

# **3. Processing Variables**

## **Preface**

This chapter is focused on the first and second objectives of this research. Specifically, it is shown that pregenerated microcomposites can be produced using PET as a matrix. Additionally, the influence of several processing variables on the mechanical properties of pregenerated microcomposites are presented. This chapter is organized as a manuscript for future publication.

# The Influence of Processing Variables on the Mechanical Properties of Injection Molded Pregenerated Microcomposites

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(ABSTRACT)

This work was concerned with addressing how injection molding process variables affected the final mechanical properties of composite materials based on poly(ethylene terephthalate) (PET) reinforced with pregenerated thermotropic liquid crystalline polymer (TLCP) fibrils, where the TLCP had a higher melting point than the PET. These composites, referred to as pregenerated microcomposites, were produced using a two step processing scheme. First, a novel dual extrusion process was used to spin composite strands of PET/TLCP containing continuous lengths of TLCP fibrils. Second, these composite strands were subsequently chopped into pellets and injection molded below the melt processing temperature of the TLCP but above that of the matrix. This allowed the high modulus TLCP fibrils generated in the spinning step to be retained in the final injection molded sample. The influence of several injection molding variables on the final composite properties was examined. These variables included 1) injection molding temperature, 2) nozzle exit diameter, and 3) the type of diluting matrix used. These variables were shown to affect the final mechanical properties of the composites, with the best mechanical properties being achieved using low injection molding temperatures, a large nozzle exit diameter, and poly(butylene terephthalate) as the diluting resin.

## 3.1 Introduction

The use of thermotropic liquid crystalline polymers (TLCPs) to reinforce commodity thermoplastics has attracted considerable interest since the mid to late 1980's [1 - 5]. One reason for this interest has been due to the fact that when blends of a thermoplastic and a TLCP are subjected to extensional deformation, the TLCP phase is deformed into fibrils. These TLCP fibrils are found to provide mechanical reinforcement to the matrix, producing light weight, wholly thermoplastic composites. Because the reinforcing fibrils are formed during the melt processing step, Kiss [3] called the resulting materials *in situ* composites.

There are several reasons that TLCPs are potentially viable alternatives to traditional reinforcing materials like glass fiber. One significant reason is their combination of low density and high mechanical properties. It has been shown that neat TLCPs can possess moduli of up to 100 GPa and strengths of 1 GPa and greater when they are highly oriented, while having densities of only around 1.4 g/cm<sup>3</sup> [6 - 8]. These properties are competitive with other forms of reinforcement, such as glass fiber, which has a tensile modulus of 69 to 83 GPa, a tensile strength from 1.72 to over 2.07 GPa, and a density of 2.52 to 2.61 g/cm<sup>3</sup> [9 - 12]. Therefore, if the full reinforcing potential of the TLCP is realized, it would be possible to produce wholly thermoplastic composites which would have mechanical properties matching or exceeding those obtained when glass and aramid fibers are used as the reinforcement. Other important reasons cited for using TLCPs as reinforcement rather than glass fiber are: 1) the melt is easier to process, 2) there is less wear on the processing equipment, 3) the ability to use compatibilization to provide interfacial adhesion between the two phases, and 4) their recycling potential [13]. Therefore, TLCPs possess several key features which make them a possible alternative to more conventional reinforcing materials.

Despite the potential of TLCPs as reinforcing materials, it has been shown that injection molded in situ composites typically have not achieved theoretically expected levels of reinforcement. For example, Datta et al. [14] produced in situ composites using polypropylene (PP) as the matrix, maleated polypropylene as a component to promote adhesion, and a polyestaramide, Vectra B950, as the TLCP. After injection molding the composite plaques, test samples were cut for making mechanical property measurements in both the machine and transverse directions. At a loading of 20 wt% Vectra B950, the machine direction modulus was 3.209 GPa and the transverse direction modulus was 1.937 GPa. Although this was significantly higher than the 1.384 GPa modulus of the neat PP, it was still well below theoretical expectations. This can be demonstrated by using the Halpin-Tsai equation to predict the modulus of the composite. Assuming random planar reinforcement and an aspect ratio of at least 100 for all of the TLCP fibrils, the Halpin-Tsai equation reduced to:

$$\text{Equation 3.1: } E_c = \frac{3}{8}\phi_f E_f + \phi_m E_m$$

where E = tensile modulus,  $\phi$  = volume fraction, subscript c = composite, subscript f = fiber, and subscript m = matrix. Qin and Yee [15] have reported that high draw ratio fibers of Vectra B950 have a tensile modulus of 75 GPa. Using this value in Eq. 3.1, a tensile modulus of 5.27 GPa is predicted for a planar isotropic plaque. Comparing the theoretically predicted modulus to the experimental values, it is clear that the full reinforcing potential of the TLCP was not utilized. The reason that the experimental properties of these composites were lower than the predicted values was because the flow kinematics during mold filling did not subject all of the TLCP to strong extensional deformation, creating a skin-core morphology with unoriented TLCP in the core [16].

Another significant drawback of injection molded in situ composites is the planar anisotropic distribution of mechanical properties, with high flow direction properties and low transverse direction properties [13, 17]. The flow kinematics during mold filling also causes this problem because the extensional deformation at the advancing front is predominantly in the machine direction. Therefore, most of the TLCP which comprises the skin is oriented in the flow direction and little reinforcement is imparted to the transverse direction. The influence of these kinematics on mechanical properties can be dramatic, as shown in a study by Bafna and coworkers [18]. In this investigation, a film-gated mold was used to produce composites containing polyetherimide (PEI) as the matrix and HX1000, a polymer believed to be composed of hydroquinone, 4-hydroxybenzoic acid, terephthalic acid, and substituted hydroquinones, as the TLCP. At a loading of 50 wt% HX1000, over a 4 to 1 ratio of mechanical anisotropy was observed for the flexural modulus. In particular, the machine direction modulus was 12.92 GPa while the transverse modulus was only 3.20 GPa. It should be noted that PEI has a modulus of 3.0 GPa, demonstrating that the TLCP did not reinforce the transverse direction appreciably.

In order to surmount many of the problems with in situ composites, investigations have been conducted where injection molded composites were produced in two steps rather than one [19 - 21]. First, the TLCP/matrix melt was spun into composite strands, orienting the TLCP molecules. Second, the strands were chopped into pellets and injection molded below the melting temperature of the TLCP to form a composite part. This two step process creates a wholly thermoplastic composite with the pregenerated TLCP fibrils stiffening the matrix; much in the same way as glass fiber is used to stiffen thermoplastics. Specifically, the fiber spinning step serves to orient all of the TLCP phase, while the injection molding step serves to form a part with the reinforcement distributed in both the machine and transverse directions. Because the TLCP fibrils were formed prior to the injection molding step and had diameters of the order of a micron, Handlos and Baird [21] called the resulting materials *pregenerated microcomposites*.

Because the TLCP fibril reinforcement in the pregenerated microcomposites is created in the spinning step, it is essential that the composite strands have the best possible mechanical properties. However, using the conventional approach of plasticating both the TLCP and matrix in the same extruder can significantly limit the mechanical properties. First, relying on the mechanism of droplet deformation to create the TLCP fibrils poses a problem because if the droplets are not deformed to aspect ratios of at least 100, the fibrils will not behave like continuous reinforcement and the highest possible stiffness will not be achieved [22]. Second, both the matrix and TLCP must have overlapping processing temperatures, restricting the use of high melting TLCPs. Third, even if the TLCP and matrix have overlapping processing temperatures, problems can still occur because of the presence of high melting crystallites in the TLCP phase. For example, it has been shown that although Vectra A950 has a melting temperature of 283°C, it must be briefly taken to 320 to 330°C to eliminate all residual crystallites from the melt [23, 24]. If the residual

crystallites are not removed from the melt, the reinforcing ability of the TLCP will be lowered [25, 26]. Fourth, to achieve high draw ratios in the composite strands, the TLCP must be kept deformable as it is cooled. Often the deformability is strongly influenced by previous thermal history, with exposure to higher temperatures allowing the melt to be cooled to lower temperatures before solidifying [27, 28]. However, these higher temperatures can not be used because they degrade the matrix, restricting the temperature the TLCP can be exposed to and making the melt more difficult to draw.

To overcome these difficulties, a patented dual extruder system was developed [29, 30]. In this process, the matrix and TLCP are plasticated in separate extruders. The TLCP is then cooled and introduced into the matrix as continuous streams, using a phase distribution system at the tee connecting the two extruders. Immediately following the phase distribution system, the blend is pushed through a series of static mixers to distribute the TLCP evenly in the matrix and to divide the continuous streams more finely. The melt is subsequently passed through a capillary die and drawn to produce a composite strand.

This novel design overcomes the problems encountered with using a single extruder in two key ways. First, using separate extruders allows different thermal histories to be applied to the two polymers before mixing. Therefore, the TLCP can be taken to a high temperature to eliminate high melting crystallites and to maximize supercooling behavior, then cooled to avoid degradation of the matrix as it is introduced into the matrix stream. By cooling the TLCP, it is possible to produce composite strands even when the processing temperatures of the two components do not overlap, expanding the range of possible TLCP/matrix combinations. Second, the continuous streams of TLCP in the matrix produce composite strands with infinite aspect ratio reinforcement, eliminating droplet deformation as the mechanism for forming high aspect ratio fibrils.

Using pelletized composite strands generated with the dual extruder process, Handlos and Baird [21] injection molded pregenerated microcomposite plaques and demonstrated that the problem of planar anisotropy was significantly reduced. In this study, the matrix was PP while two TLCPs were used as the reinforcing phase. The first was Vectra A950, a copolyester of 4-hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA) (73/27 mol%) produced by Hoechst Celanese, while the second was HX 6000, a polyester believed to be composed of hydroquinone, 4-hydroxybenzoic acid, terephthalic acid, and substituted hydroquinones produced by DuPont. Also, it should be noted that the PP contained 10 wt% maleated PP (MAP) to promote adhesion between the matrix and the TLCP. For PP (10 wt% MAP)/Vectra A950 (80/20 wt%) pregenerated microcomposites, the machine direction tensile modulus was 2.31 GPa and the transverse direction tensile modulus was 2.18 GPa, making the ratio of the two moduli 1.06. Similar results were observed with PP(10 wt% MAP)/HX6000 (80/20 wt%) pregenerated microcomposites, with the machine direction modulus being 3.23 GPa, the transverse direction modulus being 2.44 GPa, and the ratio of the two moduli being 1.31.

This degree of anisotropy compared favorably with PP containing 20 wt% glass fiber, which showed a machine to transverse direction moduli ratio of 1.31. This suggested that the TLCP fibrils and the glass fibers were distributed similarly in the plaques.

On the other hand, the pregenerated microcomposites did not reach their theoretically predicted levels of stiffness. Handlos and Baird [21] showed that the PP(10 wt% MAP)/HX6000 (70/30 wt%) pregenerated microcomposites had a machine direction modulus of 3.98 GPa and a transverse direction modulus of 2.91 GPa. Although these values were significantly greater than the modulus of 1.0 GPa of the neat PP, they were below what was predicted using composite theory. From the theoretical calculations, it was determined that a planar isotropic stiffness of 5.20 GPa would be achieved if all of the fibrils had aspect ratios over 100 and a modulus of 43 GPa. Three reasons cited as possible causes for the discrepancy between the experimental and theoretical moduli were 1) molecular relaxation due to the TLCP becoming too hot, 2) agglomeration of the TLCP fibrils, and 3) loss of aspect ratio due to the shear stresses in the injection molding step. Still, the morphology showed that fibrils were present throughout the thickness of the specimens. Hence, if the fibrils were not damaged in the injection molding step, it should have been possible to reach the maximum predicted modulus.

The purpose of this paper is to understand which injection molding variables contribute to a reduction in pregenerated microcomposite mechanical properties. By understanding the influence of each of these variables, it will then be possible to process these materials in a way to minimize the damage to the TLCP fibrils and thereby maximize the mechanical properties of the final injection molded composites. In particular, the influence of injection molding temperature, nozzle exit diameter, and diluting matrix on the mechanical properties is investigated.

## 3.2 Experimental

### 3.2.1 Materials

The TLCP used in this study was HX1000, an amorphous TLCP produced by DuPont with a glass transition temperature of approximately 160°C and a density of 1.25 g/cm<sup>3</sup>. For processing, it typically has to be taken to a melt temperature of at least 310°C. It is believed to be composed of an unspecified ratio of terephthalic acid, 4-hydroxybenzoic acid, hydroquinone, and hydroquinone derivatives, with bulky substituents on the main chain which make it amorphous [7, 31, 32].

Poly(ethylene terephthalate) (PET) was used as the matrix in the spinning step. The grade used was PT 7067 and was supplied by DuPont. It has a glass transition temperature of 84°C, a melting temperature of 255°C, and a density of 1.33 g/cm<sup>3</sup>. In the injection molding step, the chopped composite strands were dry blended with pellets of

one of two resins: 1) Rynite, an injection molding grade of PET, and 2) Celenex 1600A, an injection molding grade of poly(butylene terephthalate) (PBT). Rynite is an experimental grade of PET produced by DuPont which contains a nucleating agent to promote crystallization. It has a density of  $1.36 \text{ g/cm}^3$ , a glass transition temperature of around  $88^\circ\text{C}$ , and a melting temperature of  $257^\circ\text{C}$ . Celenex 1600A is produced by Hoechst Celanese and has a density of  $1.31 \text{ g/cm}^3$  and a melting temperature of  $228^\circ\text{C}$ . PET reinforced with 30 wt% glass (Rynite 530) was also injection molded. All polymers were dried in a vacuum oven set at  $110^\circ\text{C}$  for at least 24 hours before processing.

### 3.2.2 Composite Strand Processing

Composite strands of 50 wt% PT 7067 and 50 wt% HX1000 were generated using a patented dual extrusion process, which has been extensively described elsewhere [29, 30, 33]. The equipment consisted of two Killion KL-100 extruders having a screw diameter of one inch and a  $L/D = 24$ . The HX1000 was processed in one extruder, with the melt conveying zone set at  $310^\circ\text{C}$  to  $330^\circ\text{C}$ , while the PT 7067 was plasticated in the second extruder, with the melt conveying zone set at  $275^\circ\text{C}$  to  $285^\circ\text{C}$ . The mass flow rate of TLCP was accurately metered by using a Zenith gear pump (Model HD-556,  $1.725 \text{ cm}^3/\text{rev}$ ), with the strand composition determined from the total mass flow rate of the blend and the controlled mass flow rate of HX1000. After passing through the gear pump, the HX1000 stream was cooled to  $300^\circ\text{C}$  before being introduced into the PT 7067 using a tee connecting the two extruders. Immediately following the tee, the 50/50 wt% PT 7067/HX1000 blend was passed through a mixing head containing three helical elements and a Koch static mixer with four elements to further divide the HX1000 into smaller continuous streams. The melt was then passed through a capillary die ( $L/D < 1$ , exit diameter = 1.8 mm), drawn to orient the HX1000, quenched in a water bath, and collected on a take-up roll. It should be noted that the drawing was performed using a vertical drawing chimney that was approximately 4 meters long. The chimney insulated the spinning line from air currents in the building, helping keep the spinning process stable and assisting in reaching high draw ratios.

### 3.2.3 Injection Molding

The injection molder used in this work was an Arburg Allrounder Model 221-55-250. It has a screw with a 22 mm diameter, a check ring non-return valve, and an insulated nozzle tip. The polymer was injected into a film-gated mold having dimensions of 75 mm by 80 mm by 1.60 mm. The injection pressure (5 MPa), holding pressure (10 MPa), mold temperature ( $110^\circ\text{C}$ ), and screw speed (200 rpm) were held constant. The cooling time in the mold for the pregenerated microcomposites was 8 seconds.

The injection molded composites were produced with loadings of 10, 20, and 30 wt% TLCP. This was done by taking the chopped strands and dry blending them with the Rynite or Celenex 1600A pellets to the desired TLCP concentration.

The zone temperatures were varied according to the material being injection molded. For the pregenerated microcomposites created using PBT as the diluting resin, the zone temperatures were consistently kept as low as possible. Progressing from the solids conveying zone to the nozzle, the temperatures were: zone 1 = 240°C, zone 2 = 250°C, zone 3 = 240°C, and zone 4 = 230°C. Meanwhile, when Rynite pellets were dry blended with the chopped strands, two different sets of temperatures were used to determine the influence of barrel temperature on the pregenerated microcomposite properties. For the first set, the barrel was kept as cold as possible without having solidification in the nozzle tip: zone 1 = 245°C, zone 2 = 250°C, zone 3 = 250°C, and zone 4 = 250°C. The temperatures of the second set were significantly higher, but still below the normal processing temperature for neat HX1000: zone 1 = 250°C, zone 2 = 265°C, zone 3 = 270°C, and zone 4 = 270°C. In situ composites were also produced using Rynite, PT 7067, and HX1000. For these composites, the temperatures were: zone 1 = 285°C, zone 2 = 285°C, zone 3 = 285°C, zone 4 = 310°C.

### 3.2.4 Mechanical Properties

All of the tensile properties of the individual composite strands were measured using an Instron Mechanical Tester (model 4204) equipped with a 1 kN load cell. The gage lengths were approximately 250 mm, with the fiber ends wrapped with masking tape to provide uniform gripping of the strands. The crosshead speed was set at 1.27 mm/min. The tensile and flexural properties of the injection molded composites and compression molded strands were also measured using an Instron Mechanical Tester (model 4204), with the tensile tests performed using a 5 kN load cell and the flexural tests performed using a 1 kN load cell. To perform the tests, specimens which measured approximately 75 mm long by 12.5 mm wide were cut from the plaques. These specimens were then carefully sanded to smooth the cut surfaces. ASTM standard B 638-87B was followed for the tensile testing of these samples, with the crosshead speed kept at 1.27 mm/min. and the strain measured using an extensometer (Instron model 2630-25). For the three-point bending tests, the ASTM standard D 790M 86 was adhered to. Note that for all of the tensile and flexural test results, the reported values were an average of at least five samples. Strength, % elongation, and toughness values were all determined based on yield rather than at fracture, if the sample yielded before breaking.

### 3.2.5 Morphology

The morphology of the strands and plaques was examined using a Stereoscan S200 scanning electron microscope with an accelerating voltage of 15 kV. To prepare the

samples, they were immersed in liquid nitrogen for at least two minutes, then fractured. They were subsequently attached to mounting stubs and coated with a layer of gold using an SPI sputter coater to enhance conductivity.

## **3.3 Results and Discussion**

### **3.3.1 Tensile Properties of Neat Materials**

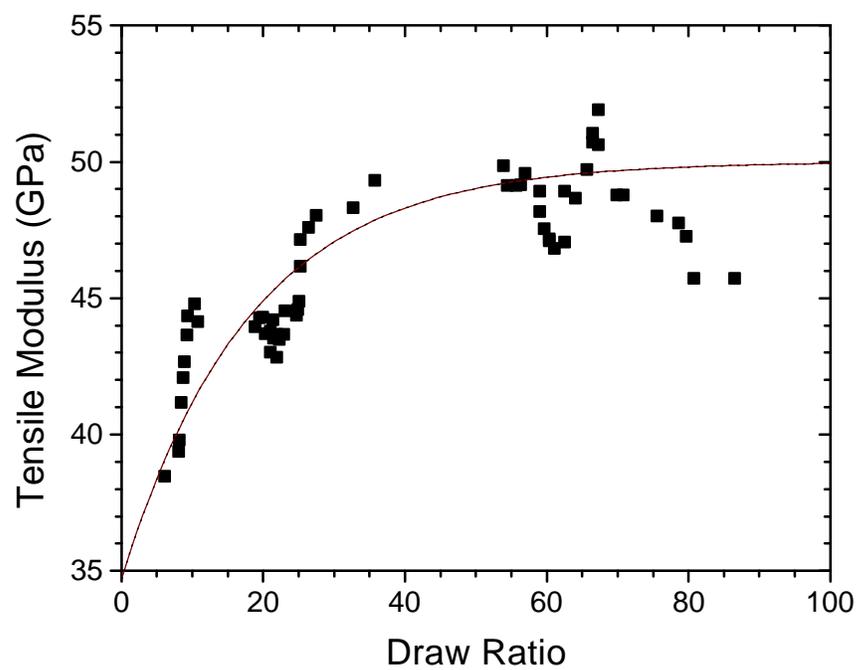
Neat HX1000 strands were extruded and spun to determine the relationship between draw ratio and mechanical properties. The modulus of the neat HX1000 showed a dramatic rise with increased draw ratio up to about 50 (Figure 3.1). After reaching a draw ratio of 50, the modulus leveled off at a value of about 50 GPa. This closely matches the results reported by Sabol et al. [20], where the tensile modulus was 53.3 GPa for draw ratios greater than 50.

Meanwhile, the tensile strength and percent elongation values for the strands did not show a statistically discernible dependence on draw ratio beyond a draw ratio of 10. For the HX1000 fiber, the tensile strength was 271.4 (86.6) MPa while the percent elongation was 0.773 (0.303) (standard deviations are shown in parentheses). The reason that it was difficult to discern a trend in the tensile strength and percent elongation values was because the brittleness of the strands. Experimentally, this led to problems such as the fibers breaking in the grips, which in turn made the standard deviations very large.

PT 7067, Rynite, and Celenex 1600A were found to have moduli of 2.18 (0.07) GPa, 2.42 (0.22) GPa, and 2.02 (0.19) GPa, respectively. These values are well below the 50 GPa measured for high draw ratio HX1000 strands. This indicates that adding highly oriented HX1000 fibrils to these matrices would result in an appreciable increase in stiffness.

### **3.3.2 Tensile Properties of HX1000/PT 7067 Composite Strands**

The composite strands of HX1000/PT 7067 (50/50 wt%) followed the same trends as the neat HX1000 strands, with higher draw ratios causing the modulus to rise (Figure 3.2). The composite strand moduli were compared to theoretically predicted values based on the rule of mixtures for uniaxially oriented systems and values for neat TLCP shown in Figure 3.1. As illustrated in Figure 3.2, it was found that the experimental modulus of the composite strands generally matched the theoretical predictions. Specifically, it



**Figure 3.1:** Tensile modulus versus draw ratio for neat HX1000 fiber.

should be noted that at high draw ratios, the modulus reached a plateau and additional drawing did not produce any further increase in modulus. Hence, it can be concluded that the full reinforcing ability of the HX1000 is being attained in the high draw ratio composite strands, with the HX1000 fibrils having a tensile modulus of about 50 GPa.

The tensile strengths of the composite strands also appear to show a trend of increasing strength with draw ratio, although the error in the strength measurements is large (Figure 3.3). Examining the higher draw ratios of 52.90, 66.47, and 108.5, the strength values lie between 175 MPa to 200 MPa. This range of strengths is significantly greater than the 83.56 MPa value measured for the strands with a draw ratio of 9.521. Therefore, to maximize both the strength and modulus of these composites, it is necessary to reach draw ratios of at least 50.

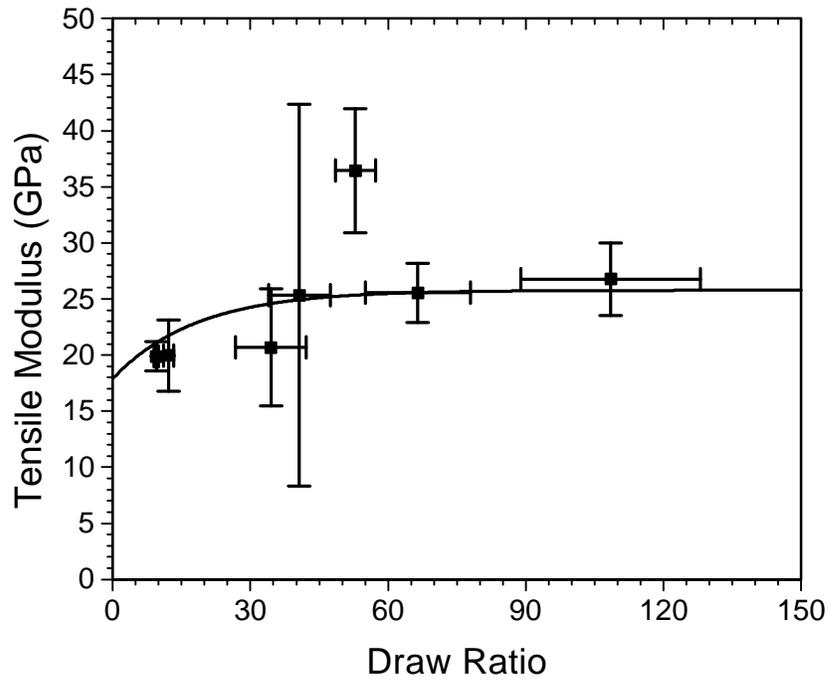
### **3.3.3 Uniaxially Compression Molded Composite Strands**

To understand the effect that temperature would have on the HX1000 fibrils in the composite strands, the strands were consolidated into uniaxially reinforced composites. It has been shown in previous work that the mechanical properties measured in individual strands were retained in uniaxially compression molded composites of PP/HX1000 [20] and PP/Vectra B950 [34]. Therefore, large losses in modulus for the HX1000/PT 7067 composites could be ascribed to the effect of temperature on the HX1000 fibrils.

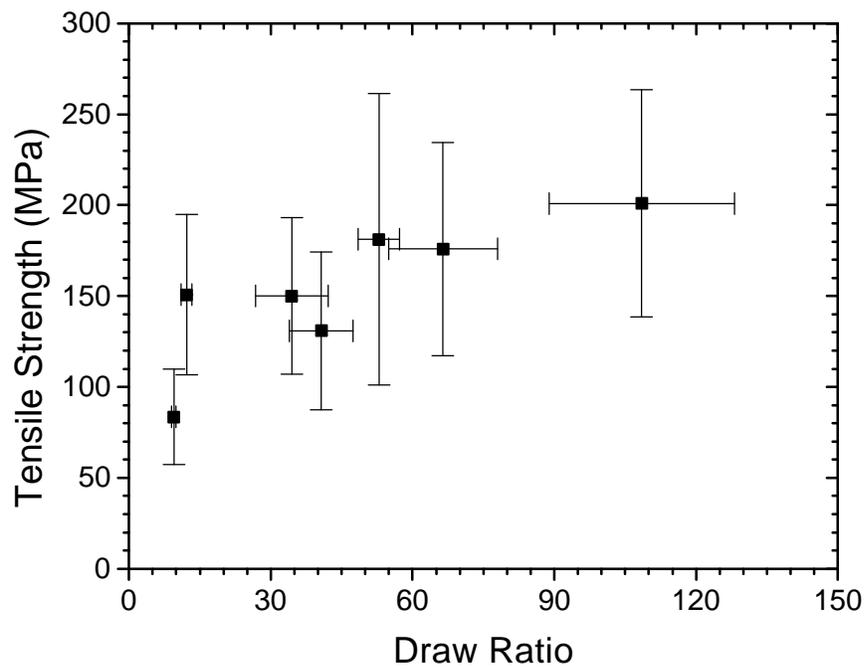
Testing the uniaxially compression molded composites, a slight drop in mechanical properties with consolidation was observed (Figure 3.4). The individual strands possessed a tensile modulus of about 25.5 GPa, while after consolidation the modulus fell to 22 GPa. However, continued exposure to 260°C after consolidation did not cause the stiffness to decline any further. This result indicates that any losses due to heat occurred quickly during the consolidation step, with additional exposure to 260°C having no appreciable effect. However, it needs to be recognized that fiber misalignment and breakage during consolidation could also explain the reduction in modulus. Specifically, it was determined that fiber misalignment in the uniaxial composites accounted for a loss in modulus of 0.5 GPa [35]. Therefore, the behavior of the consolidated strands shows that most of the reinforcing potential of the HX1000 fibrils was retained when they were exposed to high temperatures and that the reduction in modulus was likely due to fibril damage and misalignment during consolidation.

### **3.3.4 Injection Molded Pregenerated Microcomposite Properties**

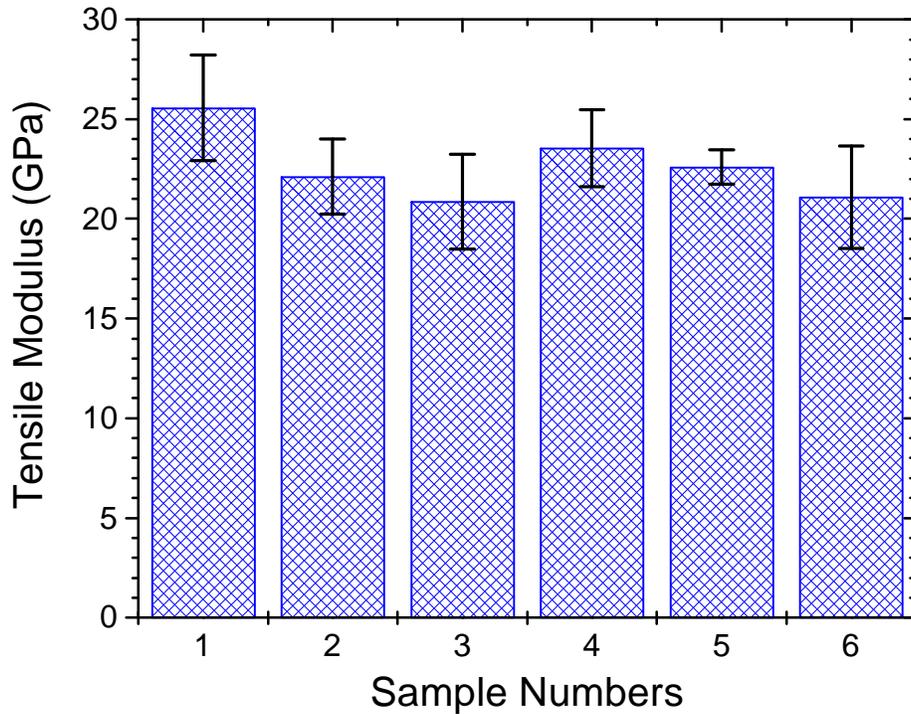
Having shown that the strands could be compression molded and retain a high modulus, it was then necessary to determine the effect of injection molding temperature on mechanical properties. To do this, composite strands of PT 7067/HX1000 (50/50 wt%) with a draw ratio of 40.67 were chopped and processed to make composites using



**Figure 3.2:** Tensile modulus versus draw ratio for HX1000/PT 7067 strands (50/50 wt%): (■) are the experimental data and (—) is the rule of mixtures prediction based on the neat HX1000 strand modulus.



**Figure 3.3:** Experimental tensile strength versus draw ratio of HX1000/PT 7067 strands (50/50 wt%).



**Figure 3.4:** The effect of temperature on composite strands of HX1000/PT 7067 (50/50 wt%) strands with a draw ratio of 66.47. (1) = individual strands, (2) = consolidated strands, (3) consolidation + 5 min., (4) consolidation + 15 min., (5) consolidation + 30 min., and (6) consolidation + 60 min. Note that all consolidation was at 260°C for 3 minutes and the additional time represents the exposure to 260°C without the application of pressure.

**Table 3.1:** Tensile Properties for PET Composites Reinforced with HX1000.

	Machine Direction			Transverse Direction		
<b>HX1000/PT 7067/Rynite (10/10/80 wt%)</b>						
	Modulus (GPa)	Strength (MPa)	% Elong. <sup>d</sup>	Modulus (GPa)	Strength (MPa)	% Elong.
In situ <sup>a</sup>	3.232 (0.219)	51.85 (1.979)	1.991 (0.219)	2.884 (0.345)	44.93 (1.138)	2.028 (0.174)
High Temp. <sup>b</sup>	2.622 (0.143)	43.38 (1.424)	2.102 (0.093)	2.697 (0.207)	42.83 (1.329)	1.979 (0.067)
Low Temp. <sup>c</sup>	3.060 (0.016)	53.64 (1.220)	2.565 (0.056)	2.782 (0.323)	45.52 (1.382)	2.124 (0.235)
<b>HX1000/PT 7067/Rynite (20/20/60 wt%)</b>						
	Modulus (GPa)	Strength (MPa)	% Elong.	Modulus (GPa)	Strength (MPa)	% Elong.
In situ	3.424 (0.445)	51.26 (4.602)	1.903 (0.283)	2.825 (0.203)	47.39 (2.997)	2.086 (0.175)
High Temp.	2.869 (0.119)	41.06 (1.657)	1.724 (0.113)	2.604 (0.233)	40.19 (1.710)	1.814 (0.112)
Low Temp.	3.976 (0.177)	54.40 (4.982)	1.739 (0.187)	3.003 (0.126)	40.71 (2.261)	1.559 (0.131)
<b>HX1000/PT 7067/Rynite (30/30/40 wt%)</b>						
	Modulus (GPa)	Strength (MPa)	% Elong.	Modulus (GPa)	Strength (MPa)	% Elong.
In situ	3.678 (0.379)	49.93 (3.147)	1.712 (0.242)	3.122 (0.316)	48.86 (2.291)	2.089 (0.188)
High Temp.	3.444 (0.182)	42.13 (3.677)	1.349 (0.103)	2.966 (0.273)	41.09 (2.127)	1.694 (0.110)
Low Temp.	5.161 (0.337)	57.73 (8.788)	1.290 (0.226)	3.310 (0.252)	31.10 (5.345)	1.063 (0.246)

Notes: Standard deviations given in parentheses.

<sup>a</sup> In situ = in situ composites.

<sup>b</sup> High Temp. = pregenerated microcomposites injection molded using a maximum barrel temperature of 270°C and strands with a draw ratio of 40.67 (6.71).

<sup>c</sup> Low Temp. = pregenerated microcomposites injection molded using a maximum barrel temperature of 250°C and strands with a draw ratio of 40.67 (6.71).

<sup>d</sup> % Elong. = percent elongation

three different sets of barrel temperatures. The experimental results show that injection molding temperature is a critical parameter which can have a considerable effect on the composite mechanical properties (see Table 3.1). Consistently, using a maximum barrel temperature of 270°C rather than 250°C resulted in the pregenerated microcomposites having lower strengths and moduli and higher percent elongations in the machine direction, matching the trends shown by Handlos and Baird [21] and Sabol and coworkers [20]. For instance, at 30 wt% TLCP, the machine direction modulus of the composite injection molded using a low barrel temperature was 5.161 GPa, versus just 3.444 GPa when the high barrel temperature was used. Meanwhile, the tensile strength dropped from 57.73 MPa to 42.13 MPa and the percent elongation rose from 1.290 to 1.349 with increasing barrel temperature.

In understanding the experimental results, it is necessary to compare the temperatures used in these tests to the PET melting temperatures. The lowest barrel temperature settings, where the maximum temperature was 250°C, were determined experimentally by injection molding the dry blended pellets at as low of a temperature as possible without having premature solidification in the nozzle. Because the melting temperatures of both grades of PET are higher than 250°C, it appears that some viscous heating occurred as the polymer was conveyed down the length of the barrel, melting the PET and allowing the material to be injection molded. From the trends in mechanical properties with increasing processing temperature, it is clear that using viscous heating to plasticate the PET allows higher mechanical properties to be attained than using higher barrel temperatures. In particular, at 270°C the composite properties suggest that the HX1000 fibrils soften too much and are severely damaged by the shear forces encountered in injection molding, yielding tensile moduli only slightly greater than those of Rynite and PT 7067.

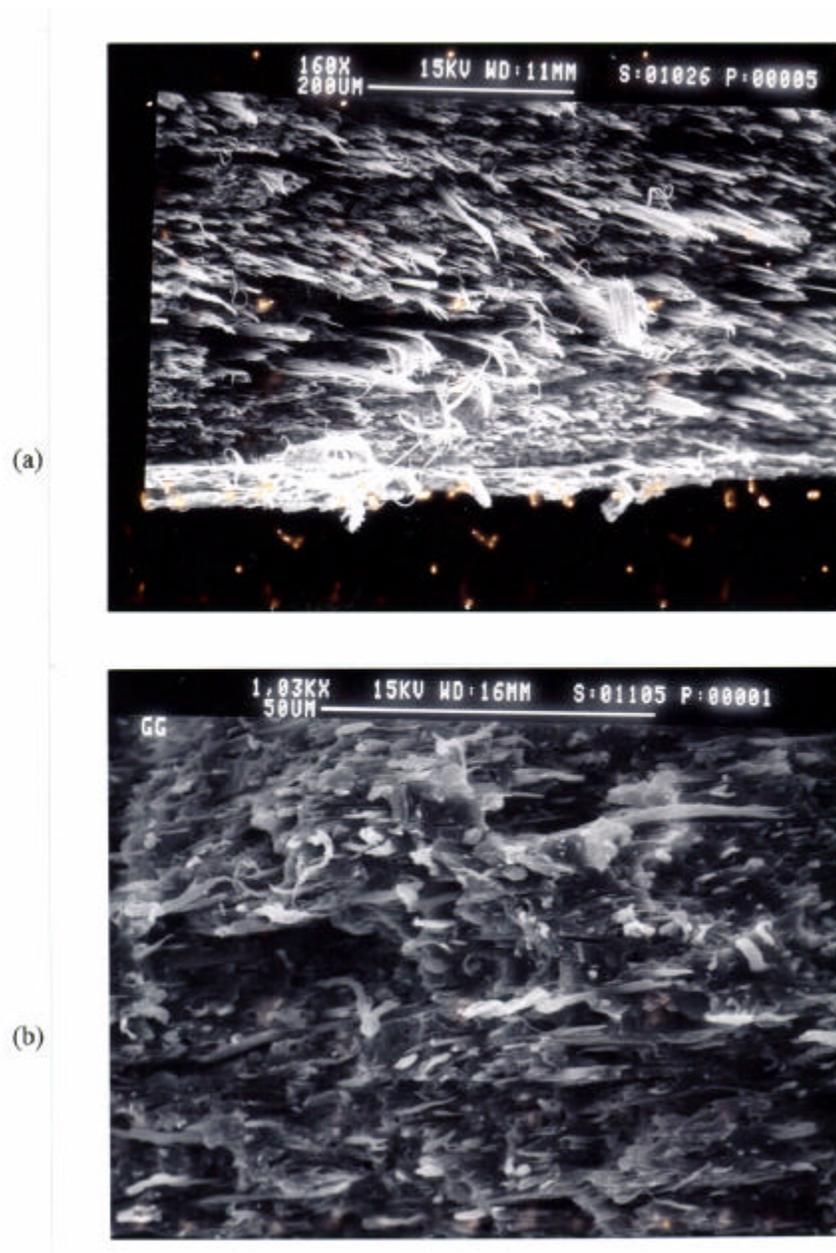
The experimental results also show that in situ composites with high mechanical properties can not be made with this combination of a spinning grade PET, an injection molding grade PET, and HX1000. This is true through the range of TLCP loadings used, with the machine direction tensile modulus consistently being only slightly greater than the transverse direction modulus. For example, at 30 wt% HX1000, the in situ composite has a machine direction modulus of 3.678 GPa and a transverse direction modulus of 3.122 GPa. Although the machine direction values are greater than the modulus of PT 7067 or Rynite, they do not match what has been observed with other in situ composites which contained HX1000. Specifically, in situ composites of polyetherimide with 30 wt% HX1000 had a machine direction flexural modulus of 7.27 GPa [36]. Also, when an in situ composite composed of 70 wt% PT 7067 and 30 wt% HX1000 was injection molded, the composite possessed a machine direction tensile modulus of 8.410 GPa [37]. By using a low viscosity, injection molding grade resin, the ratio of matrix viscosity to TLCP viscosity was not great enough to adequately deform and orient the TLCP, resulting in low mechanical properties for the in situ composites. This result demonstrates one of the

advantages that the pregenerated microcomposite process has over in situ composites; namely, it allows injection molding grade resins to be used with TLCPs to produce composite materials.

However, it also needs to be recognized that although the pregenerated HX1000 fibrils did reinforce the PET, the level of reinforcement did not reach theoretically expected levels. For the composite strands with a draw ratio of 40.67, composite theory was used to calculate a fibril modulus of 47.09 GPa. Based on the fibril modulus and assuming all of the fibrils have aspect ratios greater than 100, a planar isotropic plaque would theoretically have a tensile modulus of 4.035 GPa with 10 wt% reinforcement, 5.616 GPa with 20 wt% reinforcement, and 7.163 GPa with 30 wt% reinforcement. These values are significantly higher than the experimental values shown in Table 3.1, indicating that the full reinforcing potential of the HX1000 fibrils was not realized.

The reason that the composites produced during injection molding had properties significantly lower than those produced by compression molding can be related to the differences in shear rates and strains between the two processes. As the pregenerated microcomposite polymer melt was injection molded, it was subjected to estimated shear rates of about 150/sec in the screw channel and estimated wall shear rates of approximately 15,000/sec to 20,000/sec as the polymer was passed through the 2 mm diameter nozzle tip exit. This means the melt experienced strains of up to 1300 in the screw and nozzle tip. Meanwhile, compression molding only required uniaxially aligned strands to be pressed together to form a consolidated sample free of voids, exposing the fibrils to a very low shear rate and negligible strain. This difference in shear rate and strain had a direct effect on the morphology of the composites, as illustrated in Figure 3.5. For the injection molded composites, some of the HX1000 fibrils were bent, twisted and deformed, reducing their ability to reinforce the matrix. Meanwhile, the fibrils in the compression molded plaques were relatively unscathed, resulting in mechanical properties close to those of the individual strands. Therefore, to maximize the mechanical properties of these materials, it is necessary to process the TLCP fibrils in a way that minimizes the amount of shear to which they are exposed.

In the injection molding process, one of the places where the polymer is exposed to high shear stresses is at the nozzle tip exit. In particular, it has been shown that the properties of long fiber composites can be significantly reduced as a result of fiber breakage as the fiber reinforcement passes through this portion of the injection molder [38- 41]. This results in a lowering of mechanical properties, including flexural modulus, percent elongation, impact strength, and tensile strength for resins such as nylon 6/6, polyphenylene sulfide, and thermoplastic polyurethane. Because the TLCP fibrils also have high aspect ratios like conventional long glass fiber composites, one possible method of improving the mechanical properties is through using a nozzle tip with a larger exit diameter.



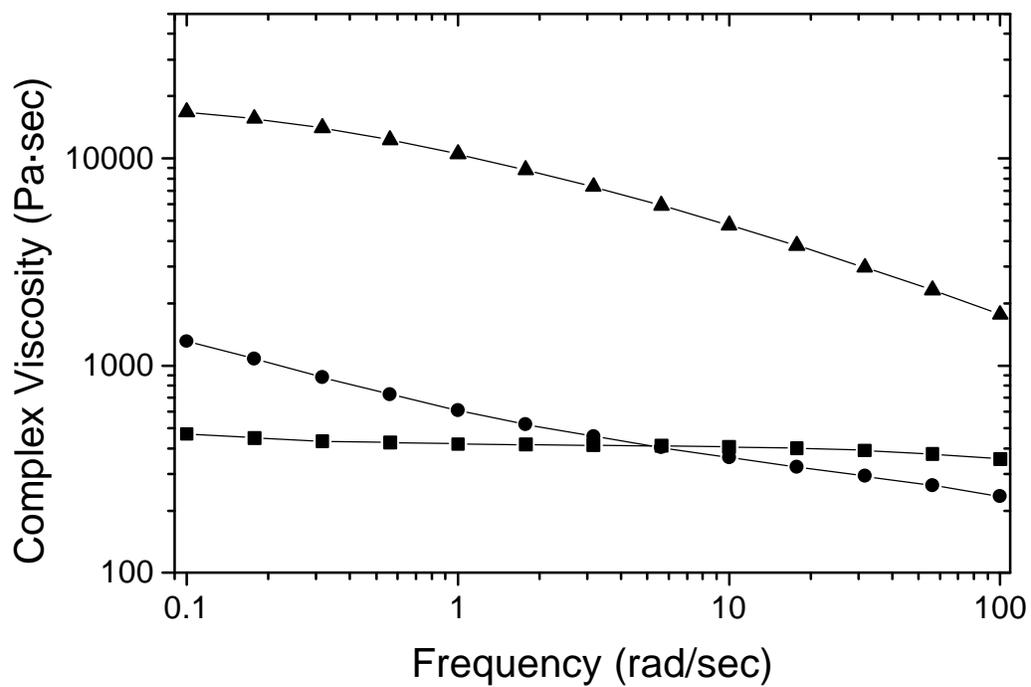
**Figure 3.5:** Scanning electron micrographs: (a) uniaxially compression molded HX1000/PT 7067 (50/50 wt%) strands and (b) injection molded pregenerated microcomposite of HX1000/PT 7067/Rynite (20/20/60 wt%).

To examine the effect of nozzle tip exit diameter on the mechanical properties of pregenerated microcomposites, two sets of pregenerated microcomposites were injection molded. Both sets of composites were produced using chopped PT 7067/HX1000 (50/50 wt%) composite strands (DR=108.5), which were dry blended with Rynite pellets to bring the HX1000 loading level to 20 wt% and injection molded at the lowest permissible barrel temperatures without having the melt solidify in the nozzle tip. The first set was injection molded using a nozzle tip with a 2 mm exit diameter, while the second set was produced with a nozzle tip having an exit diameter of 3 mm. One point which needs emphasizing is that the shear rate (and hence the shear stress) that the polymer was subjected to was significantly different between these two nozzles. Using the nozzle tip with a 2 mm diameter exit resulted in estimated wall shear rates ranging from 15,000/sec to 20,000/sec, while a 3 mm diameter exit reduced the wall shear rates to around 4500/sec to 6000/sec.

Comparing the mechanical properties of the composites produced with both nozzle tips, it appears that there was some improvement in properties by increasing the nozzle tip exit diameter. Using the 3 mm nozzle tip rather than the 2 mm nozzle tip increased the machine direction percent elongation at break from 1.477 ( $\pm 0.131$ ) to 1.869 ( $\pm 0.078$ ) and the tensile toughness from 0.409 ( $\pm 0.066$ ) MPa to 0.598 ( $\pm 0.047$ ) MPa (standard deviations given in parentheses). Meanwhile, the machine direction tensile modulus and strength showed no statistical improvement. Also, modest improvements in other mechanical properties were realized, but often these improvements were not outside the standard deviations of the data [35]. Therefore, it can be concluded that using a nozzle with a larger exit diameter does succeed in improving some of the mechanical properties, but the degree of improvement is small.

Another potential method of retaining the reinforcing ability of the TLCP fibrils is by diluting the chopped strands with a matrix resin having a low melting temperature and a low viscosity. By using a matrix with a low melting temperature, it will be possible to lower some of the barrel temperatures on the injection molder. In turn, this will expose the HX1000 fibrils to temperatures closer to the glass transition temperature of the TLCP, making them more difficult to deform and damage. Also, by using a low viscosity resin, the shear stress imposed on the fibers will be lower at a given shear rate. With a lower shear stress, the fibers should be damaged less, producing a composite with higher mechanical properties.

To explore the potential of this concept, two different resins were used to dilute the chopped composite strands to the desired level of fibril reinforcement. The first resin was Rynite, a low viscosity, injection molding grade of PET. Meanwhile, the second resin was Celenex 1600A, a low viscosity, injection molding grade of PBT. Note that these two polymers are significantly less viscous than PT 7067, as shown in Figure 3.6, so they both have the potential to help reduce the damage to the HX1000 fibrils in the



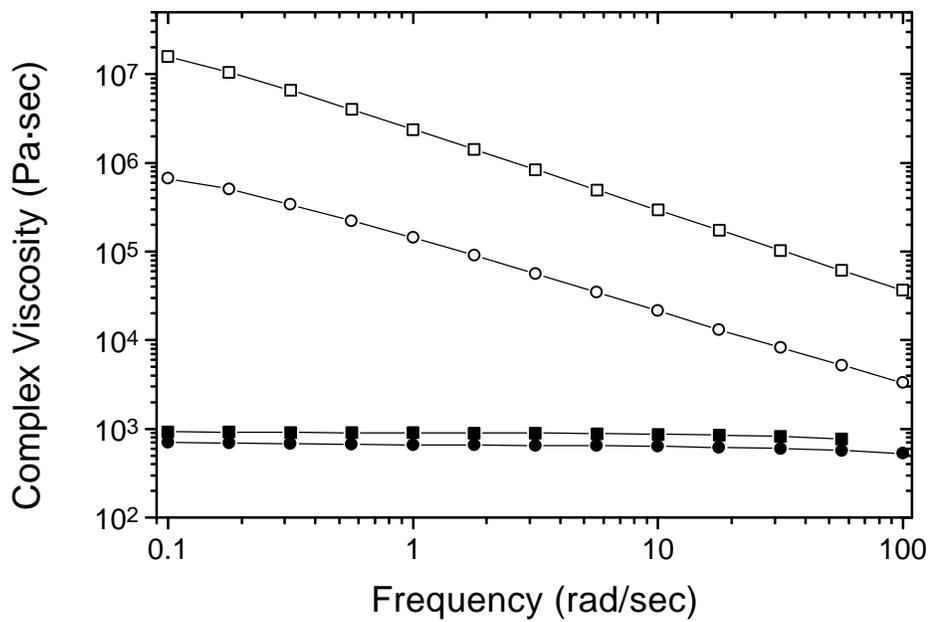
**Figure 3.6:** The complex viscosity ( $|\eta^*|$ ) versus angular frequency of the matrix polymers at 270°C. (■) = Celenex 1600A, (●) = Rynite, and (▲) = PT 7067.

injection molding step. Comparing Rynite and Celenex 1600A, Celenex 1600A had both of the desired advantages over Rynite. First, the melting temperature of Celenex 1600A was 228°C, while Rynite had a melting temperature of 257°C. With a lower melting temperature, it was possible to reduce the temperature settings of some of the zones of the injection molder barrel. With Rynite, the zone temperatures were: zone 1 = 245°C, zone 2 = 250°C, zone 3 = 245°C, zone 4 = 240°C. Meanwhile, using Celenex 1600A as the diluting phase allowed the zone temperatures to be: zone 1 = 240°C, zone 2 = 250°C, zone 3 = 240°C, zone 4 = 230°C. Second, at processing temperatures just above the melting temperature of Rynite, the complex viscosity of Celenex 1600A was significantly lower than that of Rynite (Figure 3.7). This indicates that at low processing temperatures, using Rynite rather than Celenex 1600A as the diluting resin may damage the HX1000 fibrils more because of its higher viscosity.

To explore the idea that diluting with PBT rather than PET would have an effect on the processing behavior of the dry blended pellets, polymer was solidified on the injection molder screw, removed from the screw, and examined. Specifically, as the pellets were being processed, the injection molding process was stopped and the barrel was allowed to cool. The screw was then pulled out of the barrel and the polymer unwrapped from the channels of the screw. This procedure was performed twice, once when Celenex 1600A was used as the diluting resin and once when Rynite was used. From this, features such as where the polymer began to melt and where the melt became homogeneously mixed with HX1000 fibrils could be noted.

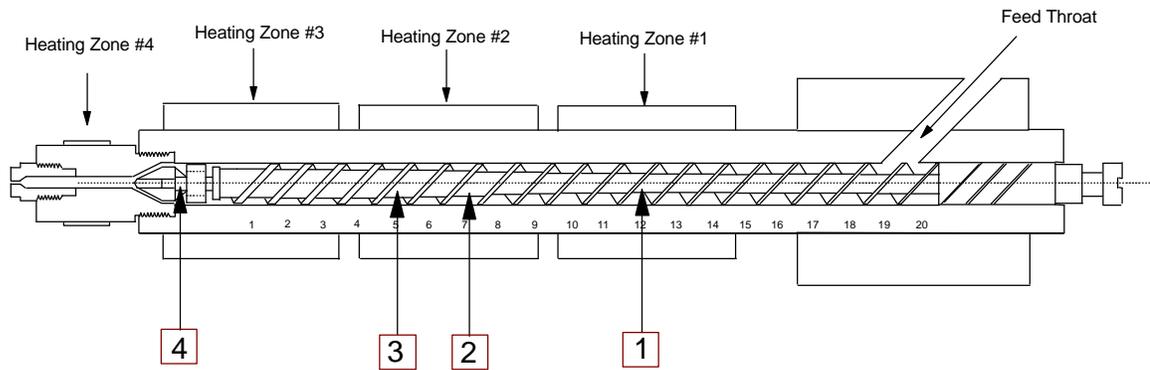
Comparing the two diluting resins, it was observed that diluting with PBT rather than PET had an appreciable effect on how the dry blended pellets behaved as they were conveyed through the barrel. First, by diluting with PBT, polymer melt began to form much earlier in the barrel, with the location shown schematically in Figure 3.8. Once the dry blended pellets reached the middle of the first heating zone, PBT began to melt and surround the chopped PT 7067/HX1000 strands. Meanwhile, when Rynite was dry blended with the chopped strands, polymer melt did not begin to form until the pellets reached the middle of the second heating zone.

Second, the order in which the matrix resins melted was affected by diluting with Celenex 1600A rather than Rynite. When Rynite was mixed with the chopped strands, it was the PT 7067 surrounding the HX1000 phase that melted in the middle of the second heating zone, not the Rynite pellets. This is an important point to note, because it influenced the quality of the melt in which the HX1000 fibrils were encapsulated. When diluting with Celenex 1600A, the PBT pellets melted first, surrounding the chopped strands with a low viscosity melt. This wetted the chopped PT 7067/HX1000 strands, helping transfer heat to the PT 7067 to melt it more quickly. Also, as the PT 7067 began to melt and release the HX1000 fibrils, the fibrils were freed into neat PBT. This contrasts sharply with what occurred when Rynite was used as the diluting resin. With



**Figure 3.7:** The complex viscosity ( $|\eta^*|$ ) versus angular frequency of the PET and PBT resins at various temperatures. Rynite: (■) = 260°C, (●) = 264°C and Celenex 1600A: (□) = 260°C, (○) = 264°C.

## Injection Molder: Cut away view



**Figure 3.8:** Cut away schematic of the injection molder. (1) = Celenex 1600A begins melting, (2) = PT 7067 surrounding the HX1000 fibrils begins melting, (3) = homogeneous PT 7067/HX1000/Celenex 1600A melt, and (4) = homogeneous PT 7067/HX1000/Rynite melt.

Rynite, the PT 7067 melted first, releasing HX1000 fibrils into a viscous melt filled with high aspect ratio HX1000 fibrils and Rynite pellets. By forming a viscous melt with such a high concentration of HX1000 fibrils, there would be a high number of fibril-fibril interactions which could damage the HX1000 fibrils and reduce their ability to reinforce the matrix, as has been observed in glass-filled systems [42, 43, 44]. Also, the high viscosity of PT 7067 (as shown in Figure 3.6) relative to Celenex 1600A could lead to more damage to the HX1000 fibrils, as has been cited for other filled polymers [44]. Therefore, using Celenex 1600A rather than Rynite to dilute the chopped strands appears to address several key areas which can affect fibril aspect ratio and reinforcing ability.

The third factor which was related to the earlier melting of the PBT in the screw channel was at what point a homogenous, thoroughly mixed melt was formed. When Rynite was used to dilute the chopped strands rather than Celenex 1600A, the dry blended pellets had to be conveyed further down the barrel. Specifically, with Rynite the melt did not become completely mixed until it had passed the check ring valve. Meanwhile, using Celenex 1600A yielded a homogeneous melt at the end of the second heating zone, well before the check ring valve. This demonstrates that using Celenex 1600A, with its much lower melting temperature, was able to more fully realize the benefits of using a low viscosity resin because it wetted the HX1000 fibrils earlier in the injection molding screw. Meanwhile, Rynite was limited by its 257°C melting temperature and the need to set the injection molder barrel temperatures at a maximum of 250°C to maximize mechanical properties.

In accordance with the observed differences in morphology, a significant improvement in mechanical properties was achieved by diluting with PBT rather than PET (see Table 3.2). For example, composites composed of PT 7067/HX1000/Rynite (30/30/40 wt%) had a machine direction flexural strength of 79.15 MPa while those with a composition of PT 7067/HX1000/Celenex 1600A (30/30/40 wt%) had a flexural strength 95.74 MPa. Tensile strength was also increased, with the PT 7067/HX1000/Rynite (30/30/40 wt%) composites having a transverse direction strength of 34.04 MPa while the PT 7067/HX1000/Celenex 1600A (30/30/40 wt%) composites had a strength of 47.92 MPa. Similar increases in tensile toughness and percent elongation were observed, while the tensile and flexural moduli stayed approximately constant. Therefore, it appears that diluting with Celenex 1600A rather than Rynite was successful in producing pregenerated microcomposites with better properties. In particular, despite the fact that Celenex 1600A has lower tensile and flexural strengths than Rynite (at 45.81 vs. 49.40 and 60.42 vs. 69.04, respectfully), it was able to be used to yield composites with higher tensile and flexural strengths. This indicates that the improvements in strength were due to better reinforcement from the HX1000 fibrils, which were probably damaged less when Celenex 1600A was used as the diluting resin rather than Rynite.

**Table 3.2:** The Mechanical Properties of the Matrix Polymers and the Effect of Matrix Type on the Mechanical Properties of Pregenerated Microcomposites <sup>a</sup>

<b>MATRIX POLYMERS</b>				
<b>Tensile Properties</b>			<b>Flexural Properties</b>	
<b>PT 7067</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	2.176 (0.067)	2.225 (0.056)	2.501 (0.092)	1.951 (0.157)
Strength (MPa)	47.87 (2.063)	50.31 (1.089)	70.16 (2.228)	61.27 (2.627)
% Elongation	3.384 (0.397)	3.655 (0.169)		
<b>Rynite</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	2.424 (0.217)	2.585 (0.246)	2.763 (0.194)	2.579 (0.085)
Strength (MPa)	49.40 (0.883)	42.85 (6.852)	69.04 (0.311)	67.45 (2.784)
% Elongation	2.760 (0.137)	1.924 (0.411)		
<b>Celenex 1600A</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	2.018 (0.188)	2.210 (0.173)	2.435 (0.112)	2.326 (0.134)
Strength (MPa)	45.81 (1.528)	49.52 (1.316)	60.42 (1.421)	62.17 (3.322)
% Elongation	3.050 (0.330)	3.186 (0.220)		
<b>PREGENERATED MICROCOMPOSITES</b>				
<b>Tensile Properties</b>			<b>Flexural Properties</b>	
<b>HX1000/PT 7067/Rynite (30/30/40 wt%)</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	5.727 (0.432)	3.362 (0.414)	6.038 (0.522)	4.216 (0.191)
Strength (MPa)	58.22 (7.814)	34.04 (7.539)	79.15 (7.212)	72.89 (4.827)
% Elongation	1.088 (0.100)	1.068 (0.150)		
Toughness (MPa)	0.330 (0.083)	0.193 (0.069)		
<b>HX1000/PT 7067/Celenex 1600A (30/30/40 wt%)</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	5.726 (0.720)	3.389 (0.401)	5.860 (0.633)	4.015 (0.289)
Strength (MPa)	65.02 (2.696)	47.92 (4.449)	95.74 (3.338)	69.49 (10.42)
% Elongation	1.286 (0.169)	1.631 (0.125)		
Toughness (MPa)	0.433 (0.069)	0.416 (0.048)		

Note: Standard deviations given in parentheses.

<sup>a</sup> Strand draw ratio = 108.5 (19.57).

Based on the previous experimental results, a final set of pregenerated microcomposites were injection molded using the best processing conditions, then tested for their mechanical properties to address several concerns. The properties of these pregenerated microcomposites are compared to those of the previous composites to show the improvement resulting from combining all of the best processing conditions. Next, the properties of these composites are compared to those of the neat PET and PBT resins to show how successful the pregenerated microcomposite process is in increasing mechanical properties. Finally, a comparison of properties to glass-filled PET is also made.

The optimum conditions were used to generate injection molded samples. Specifically, composites were molded using the lowest barrel temperatures, a nozzle tip with a 3 mm diameter exit, a mold set at 110°C, composite strands with a draw ratio of 108.5, and Celenex 1600A as the diluting resin. The barrel temperatures used were as follows: zone 1 = 240°C, zone 2 = 250°C, zone 3 = 240°C, and zone 4 = 230°C. Based on these processing conditions, pregenerated microcomposites with loadings of 10, 20, and 30 wt% HX1000 were injection molded.

Examining the properties of composites produced using the best processing conditions, it is clear that the optimum processing conditions yielded composites with generally superior mechanical properties relative to those injection molded varying just the nozzle tip exit diameter or diluting material, as shown in Table 3.3. For example, using a nozzle tip with a 3 mm exit diameter and Rynite as the diluting resin, PT 7067/HX1000/Rynite (20/20/60 wt%) composites had a machine direction flexural strength of 87.87 MPa and a transverse direction strength of 71.25 MPa. However, when Celenex 1600A was used rather than Rynite, the machine direction strength rose to 99.13 MPa and the transverse direction strength increased to 86.54 MPa. A similar effect was seen by increasing the nozzle tip exit diameter from 2 mm to 3 mm while keeping the diluting resin Celenex 1600A in both cases. For composites of PT 7067/HX1000/Celenex 1600A (30/30/40 wt%) produced with the 2 mm nozzle, the machine direction flexural strength was 95.74 MPa while the transverse direction strength was 69.49 MPa. Meanwhile, injection molding using the 3 mm nozzle yielded composites with a machine direction strength of 100.98 MPa and a transverse direction strength of 91.84 MPa. This demonstrates that increases in mechanical properties are possible by through improvements made to the injection molding process. In particular, using a nozzle tip with a large exit diameter and Celenex 1600A as the diluting resin appears to reduce the damage to the fibrils, as reflected in the higher mechanical properties relative to using just a large exit diameter or Celenex 1600A as the diluting resin. However, even with these improvements in mechanical properties, the composites are still not achieving the theoretical levels of reinforcement. Specifically, at loadings of 30 wt% HX1000, the composites experimentally showed a maximum tensile modulus of

**Table 3.3:** The Mechanical Properties of Pregenerated Microcomposites Produced Using the Optimum Processing Conditions <sup>a</sup>

Tensile Properties			Flexural Properties	
<b>HX1000/PT 7067/Celenex 1600A (10/10/80 wt%)</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	2.862 (0.185)	2.372 (0.156)	3.279 (0.134)	3.155 (0.198)
Strength (MPa)	60.61 (1.788)	51.96 (1.005)	86.42 (2.058)	81.94 (2.737)
% Elongation	4.379 (0.788)	5.665 (0.920)		
Toughness (MPa)	1.979 (0.480)	2.279 (0.436)		
<b>HX1000/PT 7067/Celenex 1600A (20/20/60 wt%)</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	4.127 (0.333)	2.701 (0.220)	4.758 (0.346)	3.499 (0.363)
Strength (MPa)	62.44 (6.371)	51.06 (3.352)	99.13 (1.349)	86.54 (3.727)
% Elongation	1.719 (0.256)	2.532 (0.146)		
Toughness (MPa)	0.614 (0.169)	0.754 (0.065)		
<b>HX1000/PT 7067/Celenex 1600A (30/30/40 wt%)</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	5.849 (0.702)	3.389 (0.598)	6.877 (0.886)	4.131 (0.722)
Strength (MPa)	72.03 (5.343)	42.61 (3.770)	100.98 (3.180)	91.84 (5.465)
% Elongation	1.414 (0.218)	1.430 (0.211)		
Toughness (MPa)	0.517 (0.101)	0.323 (0.060)		

Note: Standard deviations given in parentheses.

<sup>a</sup> Strand draw ratio was 108.5 (19.57).

5.849 GPa, while a planar isotropic composite would theoretically have a modulus of 7.258 GPa. Therefore, if additional improvements in the processing of pregenerated microcomposites can be made, the mechanical properties should be increased.

Compared to the neat PET and PBT resins, it is clear that addition of pregenerated microcomposite fibrils resulted in improved mechanical properties. This is particularly evident in the flexural properties. The neat resins had a flexural modulus of around 2.5 GPa and a strength of approximately 65 MPa, as shown in Table 3.2. This contrasts sharply with the flexural properties of PT 7067/HX1000/Celenex 1600A (30/30/40 wt%) presented in Table 3.3. This material had a machine direction modulus of 6.877 GPa, a transverse direction modulus of 4.131 GPa, a machine direction strength of 100.98 MPa, and a transverse direction strength of 91.84 MPa. Therefore, the pregenerated microcomposite processing method was successful in improving both the strength and modulus of the matrix resin.

Next, the theoretically predicted stiffnesses for both the pregenerated microcomposites and glass filled PET were calculated using the rule of mixtures and compared. For these calculations, a density of  $2.59 \text{ g/cm}^3$  and a modulus of 69 GPa was used for the glass fiber, while a density of  $1.25 \text{ g/cm}^3$  and a modulus of 49.86 GPa was used for the HX1000 fibrils. Assuming a planar isotropic distribution of fibers, the pregenerated microcomposites were predicted to have a modulus of 3.78 GPa at 10 wt% HX1000, 5.52 GPa at 20 wt% HX1000, and 7.26 GPa at 30 wt% HX1000. These values are slightly greater than those calculated for the glass filled PET, with the predicted modulus being 3.54 GPa with 10 wt% glass fiber, 5.07 GPa with 20 wt% glass fiber, and 6.80 GPa with 30 wt% glass fiber. The reason the theoretical modulus values for the HX1000 filled PET are higher is due to the fact that although the HX1000 has a lower modulus than glass fiber (50 GPa versus 69 GPa), it also has a much lower density of  $1.25 \text{ g/cm}^3$ , versus  $2.59 \text{ g/cm}^3$  ascribed to E-glass fiber. Therefore, because the rule of mixtures is based on volume fractions, the lower tensile modulus of HX1000 is offset by the fact that the HX1000 fibrils occupy a larger volume fraction of the composite than glass fiber at the same weight fraction of loading.

Comparing the experimental tensile and flexural moduli of the pregenerated microcomposites to glass filled PET showed that higher stiffnesses were achieved with glass fiber reinforcement (Table 3.4). This was the case despite the fact that theoretically, if the full reinforcing potential of both fibers was realized, the HX1000 reinforced composites would have slightly higher moduli. Examining the machine direction modulus at 30 wt% loading serves to illustrate the difference in reinforcement. At 30 wt% glass fiber, a machine direction flexural modulus of 10.05 GPa was achieved versus just 6.877 GPa for the pregenerated microcomposite. Therefore, although significant reinforcement by the pregenerated HX1000 fibrils was obtained, the level of reinforcement still fell short of the theoretically expected values and what was

**Table 3.4:** The Mechanical Properties of Glass Fiber Filled PET

<b>Tensile Properties</b>			<b>Flexural Properties</b>	
<b>10 wt% Glass Fiber Filled PET</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	3.656 (0.276)	3.476 (0.171)	4.149 (0.334)	3.492 (0.325)
Strength (MPa)	62.41 (3.999)	58.10 (2.568)	100.81 (5.215)	90.26 (5.299)
% Elongation	2.321 (0.580)	2.253 (0.634)		
Toughness (MPa)	0.979 (0.166)	0.914 (0.149)		
<b>20 wt% Glass Fiber Filled PET</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	6.269 (1.011)	4.042 (0.287)	5.773 (0.261)	4.085 (0.232)
Strength (MPa)	84.90 (4.510)	62.73 (3.245)	134.88 (6.023)	99.24 (6.386)
% Elongation	2.253 (0.333)	2.234 (0.337)		
Toughness (MPa)	1.283 (0.293)	0.929 (0.202)		
<b>30 wt% Glass Fiber Filled PET</b>				
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
Modulus (GPa)	9.209 (0.635)	4.711 (0.551)	10.045 (0.349)	4.999 (0.327)
Strength (MPa)	117.8 (5.118)	59.12 (4.268)	205.43 (4.184)	98.16 (9.178)
% Elongation	1.722 (0.090)	1.368 (0.178)		
Toughness (MPa)	1.458 (0.213)	0.843 (0.166)		

Note: Standard deviations given in parentheses.

accomplished at the same weight loadings using glass fiber. Also note that it is justifiable to compare the pregenerated microcomposite properties to the glass filled PET, despite the difference in matrix polymers. For example, the flexural moduli of two polymers manufactured by DuPont, 30 wt% glass filled PET (Rynite 530) and 30 wt% glass filled PBT (Crastin SK 605), are both reported to be 8.96 GPa [45]. Hence, regardless of whether PET or a blend of PET and PBT was being reinforced, the differences in modulus between the pregenerated microcomposites and glass filled PET can be largely attributed to the effectiveness of the reinforcing phase, not the matrix.

The difference between the glass fiber and HX1000 fibril reinforcement emphasizes that although theoretically the HX1000 reinforced composites should be slightly stiffer, the injection molding step does not have the same affect on glass fiber as it does on HX1000 fibrils. In particular, the HX1000 fibrils appear to be more sensitive to shear and thermal history, making it difficult to achieve the theoretically expected levels of reinforcement. One key reason for the difference between the two forms of reinforcement lies in the fact that during injection molding, the processing temperatures exceed the glass transition temperature of the TLCP. This means that rather than the HX1000 being in a glassy state, it is in a rubbery state, making it less resistant to the forces encountered in the injection molding step. Morphologically, this is evident in the twisted and bent shapes of some of the HX1000 fibrils after the injection molding step (as shown in Figure 3.5). This contrasts sharply with the fibrils in the uniaxially compression molded PT 7067/HX1000 (50/50 wt%) strands, which are all straight and undeformed. Therefore, for the mechanical properties to get closer to the theoretically expected levels, it appears that it is necessary to injection mold at a temperature as close to the glass transition temperature as possible. In fact, if the glass transition temperature was not exceeded in the injection molding step, the material should have behaved more like a typically fiber filled polymer melt.

In addition to having higher moduli, the glass fiber reinforced PET also consistently outperformed the pregenerated microcomposite in the categories of strength, percent elongation, and toughness. However, a few key points need to be recognized in this comparison. First, the glass fiber had a sizing agent on its surface while the HX1000 fibrils were not sized. This distinction is important because sizing agents are used to obtain good adhesion between the fiber and matrix. This means that because the HX1000 fibrils were not sized, the adhesion between the matrix and reinforcement was less than optimal, which might have accounted for the lower properties. However, it has been shown that it is possible to improve the adhesion in TLCP reinforced thermoplastics by using reactive components [46 - 48]. Therefore, higher strengths, percent elongations, and toughnesses should be possible by using a small amount of a reactive component in the injection molding step.

A second reason that the HX1000 fibril filled composites had lower mechanical properties than the glass filled composites was because HX1000 was not as strong as glass. The strength of glass fiber has been cited as ranging from 1.72 GPa to over 2.07 GPa [10, 11]. Meanwhile, neat HX1000 only had a strength of about 300 MPa. Based on the difference in strength between the two neat materials, it is not surprising that composites containing 30 wt% glass fiber are one and a half times as strong as those reinforced with HX1000 fibrils. Still, it needs to be remembered that the interfacial adhesion between the HX1000 fibrils and the matrix has not been addressed. Hence, despite the disparity in tensile strengths between neat glass fiber and HX1000 strands, improved adhesion between the matrix and the TLCP could yield strengths which are competitive with glass filled materials. Also, it should be noted that other TLCPs have higher strengths and stiffnesses, so using this processing scheme with these materials offers a method of obtaining mechanical properties more competitive with glass fiber reinforcement.

### 3.4 Conclusions

Injection molding temperature had a tremendous affect on the properties of the pregenerated microcomposites, with lower temperatures producing composites with higher properties. When processed using a highest barrel temperature of 250°C, HX1000 provided reinforcement to the PET. However, when these temperatures were increased to 270°C, the HX1000 fibrils were unable to withstand the injection molding step and the properties were worse than the in situ composites and little better than neat PET.

Nozzle exit diameter also appeared to have an influence on the pregenerated microcomposite properties, but the effect was minor. In particular, plaques produced using the nozzle with a 3 mm exit diameter had higher percent elongations to fracture and tensile toughnesses than those made with the nozzle having a 2 mm exit diameter. Yet, the machine direction tensile modulus and strength showed no statistical improvement. Considering that the overall increase in properties was small, it appears that the larger nozzle exit diameter may have helped retain longer HX1000 fibril lengths, but not as well as has been noted for long glass filled systems.

After examining the influence of diluting material on final mechanical properties, it appeared that it was better to dilute with PBT rather than PET. This was true because the PBT pellets melted before the PET encapsulating the HX1000 fibrils. By melting first, the PT X267/HX1000 pellets were surrounded by molten PBT, enhancing the heat transfer to the pellets and allowing the HX1000 fibrils to be released into a matrix with a low concentration of fibrils. Meanwhile, when diluting with Rynite, the PT X267 encapsulating the HX1000 melted first. Therefore, before the Rynite pellets melted, the melt contained a high concentration of HX1000 fibrils as well as Rynite pellets. This is speculated to have produced more fibril-fibril collisions as well as fibril-pellet collisions,

which would have damaged the fibrils more and reduced their ability to reinforce the matrix.

Using the optimum processing conditions yielded composites with the best mechanical properties. At 30 wt% reinforcement, the injection molded composites had a machine direction modulus of 5.849 GPa, 80.59% of the theoretically expected value and nearly three times that of the neat resins. The machine direction tensile strength was also approximately 50% higher. Flexural properties showed similar trends, with significantly greater moduli and strengths. Therefore, the pregenerated microcomposite processing method was shown to be an effective method of reinforcing commodity thermoplastics. However, further work appears to be necessary to reach theoretically expected values. In particular, it may be necessary to use a matrix with lower processing temperatures, a TLCP with a higher glass transition temperature, and a TLCP with a higher tensile strength and modulus.

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