamic crystallization behavior of a Polycarbonate (PC)/PET blend. They showed that the crystallization ability of PET in the blends decreased with the introduction of PC chains into the PET phase as a result of the transesterification between PC and PET. For the 20% blends even the non-solid-stated samples (I.V. =0.7) did not show any crystallization exothermal peak during the DSC measurement, despite the very slow cooling rate of 1 °C/min.

Another reason for this phenomenon could be related to the PEN presence. If the assumption of only PET crystallizing is true, the uncrystallized PEN must diffuse away from the crystal and melt interface in order for the crystallization to proceed.\[^{170}\] Higher PEN compositions therefore mean this diffusion process needs more time and that will make the dynamic crystallization of PET more difficult.

**Activation energy**

Kissinger \[^{171}\] suggested a method to determine the activation energy \(\Delta E\) for the polymer chain segments diffusing to the growing crystal surface. The method is based on the variation of the crystallization peak temperature \(T_p\) with the cooling rate as shown below:

\[
\frac{d}{d}\left(\ln \frac{x}{T_p^2}\right) = -\frac{\Delta E}{R} \quad (4.3.10)
\]
where, $x$ is the cooling rate, $R$ is the gas constant.

$\Delta E$ then can be obtained by the slope of the plot of $\ln(x/T_p^2)$ versus $1/T_p$. The results for our samples are shown in Fig. 4.3.16.

![Kissinger plots of different samples with various cooling rates](image_url)

**Fig. 4.3.16** Kissinger plot of blend samples
The activation energy values obtained using the Kissinger plot can help us better understand the blend crystallization rate constant results. As shown in Table 4.3.3, the non-solid stated blend samples have higher crystallization rate constants than the solid stated blend samples. The reason is that the non-solid stated blend samples have a lower IV and consequently lower viscosity than the solid stated samples. This relatively low viscosity will allow the polymer chains in the non-solid stated blend samples to diffuse more easily to the crystalline phases during crystallization. As a result, the activation energy ($\Delta E$) values of the non-solid stated blend samples are lower than those of solid stated blend samples, as shown in Figure 4.3.16. Non solid stated 5% and 10% PEN/PET blends had activation energy values of about 70 kJ/mol in comparison with the activation energy values of about 80 kJ/mol for the solid stated 5% and 10% PEN/PET blends.

**Isothermal Crystallization**

The isothermal crystallization behaviors of our samples were also investigated for comparison purposes. The crystallization temperatures range was from 130 °C to 180 °C. The samples were heated from 40 °C to 300 °C at 80 °C/min and held at that temperature for 5 minutes to erase the thermal history from the samples. Then the samples were quickly cooled to the crystallization temperature and held for a period of time until the crystallization was complete.

The kinetics of isothermal crystallization were studied by the Avrami equation (4.3.2) and the Avrami number and the crystallization rate constant were obtained from the slope
and the intercept of the plot of log [-ln (1 - αv)] versus log t at the primary crystallization regime. One plot of log [-ln (1 - αv)] versus log t for isothermal crystallization of the 5% PEN/PET blends solid stated samples is shown in Figure 4.3.17. Calculated results of Avrami number and the crystallization rate constant values for all the blend samples are listed in Table 4.3.5.

![Graph showing log [-ln (1 - αv)] versus log t for 5% PEN/PET blends solid stated at 200 °C for 10 hrs](image)

**Fig. 4.3.17** log [-ln (1 - αv)] versus log t for 5% PEN/PET blends solid stated at 200 °C for 10 hours
Table 4.3.5  Values of n and k of isothermal crystallization by Avrami analysis for each sample.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>5% PET/PEN blends</th>
<th>10% PET/PEN blends</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I.V.=0.7</td>
<td>I.V.=0.81</td>
</tr>
<tr>
<td>n</td>
<td>k (°C/min)</td>
<td>n (°C/min)</td>
</tr>
<tr>
<td>130</td>
<td>2.8</td>
<td>8.3×10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>2.8</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.9</td>
</tr>
<tr>
<td>150</td>
<td>2.8</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>160</td>
<td>2.7</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>170</td>
<td>2.7</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.7</td>
</tr>
</tbody>
</table>

The results showed that the Avrami exponent at each crystallization temperature for each sample is close to 3 suggesting a heterogeneous spherulite crystallization mechanism. This Avrami exponent does not change with temperature. This suggests that the mechanism of isothermal crystallization is different from that of the non-isothermal case, in which the Avrami number decreases with the decreasing temperature.

The variations of the crystallization rate constants are quite consistent with those of the non-isothermal crystallization studies, in the sense that the solid stated blend samples and higher PEN composition blend samples always have lower crystallization rates than the non-solid stated and lower PEN composition blend samples. The reasons we discussed in terms of non-isothermal crystallization also account for these isothermal process results.
4.3.3 Cold crystallization behavior

We can also study the cold crystallization behavior of the blend samples from the glassy state using DSC scans. The experiment was done by first heating the sample quickly to 300 °C and holding it for 1 min to erase the thermal history then quenching to room temperature and heating again to 300 °C at 10 °C/min to study the cold crystallization behavior.

As we can see from Figures 4.3.18 - 4.3.20, as a result of the SSP process, the cold crystallization peak temperature ($T_c$) of blend samples gradually shifts to higher temperatures and becomes broader and smaller. Meanwhile, the melting peak temperature moves to lower temperatures and the melting endotherms become smaller. This suggested that the crystallization ability and the perfection in the crystals formed by the blends samples, decreases as a result of the increase in molecular weight and the transesterification reactions, which interrupts the chain periodicity by introducing of PEN units into PET polymer chains.
Fig. 4.3.18 Second heating DSC scans of 5% blend samples with different apparent IV and RD values (Initial IV = 0.60)
Fig. 4.3.19  Second heating DSC scans of 5% blend samples with different apparent IV and RD values (Initial IV = 0.65)
Fig. 4.3.20  Second heating DSC scans of 5% blend samples with different apparent IV and RD values (Initial IV = 0.70)
It has been found that factors influencing the crystallization rate of the polymer will show the same effects, when the polymer is cooled from the melt or heated from the glassy state.\textsuperscript{[172]} More importantly it has been shown that there exists a correlation between the half time of isothermal crystallization and the peak crystallization temperature (\(T_c\)) during a non-isothermal experiment.\textsuperscript{[173]} Since \(T_c\) is more easily achieved we used \(T_c\) to represent the crystallization ability of the blends samples. From our results we found there are three factors affecting the cold crystallization temperature \(T_c\). They are IV, RD value, and PEN composition. As was done by Pilati\textsuperscript{[173]}, we propose a linear dependence of \(T_c\) on IV and also for PEN composition. It has been found\textsuperscript{[21, 23, 26]} that when the transesterification reaction is higher than a critical level it will have little effect on the crystallization of the blends samples. Therefore in order to model this relationship we choose the exponential form for RD value dependence as shown in the following equation.

\[
\ T_c = a + b \times (I.V.) + c \times [(1-exp (-RD))]^n + d \times (X_{PEN})
\]

Where, \(T_c\) is the crystallization peak temperature from the glassy state (\(^\circ\)C),

- \(IV\) is the apparent IV of the blends samples (dg/l),
- \(RD\) is the degree of randomness of the blends samples,
- \(X_{PEN}\) is the weight fraction of PEN composition in the blends.

Before performing the regression, to obtain the model constant we need to look at the surprising finding of the \(T_c\) results in terms of initial IV of the blends. As can be seen in Fig. 4.3.21 for the 5% PEN/PET, even though the IV and RD values are very similar
within each PEN composition blend group the $T_c$ values are quite different for samples with different initial IV. The samples obtained from the higher initial IV always had higher $T_c$.

This can be understood by realizing the catalyst effect on crystallization. Pilati\cite{173} pointed out that this effect came from the apparent increase of molecular weight as a result of interactions between the catalyst and the end groups of the polymer chains. Since our blends were made from the PET with different levels of degradation through the extruder, the longer thermal treatment for the lower IV PET, therefore, would weaken or destroy the linkages between the catalyst and the end groups of the polymer chains. Thus, less extent of catalyst effect on the blends with lower initial IV would be expected than for the blends with higher initial IV. In order to confirm this we conducted the SSP process for the PET samples with different initial IV (0.63 and 0.67) and performed the same DSC scans to get $T_c$. Results shown in Fig.4.3.22 confirmed our explanation. At the same values of molecular weights, PET samples starting from lower initial IV had lower cold crystallization temperatures than PET samples starting from higher initial IV. This indicates that the nature of the catalyst system has changed. It has gone from a state in which it was more soluble in the PET matrix, to one in which it exhibits a higher level of separation, in the form of a non-soluble particulate. In this changed form it can act as a more effective nucleating agent, causing cold crystallization to occur more readily at lower temperatures.
Fig. 4.3.21 Second heating DSC scans of 5% blend samples with similar apparent IV and RD values, but made from different initial IV
Fig. 4.3.22 $T_c$ values as a function of IV of PET samples made from different initial IV
Based on the above finding we calculated the constants for the model for the groups differentiated by their initial IV values, using the multiple regressions by Sigma Plot 2000® software. Results are shown below. The R squared value of each regression was around 0.98 that showed the validity of the proposed model.

Group1: Initial I.V. ~ 0.60:

\[ T_c = 66.0 + 61.2 \times (IV) + 34.4 \times [(1-\exp(-RD))]^{0.09} + 180.5 \times (X_{PEN}) \]
\[ R^2 = 0.98 \]

Group 2: Initial I.V. ~ 0.66:

\[ T_c = 28.9 + 30.7 \times (IV) + 102.6 \times [(1-\exp(-RD))]^{0.06} + 190.2 \times (X_{PEN}) \]
\[ R^2 = 0.99 \]

Group3: Initial I.V. ~ 0.70:

\[ T_c = 85.8 + 58.7 \times (IV) + 26.0 \times [(1-\exp(-RD))]^{0.07} + 180.7 \times (X_{PEN}) \]
\[ R^2 = 0.98 \]

If we fix two variables in the above models we can find the effect of the third factor. For example if we set I.V. = 0.8 for a 5% PEN/PET blend sample solid stated from precursor with I.V. of 0.60 we can obtain the following figure (Fig. 4.3.23) for the \( T_c \) dependence on RD values. We can see that after the RD value is higher than 25% the \( T_c \) changes very little.
Fig. 4.3.23  \( T_c \) values calculated from model as a function of RD value for 5 %PEN/PET blend samples ( IV =0.80)

### 4.3.4 Thermal stability (AA generation)

Acetaldehyde (AA) generation tests were conducted on non-solid stated and solid stated blend samples to investigate the effects of SSP on the thermal stability of the blends. Also for comparison the same experiments were conducted on the pure PET (IV = 0.795) and pure PEN non-solid stated resins (IV = 0.51). Table 4.3.6 lists the information for the selected blend samples. As we can see from the table, all the non-solid-stated blends have an apparent IV of around 0.7 and all the solid-stated samples have an apparent I.V. of 0.81. The AA generation tests were performed for all the samples at temperatures from 280 \(^\circ\)C to 300 \(^\circ\)C. The results are shown in Figs. 4.3.24 and 4.3.25 for the 5% blends.
Table 4.3.6. The selected blend samples for AA generation tests

<table>
<thead>
<tr>
<th>Blend</th>
<th>SSP Condition</th>
<th>Apparent I.V.</th>
<th>Blend</th>
<th>SSP Condition</th>
<th>Apparent I.V.</th>
<th>Blend</th>
<th>SSP Condition</th>
<th>Apparent I.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% PET/PEN Blend</td>
<td>No SSP</td>
<td>0.70</td>
<td>10% PET/PEN Blend</td>
<td>No SSP</td>
<td>0.71</td>
<td>20% PET/PEN Blend</td>
<td>No SSP</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>200°C, 10hrs</td>
<td>0.81</td>
<td></td>
<td>200°C 10hrs</td>
<td>0.81</td>
<td></td>
<td>200°C 10hrs</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Fig. 4.3.24 Amount of AA generation as a function of effective generation time

(5% PET/PEN blends, not solid-stated, Apparent I.V.=0.70)
Fig. 4.3.25 Amount of AA generation as a function of effective generation time

(5% PET/PEN blends, SSP@ 200°C for 10 hrs, Apparent IV=0.81)
From the experimental results we can obtain the apparent AA generation rate for each sample by assuming a linear relationship between the amount of AA generation and the effective generation time (by subtracting the induction time from the actual generation time). By the best linear fitting between these two parameters we can get the apparent AA generation rate \( (k) \) for each sample. The results are listed in Table 4.3.7 and 4.3.8.

Table 4.3.7  The apparent AA generation rate constant \( k \) (ppm/min) for different blends at different generation temperatures

<table>
<thead>
<tr>
<th>SSP condition (Temperature and time)</th>
<th>5% blend</th>
<th>10% blend</th>
<th>20% blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>280ºC</td>
<td>290ºC</td>
<td>300ºC</td>
<td>280ºC</td>
</tr>
<tr>
<td>No SSP</td>
<td>4.2</td>
<td>7.2</td>
<td>12.0</td>
</tr>
<tr>
<td>200ºC, 10 hrs</td>
<td>3.0</td>
<td>5.3</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Table 4.3.8  The apparent AA generation rate constant \( k \) (ppm/min) for virgin PET and PEN at different generation temperatures

<table>
<thead>
<tr>
<th>PET (IV=0.795)</th>
<th>PEN (IV=0.51)</th>
</tr>
</thead>
<tbody>
<tr>
<td>280ºC</td>
<td>290ºC</td>
</tr>
<tr>
<td>2.5</td>
<td>4.3</td>
</tr>
</tbody>
</table>

By comparing the \( k \) values we find that the AA generation rate decreases with the increase of apparent I.V. as a result of the SSP process. When we look at all the solid-stated blend samples, however, we do not find much difference between samples with
different PEN concentrations. We conclude, therefore, that as long as the blend samples have the nearly same apparent IV, PEN composition seem to have little effect on the thermal stability of the samples in terms of AA generation. Non-solid stated PEN has a lower IV(0.51), therefore, its AA generation rate is much higher than those of PET or PET/PEN blends.

We can also obtain the activation energies for all the samples by making Arrhenius plots. Figure 4.3.26 shows the Arrhenius plots with the calculated activation energies for 5% blends.

![Arrhenius plot](image)

**Fig. 4.3.26 Arrhenius plot of apparent rate constant of AA generation for 5 % PET/PEN blend samples**
The calculated activation energy values are listed in Table 4.3.9.

Table 4.3.9 The apparent AA generation activation energy for different samples

<table>
<thead>
<tr>
<th>Sample information</th>
<th>Activation energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% PEN/PET blends</td>
<td></td>
</tr>
<tr>
<td>No SSP</td>
<td>Apparent IV = 0.70</td>
</tr>
<tr>
<td>SSP@ 200 °C, 10 hrs</td>
<td>Apparent IV = 0.81</td>
</tr>
<tr>
<td></td>
<td>32.7</td>
</tr>
<tr>
<td>10% PEN/PET blends</td>
<td></td>
</tr>
<tr>
<td>No SSP</td>
<td>Apparent IV = 0.71</td>
</tr>
<tr>
<td>SSP@ 200 °C, 10 hrs</td>
<td>Apparent IV = 0.81</td>
</tr>
<tr>
<td></td>
<td>36.7</td>
</tr>
<tr>
<td>20% PEN/PET blends</td>
<td></td>
</tr>
<tr>
<td>No SSP</td>
<td>Apparent IV = 0.72</td>
</tr>
<tr>
<td>SSP@ 200 °C, 10 hrs</td>
<td>Apparent IV = 0.81</td>
</tr>
<tr>
<td></td>
<td>38.8</td>
</tr>
<tr>
<td>PET (IV=0.795)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39.2</td>
</tr>
<tr>
<td>PEN(IV=0.51)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.1</td>
</tr>
</tbody>
</table>

We can see from the above table that the average activation energy for each solid-stated blend sample is higher than that of corresponding non-solid-stated blend sample. The increment is small, since the original blends already have IV values of nearly 0.7. This means that the energy barriers for the AA generation reactions to occur have been increased and the thermal stabilities of the blends have been improved by the SSP process.

Pure PEN used to obtain the blends has a low activation energy value of AA generation, because it is in amorphous phase and has not been solid stated, therefore has more end groups (e.g. carboxyl end groups) to participate in the AA generation reactions. The PET resin used to prepare the blends, on the other hand has high activation energy value since
it has been through a solid state polymerization process and has fewer end groups needed for the AA generation reactions.

4.4 Conclusions

Multiple melting behaviors were observed for blends samples as a result of SSP. Medellin-Rodriguez’s model was applied to explain the multiple melting peaks and the effect of initial I.V. on the timing of the formation of a single melting peak.

For blend samples the percent crystallinity achieved during dynamic crystallization decreased with increasing sample molecular weight and PEN composition. The minimum cooling rates required to produce non-crystalline blends are predicted for 5% and 10% blends.

The non-isothermal crystallization kinetics parameters were obtained using the Ozawa equation. The Avrami exponents decreased with decreasing temperature, indicating a change in the crystallization mechanism. For all the samples the cooling function $k$ increased with decreasing temperature, within the investigated temperature range.

The activation energies for non-isothermal crystallization of different samples were calculated using Kissinger plots. The activation energies are higher for samples with
higher IV and higher PEN composition. These results are in agreement with those of crystallization rate constants. The isothermal crystallization study shows the same changing trends in crystallization rate constants as those obtained for non-isothermal crystallization. The Avrami exponent did not change with temperature. Its value is close to 3, indicating a heterogeneous spherulite crystallization mechanism.

Cold crystallization behavior was studied by DSC. The cold crystallization ($T_c$) was used to represent the crystallization ability of the blends samples. Combining the factors affecting $T_c$, a numerical model was developed to predict its value.

The SSP process improves the thermal stability of the blends samples. The AA generation rate constant $k$ decreases and the activation energy for AA generation increases as a result of SSP.
Chapter 5

Fabrication process of solid stated PEN/PET blends

5.1 Introduction

The ultimate objective of this project is to manufacture containers from the solid stated PEN/PET blends with conventional PET molds using injection molding and stretch blow molding processes. The investigation of effects of SSP on the fabrication process of PEN/PET blends is, therefore, of critical importance for fulfilling our final objective.

In the current work a two-stage stretch blow molding process was used to manufacture PEN/PET bottles. The preforms of the blends were first injection molded, then cooled to room temperature and later blown into containers using a lab scale reheat-blow (RHB) stretch blow molding machine.

An essential preform property to be considered when choosing the proper injection molding process variables is the optical clarity. Transparent preforms are always desired in producing soft drink or other beverage containers. For pure PET the transparency is secured by preventing PET from crystallizing during the cooling stage of the injection
molding cycle. The situation becomes more complex when the preforms are made of PEN/PET blends, which will appear transparent only when the two phases in the blends have achieved sufficient miscibility in addition to remaining free of crystallization. In Chapter four it has been shown that PEN/PET blends have less tendency to crystallize than PET. The main concern for blend clarity therefore, is to obtain enough miscibility between the PET and PEN components by achieving a critical transesterification level, which is 15-20%. \cite{17, 21, 23, 26 and 27} Tharmapuram and Jabarin \cite{26, 27} applied transesterification reaction kinetics to predict the critical transesterification temperatures of PEN/PET blends during extrusion. These temperatures are about 50°C higher than the equilibrium melting temperatures of the blends. These high temperatures could cause the blends to undergo thermal degradation. If copolymers are used instead of homopolymers of PET and PEN, the required processing temperature can be reduced about 20°C. PEN/PET blends subjected to SSP are expected to require lower processing temperatures, compared to non-solid-stated blends, as a result of the increased transesterification levels which can be achieved during SSP.

Stretch blow molding techniques are widely used in the production of plastic containers. There are two reasons to stretch the plastic. \cite{174} The first one is economic, since the stretching makes the bottles thinner and less expensive. The second one is that as a result of stretching and the resultant orientation, the physical and barrier properties of the plastic are improved. The orientation occurs in the rubbery state when the stretch forces make the polymer chain segments align closer to one another. This finally leads to strain induced crystallization (SIC). The critical extension ratio, at which this happens, is called
the natural draw ratio or the strain hardening point. It is very important that the preform extension ratios during stretch blow molding exceed the strain hardening point of the resin, in order to achieve optimal thickness distributions and orientation levels for the final products.

Extensive research had been conducted on the orientation of PET. Jabarin [5] studied the relationships among molecular orientation, physical properties and molecular weight of PET and their dependence on orientation variables. Bonnebat and colleagues [139] found that resin molecular weight directly controls the strain hardening point. The effect of process parameters and preheat and equilibration times on the properties of the stretch-blow bottles was investigated by Kim [175, 176]. Venkateswaran, Cameron and Jabarin [177] studied the relationship between the temperature profiles and the properties of the reheat-and-blow containers. Tharmapuram and Jabarin [26, 29] showed that the strain hardening point of the PEN/PET blend is a function of PEN composition, processing temperature, molecular weight and transesterification level. At the same molecular weight levels, the PEN/PET blends have higher strain hardening points than PET. The existing preform and stretch blow mold design can, therefore, only be applied to PEN/PET blends which have higher molecular weights and therefore strain hardening points comparable to those of PET.

In this section many important operating parameters of injection molding and stretch blow molding were investigated as functions of molecular weights and the transesterification levels of the solid stated PEN/PET blends samples. The parameters
studied included the injection molding temperature, the temperature profile of the
preform, the average stretch blow molding temperature, and the upper limit of the stretch
blow molding temperature.

By controlling the operating parameters mentioned above, two-liter bottles with optimal
properties were produced from PEN/PET blends with different compositions. Their
properties such as levels of crystallinity, tensile mechanical properties, and oxygen
barriers were analyzed and compared with those of PET bottles.

5.2 Experimental

5.2.1 Materials

The PEN/PET blends used in this study were made from PET B and PEN B as described
in section 3.2.1. The blends with apparent IV of about 0.70 were directly obtained
through the melt blending of PET B and PEN B in a twin screw extruder. Other blends
with higher IV were obtained by the SSP process. The apparent IV values shown in Table
5.2.1 were calculated from the melt viscosities of the blends. The RD levels were
measured by proton NMR.
Table 5.1.1 PEN/PET blends for injection molding experiments

<table>
<thead>
<tr>
<th>PEN composition ( wt% PEN)</th>
<th>Apparent I.V.</th>
<th>Degree of Randomness (RD %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>0.71</td>
<td>7.7%</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>13.8%</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>18.8%</td>
</tr>
<tr>
<td></td>
<td>0.83</td>
<td>26.0%</td>
</tr>
<tr>
<td>10%</td>
<td>0.71</td>
<td>9.6%</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>25.6%</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>35.7%</td>
</tr>
<tr>
<td></td>
<td>0.91</td>
<td>45.4%</td>
</tr>
<tr>
<td>20%</td>
<td>0.71</td>
<td>6.3%</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>15.9%</td>
</tr>
<tr>
<td></td>
<td>0.86</td>
<td>27.0%</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>39.0%</td>
</tr>
</tbody>
</table>

5.2.2 Method

5.2.2.1 Blending and SSP

The equipment and procedures used for preparing blends and SSP are the same as described in section 3.2.

5.2.2.2 Injection Molding

The injection molding machine used is a model ALLROUNDER 320s Arburg Injection Molding Machine. This is a 55-ton capacity, reciprocating-screw type machine, controlled by a SELOGICA control system. A single cavity three-plate mold was used to
obtain 2-liter bottle performs. Prior to the injection molding process the resins were dried overnight in a Conair SC 60 dehumidifier drier with a CH 16-4 hopper dryer system set at a temperature of 140 °C and a dew point of -40°C. During the injection molding operation the resins were transferred to the injection molding machine from the drier by an automatic loading system.

5.2.2.3. Stretch-Blow Molding

A lab-scale, reheat and stretch-blow molding machine was used to blow-mold bottles. The machine is equipped with a Sidel type heater box mounted on a carriage. The heating system consists of twelve GTE Sylvania quartz lamps rated at 1600 watts, with peak filament temperatures of 2200K at 240 volts. The heater temperature can be controlled by adjusting the heater voltage settings. During the heating process the heater box first moves toward the rotating preform, which sits on the mandrel, then passes the preform and reverses moving direction to go back to the starting position. The speed of the heater box movement can be adjusted to obtain different heating times and therefore different preform temperatures.
5.2.2.5 Evaluation of properties

Haze Measurement

A Gardner hazemeter was used to measure the percent haze of the preform and the bottle sidewall samples. In order to minimize the error of haze measurement caused by the curvature of the preform, the perform was cut in half and the inner surface was cover by black tape such that only a slit portion (3 cm × 0.3 cm) at the center of the preform was visible to the haze meter. The outside surface of the visible portion of the preform was faced toward the detector.

Density measurement

The densities of the blends samples were measured at 25°C using a density gradient column made of calcium nitrate solution and calibrated by suspending glass beads of known density.

Birefringence

A Metricon® Model 2010 Prism Coupler was used to measure the refractive indices of bottle sidewalls samples. The birefringence was calculated from the refractive indices in the three principal directions, the thickness direction ($n_x$), the axial direction ($n_y$), and the hoop direction ($n_z$). The birefringence in axial and in hoop direction is calculated using
equation (5.2.1) and (5.2.2) shown below. Birefringence for both inside and outside surface of the bottle sidewall samples were measured.

\[ \Delta_A = n_y - n_x \]  \hspace{1cm} (5.2.1)  

\[ \Delta_H = n_z - n_x \]  \hspace{1cm} (5.2.2)  

where, \( \Delta_A \) and \( \Delta_H \) are the birefringence in axial and hoop direction respectively.

**Mechanical Properties**

Mechanical properties of specimens cut in the axial and hoop directions of the bottle sidewall were determined using an Instron tensile testing machine. A standard ASTM D1708 procedure was used to measure Young’s modulus, yield stress, tensile energy absorption (toughness) and percent elongation to break at a crosshead speed of 2 in/min. The specimens were conditioned at 23 ± 2º C and 50 ± 5% relative humidity for not less than 40 hours prior to testing. The dimension of the samples is shown in Fig. 5.2.1

![Fig. 5.2.1 Dimension of samples used for ASTM D1708 tensile test](image)

- Tolerance = ± 0.051 mm (± 0.002 in)
- Thickness = thickness of bottle sidewall
- Minimum tab length, \( T = 7.9 \) mm (0.312 in)
- Minimum length, \( L = 38.1 \) mm (1.5 in)
Barrier properties

Oxygen permeability was determined by measuring the transmission rate at steady state using a Mocon OX-TRAN ten-fifty oxygen permeability tester. The measurements were carried out in a constant conditions laboratory maintained at 23°C and 50% relative humidity.

5.3. Results and discussion

5.3.1. Injection molding of PEN/PET blends

Because of the inherent immiscibility of PET and PEN, optically clear performs can only be obtained after the blends achieve a critical transesterification level as reported by Shi and Jabarin [21, 23] and Tharmapuram and Jabarin [26, 27]. The effects of several injection molding process parameters on preform clarity were studied by Tharmapuram and Jabarin [26, 27]. They concluded that the processing temperature was the most important factor. Other factors such as injection pressure and holding pressure had no visible effects. In our experiments we have, therefore, focused on the investigations of the critical injection molding temperature required for each PEN/PET blend to achieve the critical transesterification level and produce clear preforms.
Blends samples selected for these experiments have different molecular weights (apparent IV) and different transesterification levels (represented by the degree of randomness RD %) as a result of the SSP process. In this way we could study the effects of SSP of blends on the critical injection molding temperatures. For each blend sample only the injection molding barrel temperature was changed, with other parameters kept constant. The preforms produced in this way were subjected to haze measurement according to the method described earlier. When the percent haze is lower than 10% the preform appears optically clear. The results obtained for 20% PEN/PET blends with apparent IV values of 0.71 and 0.92 dl/g are shown in Fig. 5.3.1.

![Percent Haze vs. Injection Molding Temperature (20% PEN/PET blends)](image)

Fig. 5.3.1 Percent haze vs. Injection molding temperature for 20% PEN/PET blends
Preform made from 5% and 10% blends showed the similar results as shown in Fig. 5.3.2 and 5.3.3.

Fig. 5.3.2  Percent haze vs. Injection molding temperature for 5% PEN/PET blends
Fig. 5.3.3 Percent haze vs. Injection molding temperature for 20% PEN/PET blends
As we can see in the above plot, performs prepared from the solid stated blends exhibited much lower haze values than those prepared from the non-solid stated samples. This is because that the SSP process not only increased the molecular weight of the blend, but also improved the miscibility between PEN and PET in the blend system by enhancing the transesterification reactions between the two polymer molecules. The direct result of this for injection molding applications is that the critical injection molding temperature was reduced for the solid stated blends samples, as can be seen in Table 5.3.1. As a consequence, less degradation would be expected for these samples than for the non-solid stated samples. For example, for the 20% PEN/PET non-solid stated sample, the degree of randomness is only 6.3%, the critical injection molding temperature was 300°C. When the same blend was solid stated to an apparent IV of 0.92 and degree of randomness of 39%, the critical injection molding temperature was reduced to only 275°C.
Table 5.3.1 Injection molding temperature required for obtaining clear preforms for the PEN/PET blends with different Apparent IV and transesterification reaction levels

<table>
<thead>
<tr>
<th>Blend composition (% PEN)</th>
<th>Apparent IV Of Resin</th>
<th>Degree of randomness of resin (%)</th>
<th>Injection molding Temperature required for obtaining clear preform (°C)</th>
<th>Degree of randomness of preform (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.71</td>
<td>7.7%</td>
<td>285</td>
<td>14.8 %</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>13.8%</td>
<td>285</td>
<td>19.5 %</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>18.8%</td>
<td>280</td>
<td>25.8 %</td>
</tr>
<tr>
<td></td>
<td>0.83</td>
<td>26.0%</td>
<td>275</td>
<td>33.6 %</td>
</tr>
<tr>
<td>5%</td>
<td>0.71</td>
<td>9.6%</td>
<td>285</td>
<td>15.7 %</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>25.6%</td>
<td>280</td>
<td>30.8 %</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>35.7%</td>
<td>275</td>
<td>37.4 %</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>45.4%</td>
<td>270</td>
<td>48.9 %</td>
</tr>
<tr>
<td>10%</td>
<td>0.70</td>
<td>6.3%</td>
<td>300</td>
<td>22.0 %</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>15.9%</td>
<td>295</td>
<td>25.0 %</td>
</tr>
<tr>
<td></td>
<td>0.86</td>
<td>27.0%</td>
<td>285</td>
<td>31.8 %</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>39.0%</td>
<td>275</td>
<td>43.5 %</td>
</tr>
<tr>
<td>20%</td>
<td>0.70</td>
<td>6.3%</td>
<td>300</td>
<td>22.0 %</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>15.9%</td>
<td>295</td>
<td>25.0 %</td>
</tr>
<tr>
<td></td>
<td>0.86</td>
<td>27.0%</td>
<td>285</td>
<td>31.8 %</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>39.0%</td>
<td>275</td>
<td>43.5 %</td>
</tr>
</tbody>
</table>

In Table 5.3.1 the RD values are listed for the preforms produced from each blend under different injection molding temperatures. It has already been reported \cite{26, 27} that the critical RD values required to produce clear preform are about 15% -20%. This is in agreement with the results in our experiments. For example, in Table 5.3.1, we can see that for the 5%, 10% and 20% blend resins without SSP (i.e. apparent IV of about 0.71)
the minimum RD% required to obtain clear perform is from 14.8% (5% blend) to 22.0% (20% blend).

If the initial RD values of the blend resins are already beyond this minimum value as a result of SSP, the injection molding process is only for melting the resin and not for the purpose of increasing RD values for the blend resins. For example, in Table 5.3.1, we can see that the 20% blend with an apparent IV of 0.70 has only an RD value of 6.3%; therefore in order to produce an optically clear preform from this resin the required minimum injection molding temperature is 300°C to increase the RD value to about 20%. For the 20% blend with an apparent IV of 0.86 and RD value of 27.0%, however, the required minimum injection molding temperature is reduced to 285°C. This is because that the blend resin already has a high initial RD value as a result of SSP, therefore, during the injection molding process the operation temperature would not have to be as high as that in the previous case. The required minimum injection molding temperature is primarily determined by the melting point of the blend resin.

5.3.2 Stretch blow molding of PEN/PET blends preforms

5.3.2.1 Minimum stretch blowing temperature

The different stretch blowing temperatures of the preforms were achieved by adjusting the heater box movement speed of the RHB machine. A higher heater box speed gives shorter heating times, and vice versa. Immediately after leaving the heater box, the
The preform was transferred to a station where its inside and outside temperatures were measured using two infrared thermal sensors. The thermal sensors were positioned at the designated spot near the axial center area of the preform (about 7 cm from the bottom). The cooling curves were then generated for the preform with different heating times over an extended equilibration time as seen in Fig. 5.3.4.

**Preform Sidewall Temperature Profile**
(20% PEN/PET blend, Apparent IV = 0.85)

![Temperature profile of the preform sidewall (20% PEN/PET) over equilibration time](image)

Fig. 5.3.4 Temperature profile of the preform sidewall (20% PEN/PET) over equilibration time.
In our experiment the equilibration time was around 23 seconds, which offered a preferred preform temperature profile with the inside surface being hotter than the outside surface. This kind of profile is desired since during stretching the inside sidewall experiences higher extension ratios than the outside one, especially in the hoop direction. We calculated the extension ratio from the diameters of the preforms and the bottles. We found that the extension ratio in the hoop direction is about 5.3 for the inside sidewall and about 3.5 for the outside wall. The average preform temperature at blowing was calculated as the average between the inside and outside temperature and is plotted in Fig.5.3.5.

![Preform Average temperature vs. Heating box speed](image)

Fig.5.3.5  Preform average temperature vs. heating time of the stretch blow molding machine for 20% PEN/PET blend with apparent IV of 0.85)
The appearances of the bottles obtained with different perform temperatures are shown in Figures 5.3.6 - 5.3.8 for 5%, 10% and 20% PEN/PET blend respectively.

Fig. 5.3.6 Optical appearance of 5% PEN/PET bottles (resin apparent IV=0.75)
Fig. 5.3.7  Optical appearance of 10% PEN/PET bottles (resin apparent IV=0.81)
Fig.5.3.8  Optical appearance of 20% PEN/PET bottles (resin apparent IV=0.86)
From the above photographs we can see that at lower stretching temperature the bottles appeared hazy. With increased stretching temperature the bottles became clear. By looking at the bottle sidewall carefully we found that the haziness was coming from the inside surface, as it shown in Fig. 5.3.9 for a piece of sample cut from the bottle sidewall. This has been known as the stress whitening phenomena. It happens when the temperature is too low or the draw ratio is too high or both, for the polymer chain to be drawn homogeneously. Under these conditions some polymer chains would be fractured and result in microvoids \[175, 176\] along the inner wall. In our case although the inner surface was hotter than the outside surface, the extension ratio was also higher on the inside. This high extension thus caused the stress whitening to occur on the inner surface of bottles, stretched at too low preform temperatures.

Fig.5.3.9  20% PEN/PET bottle sidewall sample with inner layer peeled off
The minimum temperature needed for the blend bottles to become clear can be determined from the haze measurements of the bottle sidewall. This can be seen in Fig.5.3.10. for the 20% blends. A minimum temperature was specified as the temperature at which the percent haze is lower than 5%.

![Haze of bottle sidewall vs. Average Preform Temperature](image)

Fig.5.3.10  Percent haze of bottle sidewall vs. average preform blowing temperature (20% blend, apparent IV = 0.82)

The temperature at which the bottle became clear increased for the blends with increasing PEN composition as seen in Table 5.3.2. This is because of the glass transition temperature effect. The $T_g$ values for 5%, 10% and 20% PEN/PET blends are 80°C, 81.6°C and 85°C respectively. Blends with higher PEN composition will, therefore, require higher stretching temperatures to enable the polymer chains to have enough mobility to prevent stress whitening.
Table 5.3.2  Minimum stretch blow temperature for PEN/PET blends to get clear bottles

| PEN composition ( wt% PEN) | Minimum stretch blow temperature $T_{\text{min}}$ (°C) | $T_g$ (°C) | $T_{\text{min}} - T_g$ (°C) |
|---------------------------|--------------------------------|----------|----------------|------------------|
| 5%                        | 101                            | 80.0     | 21.0           |
| 10%                       | 103                            | 81.6     | 21.4           |
| 20%                       | 107                            | 85.0     | 22.0           |

If we plot the haze of bottle sidewall as a function of the difference between the average preform temperature and glass transition temperature for each blend (Fig. 5.3.11), we can clearly see the minimum stretch blowing temperatures are about 22°C above the glass transition temperatures of the blends with different PEN compositions. The results are also listed in Table 5.3.2.

![Percent haze of bottle sidewall vs. $(T_{\text{avg}} - T_g)$](image-url)  

**Fig. 5.3.11  Percent haze of bottle sidewall vs. $(T_{\text{avg}} - T_g)$**
As a result of the microvoids formed in the bottle sidewalls the densities of these samples were low, compared to those of bottles with clear sidewalls, as can be seen in Fig.5.3.12.

Fig.5.3.12  Bottle sidewall density vs. average preform blowing temperature (20% PEN/PET, apparent IV=0.82)

5.3.2.2 The upper limit of stretching temperature

We have seen that the stretching temperature of the preform must be above a specific lower limit in order to avoid the occurrence of stress whitening. The stretching temperature cannot be too high either. There exists an upper limit stretching temperature. For PET this temperature is usually defined as the cold crystallization temperature,
because when the amorphous PET is heated to this temperature the thermal crystallization process starts and the resultant crystallinity makes PET bottle appear hazy.

The PEN/PET blends crystallize less readily than PET thus their cold crystallization temperatures are higher than those of PET, as discussed in Chapter four. This does not necessarily mean that PEN/PET blends perform have higher stretch blowing temperature upper limits. The strain hardening point is another factor that plays an important role in determining this temperature.

The strain hardening point of the blend is a function of stretching temperature and extension ratio. When the temperature is increased the strain hardening point of the blend is also increased. The results from Tharmapuram and Jabarin \cite{26,29} showed the linear relationship between the strain hardening point and the temperature difference between actual stretching temperature and $T_g$ of the blends. If the strain hardening point of the blend was increased to a significant extent and exceeded the extension ratio achievable in the blowing mold, the strain hardening would not occur. If this happened, the bottle sidewall thickness distribution would become non-uniform. In our experiments, the body portion of the bottle will become thinner and the neck and bottom area will become thicker in comparison to those bottles which did encounter strain hardening during stretch blowing. It was also found that the temperatures at which this deterioration of thickness uniformity occurs are lower than the cold crystallization temperatures measured for each blend sample and presented in Chapter four.
From the above observations, it is therefore necessary to define the upper limit stretching temperature of PEN/PET blends as the temperature at which the thickness of the center part of the bottle body begins to drop, as illustrated in Fig.5.3.13. From the thickness measurements we specified the upper limit stretching temperature for each blend as listed in Table 5.3.3.

Fig.5.3.13  Average bottle sidewall thickness vs. stretch blow temperature ((20% PEN/PET, apparent IV=0.82)
Table 5.3.3 Upper limit stretch blow temperature of PEN/PET blends preforms

<table>
<thead>
<tr>
<th>PEN composition (wt% PEN)</th>
<th>Apparent I.V of preform</th>
<th>Upper limit stretch blow temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>0.72</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>0.76</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>122</td>
</tr>
<tr>
<td>10%</td>
<td>0.78</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>122</td>
</tr>
<tr>
<td>20%</td>
<td>0.77</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>122</td>
</tr>
</tbody>
</table>

We can see from the Table 5.3.3 that the upper limit stretching temperature is a function of the blend’s molecular weight. The higher the molecular weight the higher is the upper limit stretching temperature. This is expected since the blends with higher molecular weights will have lower strain hardening points, at the same stretching temperature.

5.3.2.3 Operation window of stretch blowing temperature

The range between the upper and lower limits of the stretching temperatures will give us the stretching temperature operating window for blends with specified apparent IV values. Results are shown in Fig.5.3.14. We can use this plot to predict the minimum apparent IV required for each blend in order to use the existing stretch blow molding equipment designed for PET.
Fig. 5.3.14  Stretch blow molding temperature operation window vs. preform apparent IV of PEN/PET blends
5.3.3. Evaluation of bottle properties

5.3.3.1 Orientation level

Birefringence can be used to measure the extent of orientation. The birefringence is calculated from the refractive index values measured by a Prism Coupler as discussed in the method section. When the preform is stretched the axial and hoop directions will be stretched to different extents as reported by Erwin. [178] The hoop and axial stresses are given by

\[ \sigma_a = \frac{Pr}{2t} \]  \hspace{1cm} (5.3.1)

\[ \sigma_h = \frac{Pr}{t} \]  \hspace{1cm} (5.3.2)

where, \( \sigma_a \) and \( \sigma_h \) are the stresses in axial and hoop direction respectively

\[ P \] is the internal pressure during stretching

\[ r \] is the radius

\[ t \] is the thickness

Therefore the hoop stress is twice as large as the axial stress. The polymer chains will be preferentially oriented in the hoop direction. Also the inside surface will experience more orientation than the outside surface as we discussed before. This explains why the birefringence in the hoop direction was higher than that in the axial direction and it was also higher for the inside sidewall than the outside as shown in Figures 5.3.15 - 5.3.16.
We chose the bottles made from blends with different PEN compositions to measure the birefringence and compare with PET bottle. The blends bottles chosen were made from 5%, 10% 20% PEN/PET blend preforms with apparent IV of 0.72, 0.78 and 0.82 respectively as listed in Table 5.3.4. They were chosen because the preforms have good operation windows as shown in Fig. 5.3.14 and the IV values of the preforms are not too high to take long SSP time for producing the resins. Another reason for these choices of IV values is because Tharmapuram and Jabarin \cite{26, 29} have predicted that blends with these IV values would have strain hardening behaviors similar to that of PET. The results of birefringence values are shown in Fig. 5.3.15 and Fig.5.3.16.

Table 5.3.4 Selected PEN/PET blends bottles for properties evaluation

<table>
<thead>
<tr>
<th>PEN composition ( wt% PEN)</th>
<th>Apparent IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.75</td>
</tr>
<tr>
<td>5%</td>
<td>0.72</td>
</tr>
<tr>
<td>10%</td>
<td>0.78</td>
</tr>
<tr>
<td>20%</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Fig. 5.3.15  Birefringence of bottle sidewalls in axial direction vs. PEN composition
Fig.5.3.16  Birefringence of bottle sidewalls in hoop direction vs. PEN composition
The results show that the orientation levels of the blends samples were comparable with those of PET. These results are expected, since the blends samples have been solid stated to higher molecular weights. If we used lower molecular weight PEN/PET blends to make bottles, the orientation levels of the bottles would be lower than that of PET, as the results by Tharmapuram and Jabarin \[26, 29\] have shown.

5.3.3.2 Strain induced crystallinity

The volume percent crystallinity in the bottle sidewalls was calculated from the density measurements. The measurements were made on the sidewall samples cut from the label panel areas of the bottle bodies. The strain induced crystallization (SIC) is different from the thermal crystallization in the way that both PET and PEN in the PEN/PET blend crystallize during SIC. Only the major component in the blend crystallizes during thermal crystallization. \[34, 35\] The volume percent SIC crystallinity was calculated as shown below:

\[
X_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (5.3.3)
\]

where, \(\rho\) is the density of the sample
\[\rho_a\] is the density of the amorphous phase,
\[\rho_a = (1-x)\rho_{a,PET} + x\rho_{a,PEN}\]
\[\rho_{a,PET} (1.333 \text{ g/cm}^3)\] and \[\rho_{a,PEN} (1.325 \text{ g/cm}^3)\] is the amorphous
phase density of pure PET and PEN respectively

x is mole fraction of PEN

ρ_c is the density of the crystalline phase,

\[ ρ_c = (1-x)ρ_{c,PET} + xρ_{c,PEN} \]

ρ_{c,PET} (1.455 g/cm³) and ρ_{c,PEN} (1.407 g/cm³) is the crystalline phase density of pure PET and PEN respectively

As expected, the percent crystallinity values of the blend bottle sidewalls were at the same level as that of PET as seen in Fig. 5.3.17. This is because the orientation levels of the solid stated blends bottles were comparable with those of the PET bottles, as determined by birefringence.

![Strain-induced Crystallinity vs. PEN composition](image)

Fig. 5.3.17 Strain induced percent crystallinity of bottle sidewall vs. PEN composition
5.3.3.3 Mechanical properties

We measured the mechanical properties of the bottles made from PET and those of the bottles made from the 5%, 10% and 20% PEN/PET blends as listed in Table 5.3.4. The results obtained for Young’s modulus and yield stress of the axial and hoop direction are shown in Figures 5.3.18 - 5.3.21.

Fig. 5.3.18  Young’s modulus of bottle sidewall in axial direction vs. PEN composition
Fig.5.3.19  Young’s modulus of bottle sidewall in hoop direction vs. PEN composition
Fig. 5.3.20  Yield stress of bottle sidewall in axial direction vs. PEN composition
Fig. 5.3.21  Yield stress of bottle sidewall in hoop direction vs. PEN composition
From the above figures we found that in general the Young’s modulus and yield stress in both axial and hoop directions increased with the increasing PEN composition. This is because the more rigid naphthalate groups present in the main chain of blends increased the stiffness of the blends and made them more difficult to deform. [26]

The results of maximum strain or elongation at break and the toughness are plotted in Figures 5.3.22 - 5.3.25.

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Fig.5.3.22  Max. Strain of bottle sidewall in axial direction vs. PEN composition
Fig. 5.3.23  Max. Strain of bottle sidewall in hoop direction vs. PEN composition
Fig. 5.3.24  Toughness of bottle sidewall in axial direction vs. PEN composition
Fig. 5.3.25  Toughness of bottle sidewall in hoop direction vs. PEN composition
From the above results we find that the maximum strain and the toughness of the blends bottles are comparable to those of the PET bottles. As has been discussed by Tharmapuram and Jabarin [26] the molecular weight has some effects on the toughness, the higher molecular weight makes the bottle wall less brittle. We have also found that the stretching temperatures affect the toughness of the bottle sidewall, as can be seen in Figures 5.3.26 and 5.3.27 for the results of stretching 20% PEN/PET blends at various temperatures.

Fig.5.3.26  Toughness of bottle sidewall in axial direction vs. stretching temperature

(20% PEN)
Toughness (MPa) in Hoop Direction vs. Average Stretch-blowing Temperature of Preform of 20% PEN/PET blend (Apparent IV=0.82)

Fig. 5.3.27  Toughness of bottle sidewall in hoop direction vs. stretching temperature

(20% PEN)
The temperature effects on toughness are clear in both axial and hoop directions. As the stretching temperatures increase, the toughness values of the bottle sidewall samples increase in both directions. The temperature at which the toughness begins to increase is near the temperature needed to obtain clear bottles. As we discussed before, with increasing stretching temperature, the polymer chains will have more ability for segmental movement and become more relaxed in the amorphous phase. When subjected to tensile tests the sample can thus absorb more energy before it fails. Therefore the values of the elongation at break will be higher for the bottles obtained at higher stretching temperatures as can be seen in Figures 5.3.28 and 5.3.29.

Fig. 5.3.28  Max. Strain in axial direction vs. stretching temperature (20% PEN)
Max. Strain In Hoop Direction vs. Average Stretch-blowing Temperature of Preform of 20% PEN/PET blend (Apparent IV=0.82)

Fig. 5.3.29  Max. Strain in hoop direction vs. stretching temperature (20% PEN)
The effect of stretching temperature on the maximum strain at break is more striking for the measurements in the hoop direction than those made in the axial direction as shown in Figures 5.3.28 and 5.3.29. This is may be due to the fact that the polymer chains experienced greater degree of stretching in the hoop direction than in the axial direction.

Since the toughness is the defined as the area under the stress-strain curve, both increases of the Young’s modulus and elongation at break would result in the increase of toughness. Our results showed that the Young’s modulus of the bottle sidewall samples changed only slightly with the changing of stretching temperature as shown in Figures 5.3.30 and 5.3.31. Therefore we can conclude that the improvement of toughness is a result of the increasing of the elongation at break when the stretching temperature is increased.

We should also notice that as the stretching temperature becomes higher and higher, the variance in the toughness also increases indicating less uniformity of the properties along the bottle sidewall. This is in parallel with the thickness distribution deterioration as we discussed earlier.
Young’s Modulus (MPa) in Axial Direction vs. Average Stretch-blowing Temperature of Preform of 20% PEN/PET blend (Apparent IV=0.82)

Fig.5.3.30  Young’s modulus in axial direction vs. stretching temperature (20% PEN)
Fig. 5.3.31  Young’s modulus in hoop direction vs. stretching temperature (20% PEN)
5.3.3.4 Oxygen barrier properties

The barrier properties of packaging materials are critical in determining the shelf life of the contained products. By introducing PEN into a PET matrix the barrier properties of the resulting PEN/PET blends or copolymers are expected to be enhanced. Increasing PEN content in PEN/PET blends or copolymers will lower the oxygen permeability. As shown by Po et al \cite{32}, an amorphous PEN and PET copolymer with 21\% NDC mole fraction has a 37\% lower oxygen permeability than that of amorphous PET. This has been explained \cite{179-181} by the free volume approach. The effect of added PEN content is to lower diffusivity D rather than solubility S of oxygen in the polymers. Diffusivity is related to the dynamic free volume which derives from the thermally accessible segmental motions and conformational changes of the polymer chain and is essential for the absorbed oxygen molecules jumping between the neighboring free volume cavities.\cite{179-181} The orientation process of cold drawn polyesters was shown to decrease the excess-hole free volume, and therefore decrease the diffusivity of oxygen in the polymer and result in lower oxygen permeability.\cite{182} Uthaisombut \cite{183} showed that the oxygen permeability of oriented 25wt\% PEN/PET film was 30-50\% lower than that of the non-oriented blend film.

The oxygen permeability values of the 2-liter bottles made from PEN/PET blends in the current work were measured using 4×4 inch (10.2×10.2 mm) sections cut from the label panel areas of the bottle sidewalls. These permeability results are shown in Fig.5.3.32. We can see that the O₂ permeability decreases as a function of PEN composition. With
increasing PEN composition from 0 wt% to 20 wt% the oxygen permeability correspondingly decreases from 5.65 cc(stp)-mil/100in²-day-atm to 3.95 cc(stp)-mil/100in²-day-atm.

Fig.5.3.32 Oxygen permeability vs. PEN composition of bottle sidewalls
The improvement in the oxygen barrier properties of PEN/PET blend bottles over that of pure PET bottles is better in the current work than had been achieved by Tharmapuram and Jabarin.\textsuperscript{[26]} Our results show a 30% decrease in O\textsubscript{2} permeability of the 20% PEN/PET blend bottle from that of the PET bottle. Tharmapuram and Jabarin\textsuperscript{[26]} had obtained only a 20% improvement for 20% PEN/PET blend. The reason for this is the better orientation levels obtained in the current work. In the case of their work, the molecular weights of the blends were quite low with an apparent IV of 0.62. This resulted in low levels of orientation and strain induced crystallinity in the bottle sidewall and consequently higher levels of oxygen permeability. In the current work, the molecular weights of the blends were increased through the SSP process. This made it possible to obtain the comparable levels of orientation and strain induced crystallinity as shown in sections 5.3.3.1 and 5.3.3.2 and thus better oxygen barrier properties.

Ophir et al\textsuperscript{[184]} also showed 27% to 35% lower oxygen permeability for a 20wt% PEN/PET blend one-liter bottle in comparison to a pure PET bottle produced using stretch blow molding with different mold temperatures. The barrier property improvement exhibited by the PEN/PET blend system can be predicted using the two phase Maxwell model as done by Hoffman and Caldwell\textsuperscript{[14]}. The model is expressed as below:

\[
\frac{P}{P_B} = 1 + \frac{(1 + G)\phi_A}{(R + G)} - \frac{(R - 1)}{(R - 1)} \phi_A
\]

(5.3.4)
Where, \( P \) is the permeability of the composite material

\[ P_B \] is the permeability of the continuous phase

\( R \) is the ratio of permeability of phase A to phase B

\( \Phi_A \) is the volume fraction of phase A

\( G \) is the geometric factor determined by the shape of dispersed phase A

In the current work the PEN content in PEN/PET blend is only from 5 wt% to 20 wt%, therefore it is reasonable to treat PET as the continuous phase and PEN as the dispersed phase. An \( R \) value of 1/5 was used by Hoffman and Caldwell \(^{14}\) for their measurements of oxygen permeability of oriented PET and PEN films. This value can also be used in the current study because the bottle sidewalls are also oriented during the stretch blowing process. The weight fraction of PEN can be used as the volume fraction of PEN in the above equation, as done by Hoffman and Caldwell \(^{14}\), because of the similar density values for amorphous phases of PET and PEN, as well as similar density values for crystalline phases of PET and PEN. The shape factor \( G \) equals 2 for spheres of phase A, it changes from zero to infinity for the planar structure of phase A depending on whether the planar structure is perpendicular or parallel to the orientation direction.

Using \( G \) value of zero (planar phase A perpendicular to the gas flow direction) we can obtain the maximum possible decrease of oxygen permeability for 20wt% PEN/PET blend. This maximum possible value calculated using equation 5.3.4 is 44% decrease in oxygen permeability for PEN/PET blend in comparison to pure PET. In the case of PEN phase (phase A) exists as spheres in the blend, \( G \) equals to 2, and the decrease in oxygen
permeability is only 14%. This shows how important it is to have a well oriented dispersed PEN phase in the blend in order to obtain optimal improvement in barrier properties.

Our result of a 30% decrease in the PO2 value is close to the maximum possible calculated value of 44%. This is different from the result of PO2 decrease obtained by Tharmapuram and Jabarin [26], which is close to 14%. The reason for this difference is that the blend bottles obtained in the current work have improved orientation over those bottles obtained by Tharmapuram and Jabarin [26]. This is true even though the same design in preform and stretch blow mold were used in both cases. The improvement in orientation is a result of the increase in the molecular weights of PEN/PET blends, through SSP in the current work, in comparison to the non-solid stated blends employed by Tharmapuram and Jabarin [26]. We conclude, therefore, that SSP is a critical process in order to obtain PEN/PET blend bottles with optimal barrier properties, utilizing a conventional injection molding and stretch blow molding process, without any changes in the machinery design.
5.4 Conclusions

The transesterification reaction that occurs during SSP enhances the miscibility between PET and PEN. As a result lower injection molding temperatures are required for obtaining clear PEN/PET blend performs.

Stretch blow molding blend preforms at temperatures lower than the lower limit stretching temperatures causes stress whitening in the bottle sidewall. The minimum stretching temperatures required for preventing stress whitening from happening were determined for each blend with different compositions. Higher PEN compositions require higher stretching temperatures. The temperature requirements can be correlated with the glass transition temperature $T_g$ of the blends. The minimum stretching temperatures are about 22 °C higher than the $T_g$ values of the blends with different PEN weight fractions.

Upper limits of the stretching temperatures were determined for each blend in order to obtain uniform thickness distributions in the bottle sidewalls. The stretching temperature operating windows increase with increasing molecular weight of the blends.

By increasing the blend molecular weights by SSP, we can produce transparent bottles from the PEN/PET blends with orientation and crystallinity levels comparable with those of PET bottles.
Bottles made from PEN/PET blends have higher Young’s modulus, yield stress and comparable toughness with respect to those of PET bottles. The barrier properties of the blend bottles are better than that of PET. The oxygen permeability of 20% PEN/PET blend bottles is 30% lower than that of PET bottles.
Chapter 6

Summary, conclusions and recommendations

6.1 Summary

The current work is a continuation of intensive research work conducted on PEN/PET blends at the Polymer Institute of The University of Toledo. Acknowledging the effects of the transesterification levels and molecular weights of the blends, on the manufacturing of final products from PEN/PET blends, we brought solid state polymerization (SSP) into the PEN/PET blends processing cycle. After the blends were prepared using an extrusion process through a twin screw extruder, they were subjected to SSP before the preform injection molding and bottle stretch blow molding processes. The expectation was that SSP would be a single process that would both enhance the miscibility of the two polymer phases and upgrade the molecular weights of the blends. These solid stated blends could then be used to produce bottles with a conventional injection molding and stretch blow molding process, without any changes in the machinery design.

Through this work the SSP has been proven to be a very effective method to improve the properties of the PEN/PET blends. Systematic investigations were conducted on PEN/PET blends with different compositions to gain insight of the kinetics and mechanisms of SSP and the accompanying transesterification reactions. Important factors
such as SSP temperatures, SSP times, blend compositions and initial IV of the precursor on these reactions, were investigated. Investigations were done to learn how the thermal properties of the blends such as melting behavior, non-isothermal crystallization behavior, cold crystallization behavior and thermal stability would be affected by the SSP process, and to establish important processing variables of injection molding and stretch blow molding of the blends.

Specifically, the major conclusions of our work are listed in the following section.

### 6.2 Conclusions

- Through approaches utilizing apparent IV and the end group concentration variations, the kinetics and mechanisms of solid state polymerization reactions were investigated using PET/PEN blends with PEN weight fractions of 5%, 10%, and 20%. Results have shown that the condensation polymerization reactions were diffusion controlled rather than chemical reaction controlled. The values of activation energy calculated from apparent IV and end group concentration methods were very close to each other. These values of about 17 kcal/mol confirmed the SSP process is controlled by the combination of byproduct diffusion and the polymer chain diffusion in the pellets. It was found that the SSP temperature and time are the major factors affecting the polycondensation reaction. The PEN composition in PEN/PET blends has not been shown to have a major effect on SSP kinetics, within our investigation range. The end groups approach is a more reliable way to obtain SSP apparent rate constants, especially when studying the initial IV effect on the
SSP reaction. The effect of the initial IV of the blend precursors on the SSP reaction was successfully illustrated by the molecular weights calculated from the end group concentrations obtained from FT-IR measurements. Samples with higher initial I.V. tend to have higher SSP reaction rates. The chain mobility difference resulting from crystallinity and the crystalline structures is responsible for this phenomenon. An optimal ratio of the mole concentration of carboxyl end groups over hydroxyl end groups ([COOH] / [OH]) seems to exist, which is apparent for the blends with the highest initial IV values in our experiments.

- The advantage of SSP for PEN/PET blends was demonstrated by the concurrent occurrence of the transesterification reaction with polycondensation reaction during SSP. The transesterification level (represented by degree of randomness RD %) increased with the increase of SSP temperature and time. The higher SSP temperatures favor higher transesterification reaction rate. The composition of PEN in different blends has little effect on transesterification kinetics. By assuming a second order transesterification reaction, the reaction rate constant and activation energy were obtained for each blend. The values of the activation energies and the entropy terms in the activation energies confirmed the proposed reaction mechanism. Higher initial IVs of the blend precursors favor higher transesterification reaction rates because of the higher chain mobility resulting from the lower crystallinity values achieved during SSP. The ratio of [COOH] / [OH] has no apparent effect on the transesterification reaction. As the result of the transesterification reaction during SSP, the number-average sequence chain lengths
of the components in the blends were shortened. The blends with higher PEN concentrations have a higher rate in the decrease of PET unit sequence lengths.

- A linear relationship exists between the transesterification reaction levels (RD %) and the molecular weights of the blends during SSP up to a certain value of molecular weight. Long SSP times at higher temperatures result in leveling off of the transesterification reactions. This phenomenon can be explained in terms of crystallization induced sequential reordering.

- The multiple melting behaviors were observed for the solid PEN/PET blends. Medellin-Rodriguez’s model on multiple melting peaks was applied to explain the effect of initial I.V. of blends precursor on the melting behavior differences of the blend samples.

- Non-isothermal crystallization was conducted to simulate crystallization during the cooling stage of injection molding. The percent crystallinity achieved during non-isothermal crystallization decreased with increasing sample molecular weight and PEN composition. The minimum cooling rates required to produce noncrystalline blends were lower for the solid stated PEN/PET blends. The non-isothermal crystallization kinetics was analyzed using the Ozawa equation. The Avrami exponents decreased with decreasing temperature during non-isothermal crystallization, indicating a change in the crystallization mechanism. The activation energies of non-isothermal crystallization calculated using Kissinger plots, were
higher for samples with higher I.V. and higher PEN compositions, indicating the reduced crystallibility of solid stated blends.

- The crystallization ability of solid stated PEN/PET blends, heated from the amorphous state, were affected by the molecular weight, PEN concentration, and transesterification level. The cold crystallization behavior was studied by DSC. A numerical model was developed to predict the cold crystallization ($T_c$) as a function of the above factors.

- Blend thermal stability was improved by the SSP process. The AA generation rate constant $k$ decreases and the activation energy for AA generation increases as a result of solid stating PEN/PET blends.

- The advantages of applying SSP to PEN/PET blends were shown by the lowering of the critical injection molding temperature required to achieve optically clear performs for the solid stated blends. This occurred as a result of the miscibility enhancement between PET and PEN through the transesterification reaction during SSP.

- By monitoring the temperature profiles of the blend preforms, the minimum stretching temperatures required for preventing stress whitening in the bottle sidewalls were determined for the blends with different compositions. Higher PEN compositions require higher stretching temperatures, which have a correlation with
the glass transition temperature $T_g$ of the blends. The minimum stretching temperature is about 22 °C higher than $T_g$ of each blend with different PEN weight fractions. Instead of the cold crystallization temperatures, an upper limit of stretching temperature was defined, based on the uniformity of the thickness of bottle sidewall. Upper limits of the stretching temperatures were determined for each blend in order to obtain uniform thickness distributions in the bottle sidewalls. The operating window of the stretching temperature increases with increasing molecular weights of the blends.

- The increased molecular weight of PEN/PET blends is the key to producing good bottles from the PEN/PET blends. These bottles will have orientation and crystallinity levels comparable with those of PET bottles, without changing any designs in either the injection molding process or the stretch blow molding mold. Better mechanical properties in terms of Young’s modulus, yield stress and comparable toughness were obtained for the bottles made from PEN/PET blends, compared to those of the PET bottle. As the result of sustained orientation and strain induced crystallinity levels the barrier properties of the blend bottles are better than those made from lower molecular weight PEN/PET blends.
6.3 Recommendations

1. The effects of many important factors such as temperature, time, blend composition and initial IV of the precursor on the solid state polymerization and transesterification reactions were investigated. A comprehensive investigation of the SSP process of PEN/PET blends should also include the study of other factors such as the different PET and PEN sources (homopolymers or copolymers), resin moisture content, and the catalyst systems used in preparation of the pure PET and PEN resins.

2. The PEN/PET blends used in the investigation of initial IV effects of blend precursors on SSP and transesterification reactions were made by the method of degrading the currently available PET resin. This method has a disadvantage originating from the degradation reactions that occurred during multiple time extrusions. If materials are available the blends with different initial IV made from the different original PET and PEN commercial resins would be better alternatives to conduct similar investigations.

3. In order to have better control of the strain hardening process of PEN/PET blends during stretch blow molding a systematic investigation of the strain hardening behavior of PEN/ET blends as a function of blend composition, molecular weight, transesterification level, and temperature will certainly be of great help. If possible, this work should be done on the PEN/PET blends sheets under biaxial stretching conditions similar to those experienced by the blend preforms in the stretch blow molding process.
4. The application of SSP into the polymer product manufacturing process could also be appropriate for the other polymer blend systems, such as other blends using PET as the major components and having similar concerns about the miscibility and strain hardening behavior similar to those for the PEN/PET blends.
Appendix A

Fig. A1  Apparent $M_n$ vs. Square root of SSP time  
(5% PEN/PET blend, initial IV=0.60)

Fig. A2  Apparent $M_n$ vs. Square root of SSP time  
(5% PEN/PET blend, initial IV=0.65)
Apparent $M_n$ vs. Square root of SSP time
(5% PEN/PET blend, initial IV=0.70)

Fig. A3  Apparent $M_n$ vs. Square root of SSP time
(5% PEN/PET blend, initial IV=0.70)

Apparent $M_n$ vs. Square root of SSP time
(10% PEN/PET blend, initial IV=0.60)

Fig. A4  Apparent $M_n$ vs. Square root of SSP time
(10% PEN/PET blend, initial IV=0.60)
Fig. A5  Apparent $M_n$ vs. Square root of SSP time  
(10% PEN/PET blend, initial IV=0.65)

Fig. A6  Apparent $M_n$ vs. Square root of SSP time  
(10% PEN/PET blend, initial IV=0.71)
Fig. A7  Apparent $M_n$ vs. Square root of SSP time  
(20% PEN/PET blend, initial IV=0.60)

Fig. A8  Apparent $M_n$ vs. Square root of SSP time  
(20% PEN/PET blend, initial IV=0.65)
Fig. A9  Apparent $M_n$ vs. Square root of SSP time
(20% PEN/PET blend, initial IV=0.70)
Appendix B

Fig. B1 $M_n$ vs. Square root of SSP time
(5% PEN/PET blend, initial IV=0.60, from end group approach)

Fig. B2 $M_n$ vs. Square root of SSP time
(5% PEN/PET blend, initial IV=0.65, from end group approach)
Fig. B3  $M_n$ vs. Square root of SSP time  
(5% PEN/PET blend, initial IV=0.70, from end group approach)

Fig. B4  $M_n$ vs. Square root of SSP time  
(10% PEN/PET blend, initial IV=0.60, from end group approach)
Fig. B5  $M_n$ vs. Square root of SSP time  
(10% PEN/PET blend, initial IV=0.65, from end group approach)

Fig. B6  $M_n$ vs. Square root of SSP time  
(10% PEN/PET blend, initial IV=0.71, from end group approach)
Fig. B7  $M_n$ vs. Square root of SSP time  
(20% PEN/PET blend, initial IV=0.60, from end group approach)

Fig. B8  $M_n$ vs. Square root of SSP time  
(20% PEN/PET blend, initial IV=0.65, from end group approach)
Fig. B9  \( M_n \) vs. Square root of SSP time  
(20% PEN/PET blend, initial IV=0.70, from end group approach)
Appendix C

Fig. C1  \( \ln\left[\frac{b}{b-r}\right] \) vs. SSP time at various SSP temperatures for 5% PEN/PET blends, initial IV=0.60

Fig. C2  \( \ln\left[\frac{b}{b-r}\right] \) vs. SSP time at various SSP temperatures for 5% PEN/PET blends, initial IV=0.65
Fig. C3  $\ln[b/(b-r)]$ vs. SSP time at various SSP temperatures for 5% PEN/PET blends, initial IV=0.70

Fig. C4  $\ln[b/(b-r)]$ vs. SSP time at various SSP temperatures for 10% PEN/PET blends, initial IV=0.60
Fig. C5  $\ln[b/(b-r)]$ vs. SSP time at various SSP temperatures for 10% PEN/PET blends, initial IV=0.65

Fig. C6  $\ln[b/(b-r)]$ vs. SSP time at various SSP temperatures for 10% PEN/PET blends, initial IV=0.71
Fig. C7  \( \ln[b/(b-r)] \) vs. SSP time at various SSP temperatures for 20% PEN/PET blends, initial IV=0.60

Fig. C8  \( \ln[b/(b-r)] \) vs. SSP time at various SSP temperatures for 20% PEN/PET blends, initial IV=0.65
Fig. C9  \(\ln[\frac{b}{(b-r)}]\) vs. SSP time at various SSP temperatures for 20% PEN/PET blends, initial IV=0.70
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