

1. Introduction

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There is a need to develop materials which are light weight, of high strength, and of high stiffness. This combination of properties would allow these materials to supplant areas that have traditionally relied on metal, such as the automotive and aerospace industries. Polymers have an advantage over metal because of their light weight, with densities around 0.9 to 1.4 g/cm^3 . Typical metals used in engineering applications have densities from 2.7 to 8.2 g/cm^3 . However, metals show superior mechanical properties, with tensile moduli of 45 to 205 GPa and tensile strengths of 90 MPa to 850 MPa [1]. The properties of commodity thermoplastics are usually much lower, with moduli of 0.1 to 3.5 GPa and strengths of 1 to 100 MPa [2].

To increase the strength and stiffness of thermoplastics, they have been combined with fibers to create composites. Typically, this reinforcement has been generated by compounding short fiber into the matrix or impregnating a fiber weave with polymer. The fiber reinforcement has ordinarily been glass, graphite, carbon, or aromatic polyamide. Glass fiber has been the most common form of reinforcement because of its low cost and the experience in using glass as a reinforcing agent [3].

However, the use of glass fiber for reinforcement possesses several drawbacks. The most important of these drawbacks for the automotive industry is its high density. A part made of polyethylene terephthalate with 30 volume percent glass has 45 percent of its weight from the glass reinforcement, resulting in a density of 1.70 g/cm^3 . This is too heavy for many applications, such as automotive door panels and floor boards. Another shortcoming is found in recycling glass-filled thermoplastics. Recycling is primarily limited to regrinding the material and reprocessing it, which causes further fiber breakage and lowering of the fiber aspect ratio. Since there is no method of recreating high aspect ratios, the recycled materials are usually mixed with virgin polymer to achieve an acceptable distribution of fiber lengths that will yield the desired performance. Addition of fiber also: 1) increases matrix viscosity, 2) causes abrasive wear which shortens the life of processing equipment, 3) can not be used in injection molding which requires fine detail, 4) produces a poor surface finish, and 5) tends not to reach optimum reinforcement potential due to fiber breakage.

The purpose of this chapter is to delineate how thermotropic liquid crystalline polymers (TLCPs) may be the material to use for surmounting some of these problems. This will include a discussion of TLCPs and the mechanical properties they possess. Blends with thermoplastics will also be presented to illustrate their potential as the reinforcing phase in composites. Emphasis will be placed on what advantages and disadvantages are observed by using TLCPs and TLCP based composites.

1.1 Liquid Crystalline Polymers

Liquid crystalline polymers (LCPs) possess a phase of matter intermediate to the isotropic liquid and solid crystal states called a *mesophase* or *mesomorphic* phase (from the Greek *mesos*, meaning middle or intermediate). There are three types of mesophases recognized by Friedel [4], which are defined by their type of ordering. Smectic mesophases show ordering in two directions, which is manifested as the polymer chains both lying parallel to one another (orientational order) and long-range stratification normal to the chain axes (positional order). These liquid crystalline phases often possess certain properties similar to those of soaps, hence the name smectic. Nematic mesophases show only orientational order, manifested as the polymer chains lying parallel to one another along one axis. This axis establishes the nematic director, or optic axis in the fluid. The term "nematic" derives from the Greek word for thread because when viewed under crossed polarizers, thread-like extinction bands are observed. A subset of the nematic mesophase is the cholesteric, or more properly the chiral nematic mesophase. It is nematic because each plane of polymer chains has a nematic director, but has the additional feature that the directors show a cumulative twist as each plane is examined in sequence. The twist is created by the chiral centers in the mesogens exerting asymmetrical intermolecular forces between the nematic layers [5]. The result of this twisting is the creation of a periodic helical structure (refer to Figure 1.1).

A distinction between types of liquid crystalline polymers can be made based on whether they are liquid crystalline in solution or in the melt. Lyotropic liquid crystalline polymers (LLCPs) exhibit liquid crystallinity in solutions. This is controlled by the solvent used, the temperature of the solvent, and the concentration of polymer. Typically LLCPs can not exhibit liquid crystallinity in the melt because they degrade before melting. Thermotropic liquid crystalline polymers (TLCPs) show liquid crystallinity when in the melt [5 - 7]. This is controlled by melt temperature and thermal history.

To form a polymeric liquid crystalline phase, the most important molecular feature needed is a rigid anisotropic unit called a mesogen [8, 9]. Mesogenic units are important because they create rodlike molecules (main chain LCPs) or branches (side chain LCPs) which can organize to form liquid crystalline order. Mesogens are usually based on stiff, aromatic units with bridging groups linking the individual aromatic units. Typical chemicals used to form mesogenic groups are 4-hydroxybenzoic acid (HBA), hydroquinone (HQ), and terephthalic acid (TA).

A LCP can be created by polymerizing one mesogen, but these polymers often have a melting temperature higher than their degradation temperature. This is a problem because they can not be melt processed using conventional techniques, so usually they are only processed from solution. Examples of these kinds of LLCs are poly(1,4-phenylene

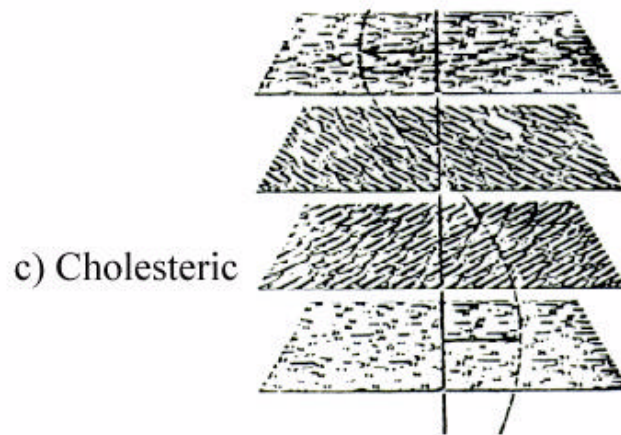
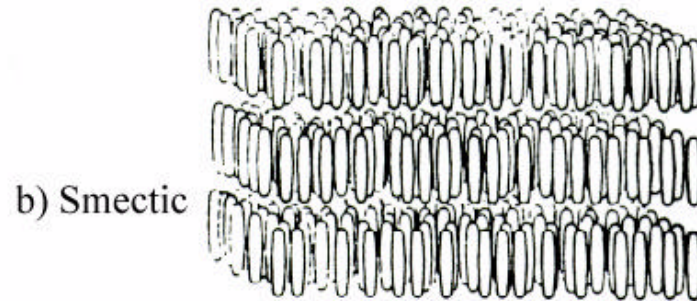
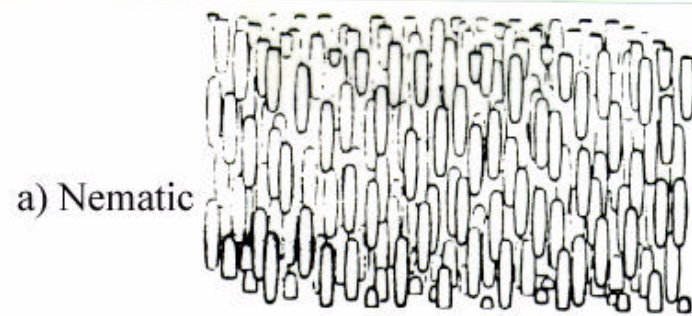
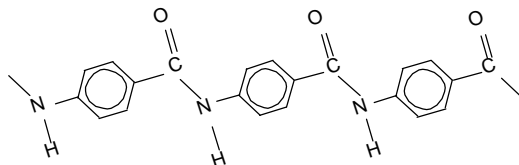
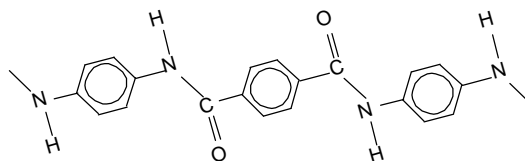


Figure 1.1: The Types of Liquid Crystals. This shows the organization present in smectic, nematic, and chiral nematic liquid crystals [10].

Lytotropic Liquid Crystalline Polymers

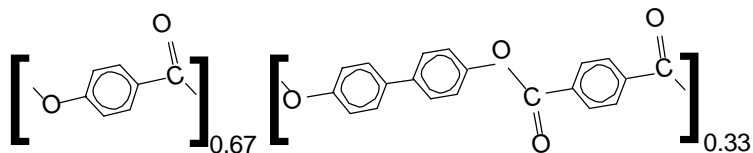


Polybenzamide (PBA)

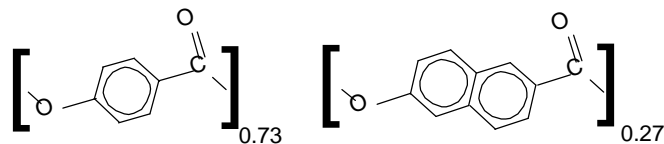


Poly(1,4-phenylene terephthalamide) (PPTA)

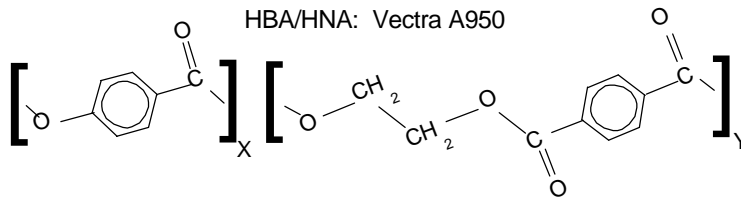
Thermotropic Liquid Crystalline Polymers



HBA/BP-TA: Xydar (formerly Ekkcel I-2000)



HBA/HNA: Vectra A950



HBA/PET: Rodrun (formerly XG-7)

Figure 1.2: Liquid Crystalline Polymer Structures. This includes both lyotropic liquid crystalline polymers (LLCPs) and thermotropic liquid crystalline polymers (TLCPs). Note X and Y for the Rodrun structure represent mole percentages, with X typically being 60 or 80 and Y being 40 or 20.

terephthalamide) (PPTA) and polybenzamide (PBA), with PPTA being more commonly known as Kevlar[®] [11] (refer to Figure 1.2).

To create thermotropic LCPs, the polymer's melting temperature must be below the degradation temperature, and the chains must retain their rodlike character. On a molecular level, this is accomplished by disrupting the regularity in the LCP's chain structure. Two methods exist for doing this: 1) using more than one mesogenic unit in the polymer and 2) incorporating flexible spacers between the mesogens [9]. Those which use two or more mesogenic units rather than flexible spacers are called wholly aromatic, main-chain TLCPs or semirigid TLCPs. Typical semirigid TLCPs include Xydar[®], a copolyester of 4,4'-dihydroxybiphenol (BP), TA, and HBA (25/25/50 mole %), and Vectra A950[®], a copolyester of HBA and 2-hydroxy-6-naphthoic acid (HNA) (73/27 mole %). Those which use flexible spacers between the mesogens are semiflexible TLCPs. Typical semiflexible TLCPs include copolyesters of polyethylene terephthalate (PET) and HBA, with the HBA usually constituting 40 to 80 mole % of the polymer and the PET acting as the flexible spacer.

TLCPs have several useful properties which could lead to commercial applications. For example, they exhibit low permeability to many gases relative to other thermoplastics [7, 12, 13, 14]. Thomas and Roth [12] examined the oxygen permeability of a wide variety of polymers at 23°C and found that Vectra A900 film had a permeability of $1.2 \cdot 10^{-7}$ (cm³-cm)/(cm²-day-atmo.). This is over 100 times lower than the value for PET and 5000 times lower than the value for PP. TLCPs exhibit low coefficients of thermal expansion and excellent electrical property values [7, 15 - 21]. Hoechst Celanese [19] has reported the coefficient of linear thermal expansion to be $-5 \cdot 10^{-6}$ cm/cm/°C in the flow direction and $40 \cdot 10^{-6}$ cm/cm/°C in the transverse direction, versus $65 \cdot 10^{-6}$ cm/cm/°C for neat PET [22]. They are extremely resistant to chemical attack because of their negligible solubility to many fluids, leading to a retention of mechanical properties [17, 18, 21, 23, 24]. After a three month exposure to various automotive fluids (transmission oil, engine oil, unleaded gasoline) at room temperature, TLCP test samples composed of substituted hydroquinones retained greater than 90% of their tensile strength and modulus [24]. Also, because there is a little change in density upon cooling, they can be used to injection mold highly complicated shaped articles, such as electrical conductors, which can not be produced with commodity thermoplastics [14, 17, 18, 21, 25, 26].

The mechanical properties of TLCPs can also be exceptional. In particular, fibers and injection molded samples can exhibit high modulus and strength values. Fiber spinning without any annealing post-treatment often yields fibers with tensile strengths over 1 GPa and tensile moduli of 40 to 100 GPa [27 - 40], while typical nylon and polyester yarn have strengths of around 1 GPa and moduli from 6 to 14 GPa [41]. This shows that when both TLCPs and commodity resins are highly oriented by the spinning process, TLCPs excel. They have modulus values which greatly exceed either nylon or

PET commodity yarns while giving strengths which match or slightly exceed those same materials.

More important than the comparison of properties to other thermoplastics is the comparison to common reinforcing materials such as glass. In work reported by Baird and coworkers [42 - 46], the tensile moduli of the TLCP phase in composite strands was found to fall in the range from 50 to 100 GPa. Also, the strength of neat TLCP fibers has been reported to be in the range of 1 GPa as spun and over 2 GPa when annealed [41]. Glass fiber 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/cm³ [47- 50]. (Note: For undamaged pristine fibers, tensile strength values are reported to be in the range of 3.4 to 4.1 GPa). This indicates that the properties of the TLCP fibers compete well with what glass fibers can provide. They have equal moduli and although glass is two times as strong when compared to unannealed TLCP fibers, some annealed fibers have strengths matching those of glass.

When the properties of the TLCP are normalized by their density, then they are more attractive as reinforcing materials than glass. The specific mechanical properties, assuming a density of 1.4 g/cm³ for the TLCP and 2.5 g/cm³ for the glass fiber, are shown as follows. The specific strength of unannealed (HBA/HNA based) TLCP fiber is around 0.7 GPa·cm³/g, with annealed fiber rising to values of 1.4 GPa·cm³/g [17, 18, 41]. Meanwhile, glass fiber only matches the unannealed fiber with values of 0.69 to 0.83 GPa·cm³/g [47 - 50]. The values for the specific modulus are even more impressive. The specific modulus of TLCPs is around 35 to 71 GPa·cm³/g [42, 43], while the specific modulus of glass fiber is significantly lower, being at 28 to 33 GPa·cm³/g [47 - 50]. This shows that on a weight basis, TLCP fibers have the potential to match or outperform glass as a reinforcing material.

Exceptional mechanical properties are also observed when neat TLCP samples are injection molded. An example of this was shown in Jackson and Kuhfuss' study [20], where neat PET/PHB (40/60 mole %) was injection molded into a one-eighth inch thick end-gated plaques and tested for tensile and flexural properties. Tensile strengths of 107 MPa along the flow (machine) direction and 29.0 MPa across the flow (transverse) direction were obtained. Neat PET was shown to have a tensile strength of 55 MPa, with no significant difference noted between the two testing directions. The trends from flexural tests were similar, with PET/PHB plaques having flexural moduli of 11.8 GPa in the machine direction and 1.6 GPa in the transverse direction, while PET had a flexural modulus of 2.3 GPa. This showed that in the flow direction, TLCP tensile and flexural properties exceed those of neat PET. However, injection molding has a problem of producing anisotropic specimens which have low transverse direction properties (refer to Figure 1.3).

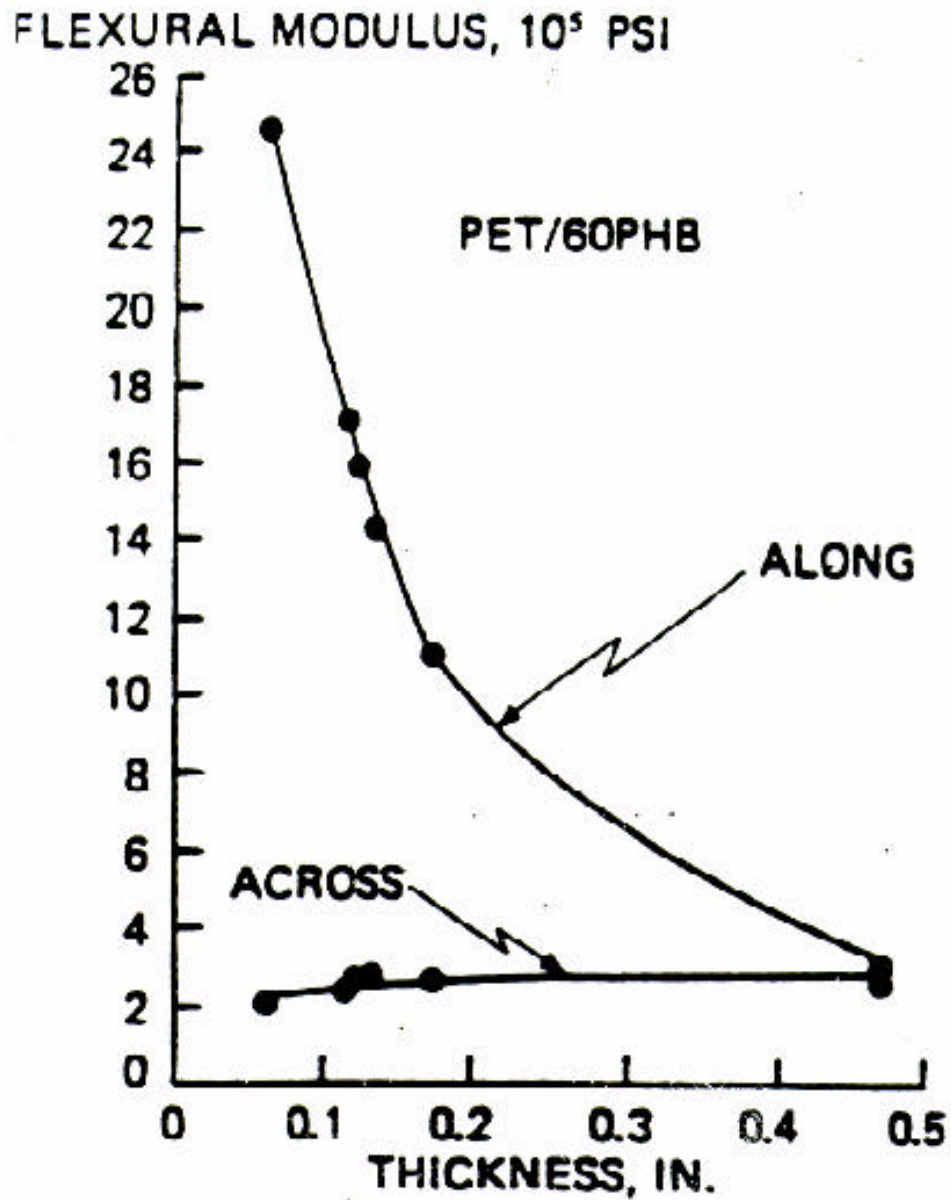


Figure 1.3: Anisotropy of Injection Molded TLCP Plaques. Comparing flexural modulus versus mold thickness for the copolyester PET/PHB (40/60 mole %) [20].

Some mechanical properties of neat TLCPs even exceed those of reinforced matrices, such as glass-filled thermoplastics. Comparing the tensile strengths between Vectra B950 and 30 weight percent glass fiber reinforced PET shows that the fiber-filled PET is weaker, with a strength of 160 MPa versus 227 MPa for the Vectra B950 [19, 51, 52]. Similar results were observed with in flexural tests. In one study, the machine direction flexural modulus of the TLCP was over three times greater than the modulus for glass-filled PET (32.5 GPa versus 9.7 GPa) [53]. These remarkable values are obtained despite the fact that the full reinforcing capacity is not being realized in these injection as molded plaques, because injection molding does not orient the TLCP molecules as well fiber spinning. This indicates that if more of the TLCP could be oriented, the resulting part could greatly exceed what is observed with glass filled systems.

Attempts have been made to reduce anisotropy and orient more of the TLCP by changing the flow kinematics. Studies have shown that TLCPs can be processed by means of film blowing [54- 57] and blow molding [58, 59], with the emphasis on using biaxial stretching to create a less anisotropic product. Center gated injection molding has also been shown to reduce anisotropy through the flow kinematics during mold filling [60, 61]. The core material is oriented in the circumferential or hoop direction while the skin material is oriented in the radial direction.

Meanwhile, specially modified injection molding equipment has been shown to have success in orienting more of the TLCP phase, such as the multiple live feed injection molding (MLFIM) system [21, 25, 62, 63, 64] and the "push-pull" or Gegentakt system [21, 62], both of which promote material flow in the mold after injection. This approach attempts to orient more TLCP in injection molding by deforming the melt as it cools, continuing until the core of the specimen has solidified. Wang et al. [64] injection molded Vectra A950 in a double gated mold with and without the MLFIM processing scheme. From the tensile testing performed on the injection molded samples, it was found that the addition shear deformation in the mold improved stiffness and healed weld lines, resulting in increased tenacity. Using a 3 mm thick mold, the modulus of MLFIM bars was 15.8 GPa and the tenacity was 244.3 MPa, while conventional injection molding made samples with a modulus of 6.3 GPa and a strength of just 15.3 MPa. Even with samples without weld lines (injection molded using a single gate fill), the MLFIM samples still had higher mechanical properties. The single gate filled specimens had a modulus of 12.1 GPa and a strength of 168.4 MPa, well below the modulus of 1.58 GPa and strength of 244.3 MPa for the MLFIM specimens. It should be recognized that all of these results were for the machine direction, so additional research needs to be done with this injection molding technique to show how effective it may be in reducing or eliminating anisotropy. Also, this system usually requires relatively long cycle times, which may limit its usefulness.

Besides the anisotropy present in many melt processed parts, TLCPs have an additional drawback due to their expense [25, 26]. The costs of unfilled TLCPs are

currently \$26 to \$48/kg, while commodity thermoplastics such as polyethylene and polypropylene cost around \$1.00/kg and polyamide 6/12, a relatively expensive thermoplastic, only reaches \$7.70/kg [65]. Comparing the price of TLCPs to other forms of reinforcement, its cost is about the same as the average cost of carbon fiber (\$46/kg) [66] and aramid fiber (\$33/kg) [67], but is still significantly higher than the price of glass fiber (\$1.65/kg) [68]. This high cost has caused TLCPs to develop only niche markets, such as in the electronics industry, rather than any of the high volume markets currently enjoyed by commodity thermoplastics.

In summary, TLCPs possess a combination of high mechanical properties and light weight which suggests they could be competitive with glass fibers as reinforcing agents. The TLCP fibers have specific tensile strengths and moduli which match or exceed glass fibers, demonstrating their reinforcing potential. However, the use of neat TLCPs has two major drawbacks: 1) their high cost and 2) the forming of highly anisotropic parts.

1.2 In Situ Composites

One way to use TLCPs to reinforce thermoplastics is by forming what are known as *in situ composites* [69]. These are created by processing both the thermoplastic and TLCP as a molten blend and forming that blend into a final part. This processing technique has two distinct advantages: 1) the reinforcing phase is fully wetted by the matrix and 2) no compounding step is needed because the reinforcement is generated in the melt. The main processing methods which have been used to generate in situ composites are sheet extrusion, injection molding, and fiber spinning.

Production of in situ composite sheets and films is typically done by sheet extrusion, with draw ratios up to fifty-five being achieved. At the lower draw ratios, some of the in situ composites have improved properties while others show no reinforcement [58, 70- 83]. Ramanathan et al. [58] showed that in a polycarbonate/TLCP blend, the LCP can double the blend's tensile modulus from 2.5 to 5.3 GPa as it is taken from a draw ratio (DR) of 1.45 to 5.60. The work of Sukhadia et al. [72] on blends of PET/Vectra A900 and PET/HX4000 did not give a similar improvement. These blends showed no discernible increase in mechanical properties for draw ratios up to 6.6. The explanation for this was the inability to apply high strains. This resulted in low molecular orientation and consequently low mechanical properties. Where it has been possible to apply higher draw ratios, a more pronounced improvement in mechanical properties can be attained [76, 81]. For example, in dynamic mechanical testing, polyetherimide containing 30 wt % Vectra A900 showed a storage modulus of $1.0 \cdot 10^{11}$ Pa at a DR of 19 while only $4.0 \cdot 10^9$ Pa at a DR of 3.3 [76]. However, it is generally demonstrated in the research literature that sheet extrusion is unable to achieve high draw ratios because of necking of the sheet and equipment limitations. The result is the TLCP phase is not fully deformed and oriented, so the full reinforcing potential of the TLCP is not realized.

In injection molding of in situ composites, optimizing the reinforcing potential of the TLCP phase is complicated by the presence of several variables which do not exist in other forms of processing. O'Donnell and Baird [53, 84] investigated the effects some of these variables had on mechanical properties by varying mold thickness, fill time, and mold temperature. This was done using blends of polypropylene (PP), maleated polypropylene (MAP), and Vectra B950, at a weight concentration of 70 percent PP/MAP mixture (10 wt % MAP) and 30 percent Vectra B950. It was found the mechanical properties were more sensitive to fill time and mold thickness. Moduli reached maximum values at the shortest fill times. Using a fill time of 1 second, the flexural modulus was 5.10 GPa while a 10.7 second fill time produced a modulus of only 3.21 GPa. Unlike the neat TLCP plaques, the best properties were not obtained when using the thinnest mold (1.0 mm thick) but rather the two thicker molds (1.5 mm and 2.3 mm thick). The best flexural properties of the 1.0 mm thick plaques was a modulus of 3.82 GPa and a strength of 56.3 MPa while the 1.5 mm thick plaques had a modulus of 5.10 GPa and a strength of 60.5 MPa. The conclusion from this work was that using a fast fill time with a moderately thick mold utilizes the reinforcing potential of the TLCP most effectively.

The anisotropy present in neat injection molded TLCPs is likewise found in in situ composites. Bafna and coworkers [85] showed this in a thorough study of polyetherimide (PEI)/TLCP composites. In this investigation, a film-gated rectangular mold was used to produce plaques, from which samples were cut and the machine and transverse flexural moduli were measured. At loadings of 50 wt% TLCP, over 4 to 1 anisotropy was found. The PEI/HX1000 (50/50 wt%) plaques had a machine direction flexural modulus of 12.92 GPa while the transverse direction was only 3.20 GPa. The PEI/HX4000 (50/50 wt%) plaques showed similar results, with a machine direction modulus of 12.25 GPa and a transverse direction modulus of 2.71 GPa (refer to Table 1.1).

The anisotropy typical of in situ TLCP composites is also greater than that found with their glass fiber filled counterparts [85]. This was demonstrated by contrasting the effect of loading polyetherimide (PEI) with 30 wt% of three different materials: 1) HX1000, 2) HX4000 and 3) glass fiber. HX1000 and HX4000 are two TLCPs composed of hydroquinone, terephthalic acid, and hydroquinone derivatives, so this directly compares TLCP reinforcement to glass fiber reinforcement. The PEI/glass fiber (70/30 wt%) composite had a ratio of machine direction to transverse direction flexural moduli of 1.88. The PEI/TLCP (70/30 wt %) ratios were significantly higher, with the PEI/HX1000 blend having a value of 2.27 and the PEI/HX4000 blend possessing a value of 2.18.

Table 1.1: Anisotropy of In Situ Composites. These results are from flexural tests of samples cut from film-gated rectangular plaques [85]. Ultem 1000 is an unfilled grade of polyetherimide while HX1000 and HX4000 are two types of thermotropic liquid crystalline polymers.

Ultem 1000/HX1000			Ultem 1000/HX4000		
Weight Percent (PEI/HX 1000)	Mach. Dir. Flex. Mod. (GPa)	Trans. Dir. Flex. Mod. (GPa)	Weight Percent (PEI/HX 4000)	Mach. Dir. Flex. Mod. (GPa)	Trans. Dir. Flex. Mod. (GPa)
100/0	3.00	3.05	100/0	3.00	3.05
80/20	6.20	***	80/20	5.31	3.12
70/30	7.27	3.20	70/30	7.00	3.21
50/50	12.92	3.20	50/50	12.25	2.71
30/70	15.83	2.70	30/70	14.75	2.62
0/100	15.60	2.40	0/100	14.00	2.36

The explanation provided for this difference was how each method of reinforcement is generated by the flow kinematics. In situ composites rely mostly on extensional flow kinematics to first generate the TLCP fibrils and then orient them in a specific direction; shear flow does not significantly deform the TLCP and does not contribute to property improvement. For injection molded film-gated plaques, this extensional deformation occurs only at the advancing front as the melt flows in the machine direction. Because the extensional deformation is predominantly in the machine direction, that is the only direction in which the plaques are reinforced.

Meanwhile, glass fiber filled polymers are less anisotropic because the flow kinematics only orient the reinforcement. As with the in situ composites, the advancing front during molding filling produces a skin with fibers oriented in the machine direction. However, the shear flow which follows the advancing front is also important for glass filled systems. In end gated plaques, the shear flow tends to position fiber orientation in the transverse direction, especially near the core of the plaque [86]. By having reinforcement in both directions, the composite plaques are less anisotropic.

Despite the problem of anisotropy, in situ composites are competitive with glass reinforcement when just the machine direction mechanical properties are compared [85, 87]. PEI with 30 wt% glass fiber was shown to have a machine direction tensile modulus of 9.2 GPa, while loading the PEI with 30 wt% HX4000 gave a slightly higher modulus of 9.8 GPa. When the density difference between the two composites is considered, the in situ composite shows significantly superior mechanical properties. The specific modulus of the PEI/HX4000 blend is $7.4 \text{ GPa}\cdot\text{cm}^3/\text{g}$ versus only $6.1 \text{ GPa}\cdot\text{cm}^3/\text{g}$ for the PEI/glass composite. These results confirm the potential of TLCPs as a reinforcing agent.

Comparing the moduli of various in situ composites, composite fibers are typically stiffer than injection molded composites. An example of this can be shown by comparing the tensile modulus of PP/Vectra B950 (80/20 wt% composites). O'Donnell, Datta, and Baird [52] found that injection molded film-gated plaques had a machine direction modulus of 3.209 GPa. Meanwhile, Robertson [43], using the same PP/Vectra B950 (80/20 wt%) composition, were able to spin in situ composite strands with a modulus of 13 GPa when drawn to draw ratios over 50.

The reason for this difference is primarily associated with the flow kinematics found in fiber spinning versus injection molding. In fiber spinning, high uniaxial extensional strains, as evidenced by high draw ratios, can be applied to all of the TLCP domains. In injection molding, extensional deformations are formed primarily at the advancing front with shear deformation in the core. Therefore, only TLCP domains which reach the advancing front have the potential to be subjected to high extensional strains.

Fiber spinning has the advantage of being able to apply high strains of purely uniaxial extensional deformation [72, 75, 77, 88-105], resulting in exceptional properties. The high strains are reflected in the fiber draw ratios, with values over 50 not uncommon. Lin et al. [102] blended polycarbonate/Vectra B950 (74.1/26.9 volume %) and drew it to a draw ratio of 34. These fibers had moduli of 19.0 GPa and tensile strengths over 140 MPa. This modulus is much higher than that of neat polycarbonate, which is only 2.5 GPa.

Several workers have shown excellent fiber properties using a patented dual extruder process [42, 43, 72, 106-109]. This process has succeeded in producing fibers of PP/Vectra B950 (50/50 wt%) with tensile moduli of 44 GPa, tensile strengths around 400 MPa, and draw ratios over 200 [43]. Using the rule of mixtures composite theory, the calculated tensile modulus of the Vectra B950 phase was approximately 100 GPa. Other blends have produced similar results, such as fibers of PP/HX1000 (73/27 wt%) having tensile moduli of 12 GPa [42]. Using the rule of mixtures, the tensile modulus of the HX1000 phase was calculated to be around 50 GPa. These results suggest that any post processing techniques should use spun fibers if the maximum possible mechanical properties are desired.

In summary, blends of neat TLCPs and inexpensive commodity resins have several useful features. By blending the TLCP with inexpensive commodity resins, the formed part is less expensive than it would be using neat TLCP resin [25]. In situ composites are successful in exploiting the mechanical properties of TLCPs, with the blend fibers in particular showing exceptional mechanical properties. On a weight basis, the blends can be competitive with glass reinforcement, as shown by comparing machine direction properties of injection molded in situ plaques with glass-fiber reinforced plaques. However, unlike other forms of short fiber reinforcement, no compounding step is necessary because the production of in situ composites simultaneously generates and fully wets the reinforcement. This is a significant advantage over other composites, since compounding fibers into a molten matrix reduces mechanical properties by damaging the fibers and adds another processing step.

However, in situ composites still possess disadvantages. At similar weight fractions, the material cost of TLCP-based composites is higher than glass fiber reinforced composites because TLCPs are more expensive than glass fiber. Also, injection molded in situ composites are more anisotropic than short fiber reinforced composites.

1.3 Post Processing of In Situ Composites

One way to overcome the anisotropy associated with in situ composites is by using various post processing techniques. Several methods of post processing have been investigated, including shear free deformation, thermoforming, compression molding, and

fiber weaving. These can be divided into two groups: 1) those which deform the TLCP phase and 2) those which avoid deforming the oriented TLCP. Shear free deformation, compression molding injection molded plaques, and thermoforming are in the first group, relying on imparting extensional deformation in the post processing step. This seeks to reduce anisotropic behavior by stretching the TLCP in its weakest direction and simultaneously orienting any unoriented TLCP. Conversely, the work done compression molding and weaving fibers attempts to retain orientation acquired in the fiber spinning step. This approach seeks to reduce anisotropy by forming the fibers into a final sample without deforming the TLCP. Both of these post processing approaches will be evaluated to determine their strengths and weaknesses.

Shear free deformation experiments have shown success in reducing anisotropy by orienting TLCP in the direction with the lowest properties. The ability of shear free deformation to stretch the TLCP phase in a TLCP/matrix blend has been demonstrated using sheets, injection molded plaques, and fibers [87, 104, 110, 111]. One investigation into this approach used injection molded plaques composed of PEI/HX1000 (80/20 wt %) [110, 111]. Planar strain was applied to injection molded samples by placing constraints on the machine direction and stretching the sample in the transverse direction. This succeeded in creating a nearly isotropic sample, with a tensile modulus just over 5.0 GPa, a tensile strength of around 70 MPa, and a percent elongation of about 1.5 for the PEI/HX1000 plaque. The theoretical modulus of this blend is 7.432 GPa, assuming that all the fibrils have aspect ratios over 100. However, the aspect ratios of the fibrils in these composites was not determined, so if there were a significant number of fibrils with aspect ratios under 100, the predicted theoretical modulus of 7.432 GPa may be an overestimation of the actual possible maximum. Nevertheless, these results demonstrate that planar stretching of injection molded plaques can eliminate anisotropy and produce favorable mechanical properties.

Compression molding has been performed on both in situ sheets and fibers, with the focus being on retention of fiber properties and determining if compression molding can yield a planar isotropic sample [46, 91, 107, 112-122]. This process has the advantages of accurate process control and the ease in doing these studies on a laboratory scale. In a study by Sabol et al. [117], a blend of polypropylene with an amorphous TLCP, HX1000, was comprehensively examined. This work showed that the most highly drawn strands, aligned uniaxially and compressed, gave a tensile modulus of 13.55 GPa and a tensile strength of 67 MPa. This matched what was observed with the original strands and expectations from composite theory. When 30 mm long strands were randomly aligned, a tensile modulus of 4.42 GPa and a tensile strength of 34.9 MPa were measured, again matching composite theory. These results prove that it is possible to retain the mechanical properties of the spun strands in this form of post processing.

It was speculated that if thermoplastic/TLCP fibers were woven into preforms, it could be possible to shape them in a mold, consolidate the material into a final part, and retain the properties of the TLCP [112]. This concept has recently been tested by Robertson et al. [43 - 45] and Krishnaswamy and Baird [123]. For blends of PP/Vectra B950, it was shown that these preforms could be thermoformed into a rectangular mold. The mechanical properties of the composites based on these preforms were also favorable, with a tensile modulus of 10.3 GPa and a tensile strength of 63.8 MPa at a loading of 31.5 wt% Vectra B950. This is a ten-fold increase in neat PP modulus and a two and a half increase in tensile strength, demonstrating that the TLCP/thermoplastic preforms can be consolidated and thermoformed while maintaining the mechanical properties.

Problems are still present with each of these post processing procedures, though. Many of these techniques can only be run as a batch operation, so they require long cycle times to produce each sample. Some of the techniques can not be used in forming complex shapes because of inherent process limitations. Also, in methods which require continuous lengths of fiber, problems of fibers buckling and breaking can exist.

1.4 Pregenerated Microcomposites

For some applications, an ideal processing scheme would maximize the reinforcing potential of the TLCP, have fast cycle times, and allow a versatile range of sizes and shapes to be formed. When reinforcing with glass, the most flexible method uses fiber-filled pellets in an injection molding process. A similar approach can be used with matrix/TLCP blends. They can first be spun into strands, generating oriented TLCP fibrils and maximizing its reinforcing potential. These strands can be chopped, creating pellets containing oriented fibrils as the reinforcing phase. The pellets can then be injection molded below the melting temperature of the TLCP, forming the desired part. The combination of these steps creates what have been called *pregenerated microcomposites* [108]. They differ from in situ composites because of the requirement for two distinct processing steps: one to orient the liquid crystalline phase and a second to form the final part. They also differ from the other post processed composites because of the versatility of the process and its resemblance to injection molding with glass-filled resins. It is believed that these features offer a means to provide the desired characteristics of being able to reinforce complex geometries using fast cycle times.

The attraction to the pregenerated microcomposite processing technique is the potential to obtain a composite with mechanical properties like glass but without several of its drawbacks. The density of glass creates difficulties because it makes a heavy composite. Other limitations center around the physical size of the glass fiber. Glass fiber is typically 10 μm in diameter or larger [3, 47] while TLCP fibrils are often an order of magnitude smaller. The larger size of the glass fiber makes it more difficult to retain an fiber aspect ratio over 100, which is required for maximum theoretical reinforcement

[124]. The larger size also is more abrasive to the processing equipment, since smaller TLCP fibrils can more readily pass through their tight tolerances. When injection molded, the mold cavity can have only limited detail because the size of the glass prevents detail on the mold from appearing on the sample [69]. Injection molded parts are also known to have a poorer surface finish due to surface waviness, sink marks, and a loss of glossiness [125, 126]

The research regarding pregenerated microcomposites has been performed with a limited number of materials [42, 108, 127]. The only matrix material used has been polypropylene (PP), chosen because of its wide range of processing temperatures. For the reinforcing phase, just two TLCPs have been investigated: Vectra A950 and HX6000. Although this proved the tenability of the concept, it has not been extended to additional matrices which have a significantly smaller window of processing temperatures.

The effect of temperature on pregenerated microcomposite properties has been determined in flexural and impact tests of PP/Vectra A950 blends. Heino et al. [127] investigated an 80/20 weight fraction blend that was melt blended in a twin screw extruder at 290°C and spun to draw ratios of 1.1 and 6.1. The blend was subsequently chopped into 2 mm long pellets and injection molded at various temperatures, establishing three separate injection molding regions. The first was from 180°C to 200°C, where the Vectra A950 was rigid. The second was from 230°C to 250°C, where the Vectra A950 became a softened solid. The test samples from both of these regions were pregenerated microcomposites, since the TLCP was oriented in the spinning step. The last was from 280°C onward, where the TLCP became fluid and the injection molded plaques were simply in situ composites. The pregenerated microcomposites from the second region showed poorer properties than those from the first. This was attributed to the fibrils deforming and agglomerating into clusters, as confirmed by optical microscopy. The greatest flexural properties for the pregenerated microcomposites was a flexural modulus of 1.77 GPa and a flexural strength of 45 MPa. This was greater than the neat PP and comparable to the in situ composite values of 1.97 GPa and 42 MPa. They also noted that the PGMC had a much greater Charpy impact strength relative to the in situ composite, 39 kJ/m² versus 22 kJ/m² (refer to Table 1.2).

The effect of fiber draw ratio on composite properties was examined by Handlos et al. [108]. The investigations used blends of PP/Vectra A950 and PP/HX6000, where the strands were spun to draw ratios of 30 and 25 at a concentration of 60/40. Instead of melt blending these at the same temperature, a patented dual extrusion process [106] was used to apply different thermal histories to each polymer and thereby avoid degrading the PP. The chopped strands were then diluted by adding more PP and post processed using injection molding, sheet extrusion, and extrusion blow molding. When injection molding a pregenerated composite of PP/Vectra (80/20 wt%), a tensile modulus of 2.31 GPa and a

Table 1.2: Pregenerated Microcomposite Mechanical Properties. These are the flexural and impact properties of pregenerated microcomposites based on PP and Vectra A950 (80/20 weight percent) [127].

Injection Molding Feedstock	Flexural Modulus E (GPa)	Flexural Strength σ (MPa)	Displacement at Yield (Flex.) ϵ_Y (mm)	Charpy Impact Str. (kJ/m ²)
PP (180°C)	1.39 (0.05)	39 (1)	12 (1)	not broken
Li (180°C)	1.58 (0.04)	40 (1)	12 (1)	41 (5)
Hi (180°C)	1.77 (0.04)	45 (1)	12 (1)	39 (5)
Li (280°C)	1.90 (0.15)	41 (1)	11 (1)	22 (3)
Hi (280°C)	1.97 (0.11)	42 (1)	10 (1)	22 (1)

Temperatures in parentheses are the highest injection molding temperatures. Values in parentheses are the standard deviation.

Li = Low Draw Ratio Fibers (DR=1.1) with 20 wt% Vectra A950 and 80 wt% polypropylene.

Hi = High Draw Ratio Fibers (DR=6.1) with 20 wt% Vectra A950 and 80 wt% polypropylene.

strength of 37.6 MPa was attained. Similar results were obtained with injection molded PP/HX6000 (80/20 wt %), showing a modulus of 3.23 GPa and a strength of 35.8 MPa.

While these plaques did show properties higher than neat PP, the tensile moduli did not reach the theoretical values. Theoretically, the 20 wt% Vectra A950 and HX6000 blends should have had moduli of 3.85 GPa and 4.08 GPa, respectively. This means the tensile modulus of the PP/Vectra A950 composite was only at 60% of its theoretical maximum while the PP/HX6000 composite was at 79%. The discrepancy between the theory and experimental results was explained as being due to the fibers having a low aspect ratio and a reduction of the effective aspect ratio of the reinforcing fibers by agglomeration of the TLCP phase. This research showed that it is possible to reinforce PP by using the PGMC processing method and reduce the anisotropic mechanical properties characteristic of in situ injection molded samples. However, it appears that the process is still not well understood and has difficulties which warrant further investigation. These points are the subject of the proposed research and are delineated in the following section.

1.5 Research Objectives

The pregenerated microcomposite processing technique has been pursued because of its ability to provide reinforcement using TLCPs which is both planar isotropic and offers versatility in processing. TLCPs also have the potential to provide stiffnesses greater than glass fiber on a weight basis, a specific strength which matches glass fiber, and eliminate or reduce many of the problems encountered with glass-filled systems. The research in this area has established that the technique does reinforce polypropylene and lower the anisotropy relative to in situ composites. However, the mechanical properties were found to be below the theoretical expectations. To determine the possibilities for this processing scheme, further research must be undertaken. It is the goal of this research to clarify these possibilities and attempt to overcome the limitations encountered in the previous work.

1.5.1 Research Objective #1

It remains to be proven that this method of reinforcement can be applied to other matrix polymers. Polypropylene is unusual in it has a very broad processing temperature range, melting at 165°C and degrading at around 290°C. Most polymers do not offer such flexibility. Realizing that this may severely limit the possible thermoplastic/TLCP combinations, other thermoplastics need to be investigated. Therefore, the first research objective is:

Demonstrate that poly(ethylene terephthalate) (PET) can be used in the pregenerated microcomposite process without losing the

reinforcing ability of the TLCP fibrils. This includes finding an appropriate TLCP suitable for processing with PET.

1.5.2 Research Objective #2

Although it has been shown that the PGMs have properties below the theoretical limit, there has been no comprehensive study undertaken to see what factors are the most important in causing this deviation. The difference has been dismissed as being due to agglomeration of TLCP fibrils. Many questions still remain concerning these losses. Is this the sole cause of property loss or are other factors important? Is there a specific point in the injection molding process which causes the agglomeration? If the fibrils avoid the rigorous shear encountered in the injection molder's screw, will mechanical properties come closer to theoretical expectations? These questions lead to the second research objective:

Perform a comprehensive study of the pregenerated microcomposite process to determine where property losses are occurring. Develop processing options to overcome these problems.

1.5.3 Research Objective #3

None of the previous studies used fibers with optimally oriented TLCP fibrils; further drawing of the blend would have both increased the fiber's mechanical properties and reduced the diameter of the fibrils. These fibrils should be both more highly oriented and more readily pass through the tight equipment tolerances in the injection molder, offering the potential of greater mechanical properties. Recognizing this possibility, the third research objective is:

Determine the effect of fiber draw ratio on mechanical properties by using fibers with optimal mechanical properties.

1.5.4 Research Objective #4

Because the dual extruder process relies on the supercooling behavior of the TLCPs, it would be desirable to control this behavior. If this were to be accomplished, it would be possible to select specific TLCPs for use with specific matrices, expanding the possible range of composites which could be made. Towards this goal, the fourth research objective is:

Determine if the supercooling behavior of a high melting point TLCP can be modified by melt blending with a second, lower melting point TLCP.

The remaining chapters provide the detailed background information and discussion of experimental results needed to demonstrate that the goals of this research were fulfilled. Chapter 2 is a detailed literature review of subject matter pertinent to this research. The three subsequent chapters are manuscripts in which the research performed to satisfy the objectives is discussed. Chapter 3, entitled “The Influence of Processing Variables on the Mechanical Properties of Injection Molded Pregenerated Microcomposites”, is concerned with satisfying the first two research objectives. Chapter 4, entitled “Injection Molding of PET Reinforced with Pregenerated TLCP Micro-Fibrils”, addresses the third research objective as well as provides information which also helps to satisfy the second objective. Chapter 5, “The Crystallization Behavior of Blends of Thermotropic Liquid Crystalline Polymers”, fulfills the fourth research objective. After Chapter 5 is a Recommendations section which notes areas which warrant further investigation based on the results of this research. Note that Appendix A is a preprint which discusses coinjection molding of pregenerated microcomposites, which also serves to help satisfy the second objective.

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