

INJECTION MOLDING OF WHOLLY THERMOPLASTIC COMPOSITES

*W. Huang, J. Huang, and D.G. Baird**
Center for Composite Materials and Structures,
Virginia Tech, Blacksburg, VA 24061
** dbaird@vt.edu*

Abstract

Thermotropic liquid crystalline polymer reinforced thermoplastic polymer strands were spun and used in injection molding to form wholly thermoplastic composite materials. While keeping the strand size suitable for injection molding, an effort was made to increase the orientation and aspect ratio of the reinforcing TLCP fibril. The pelletized strand was injection molded without disturbing the TLCP reinforcing fibrils. The samples have similar mechanical properties, lower density and smoother surfaces compared with glass fiber reinforced samples.

Introduction

There has been considerable interest in recent years in reinforcing thermoplastics (TPs) with thermotropic liquid crystalline polymers (TLCPs) (1-3). The most commonly used method is to subject a blend of a TP and a TLCP to extensional deformations such as those that occur in injection molding or fiber spinning to form highly oriented TLCP fibrils (4,5). Although this is a highly desirable approach for forming composites, there are a number of limitations including highly anisotropic mechanical properties, and overlapping processing temperatures of the two polymers. More recently, Baird and coworkers (6-9) have reported on the development of a technique for forming thermoplastics reinforced with TLCPs of higher melting and processing temperatures than the matrix. Composite monofilaments consisting of polyethyleneterephthalate and polybutyleneterephthalate (PBT) reinforced with a TLCP were produced using a novel dual-extruder process, and then injection molded at a temperature below which the TLCP would lose molecular orientation but above which the matrix would melt (9). The properties of the injection molded samples were about 20% lower than those of similar glass-reinforced matrices but the surfaces were much smoother (9).

One of most important discoveries from these works is that the draw ratio of the strand plays an important role in determining the mechanical properties of the strand. To get optimal mechanical properties, minimum draw ratios necessary were in the range of 20-30 (9). However, due to the limitation of the spinning die (1.8 mm in diameter) used (9), the strand with this draw ratio actually has diameter of only 0.3 to 0.4 mm. This size is too small to

be used in the injection molding, especially on an industrially featured injection molding machine.

The main objective of this present work is to increase the strand size while retaining the draw ratio to ensure the high molecular orientation of TLCP. We will show that this can be accomplished by replacing the existing spinneret with one having a monofilament die of large diameter. However, the conventional cooling scheme must be modified or innovated to suit the change in the solidification process of the strand. In accordance with these changes, the mechanical properties of the TLCP/TP strands are studied as a function of spinning temperature, draw ratio and the distance between the spinneret and the water bath or quenching point. All these variables are very important in generating TLCP/TP composite stands with optimal mechanical properties.

Experimental

Materials: The liquid crystalline polymers in this work were HX3000 and HX6000 provided by DuPont Company. The copolymers are believed to be composed of unspecified ratios of terephthalic acid, 4-hydroxybenzoic acid, hydroquinone and hydroquinone derivatives. These semi-crystalline TLCPs have no discernible glass transition temperature and a solid density of 1.38 g/cm³. The melting temperature for HX3000 and HX6000 is 320°C and 331.9°C, respectively. The thermoplastic matrix used is polypropylene (Profax 6823) purchased from the Himont Company. The polymer has a melting temperature of 161°C, flow index of 0.8 and solid density of 0.902 g/cm³.

Methods: The composite strand was spun on a novel dial extrusion spinning system consisting of two Killion 1-inch extruders and a spinning pack. The spinning pack consists of a spinneret and a mixing head including three helical elements and a Koch static mixer with four elements. The TLCP (as an illustration, HX3000 or HX6000) was processed in one extruder, with the melt conveying zone set at 350°C to 360°C, while the matrix (PP) was plasticized in the second extruder, with the melt conveying zone set at 260°C to 270°C. After passing through the gear pump, the TLCP melt was cooled to 340°C and extruded through a multi-port nozzle to form a multiple streams and join with the matrix (PP). The melt blend was then passed through a mixing head consisting of

static mixers to further divide the TLCP into smaller layers. The temperature of the mixing head and spinneret was set at 325°C to 340°C. The spinneret has a circular die with diameter of 6.35 mm and $L/D \approx 1$. Extruded through the spinning die, the melt was drawn to orient the TLCP, quenched in a water bath, and taken up with nip rollers. Through adjusting the speed of TLCP and matrix gear pumps, the composition of the strand can be controlled. The composition was then tested by use of the burning-off method. This was done by chopping the strand and putting it into an oven at 300°C for 30 minutes. Tensile mechanical properties of the strand were measured on an Instron Tensile Tester (model 4202) with 1 KN load cell. The sample grips were set 250 mm apart. At least five readings were taken to get an average value for each sample.

Results and Discussion

Figure 1 illustrates the spinning system used for generating TLCP/TP composite strand. A spinneret with a monofilament die was used to spin the composite strand. In prior work, a die of 1.8 mm in diameter was used and the tensile modulus of TLCP/PET composite strand increased significantly as the draw ratio of the strand increased to 30 (9). Note that if the draw ratio of 30 is desired, then the diameter of the strand was only about 0.33 mm as was calculated from the draw ratio and diameter of the die. Obviously, this strand size is too small to be used in the injection molding. In order to increase the diameter of the strand while retain the high draw ratio, we tried to use a monofilament die with diameter of 6.35 mm ($L/D \approx 1$) to generate the strand. The new die can produce strand with diameter of 1 mm even if the draw ratio reaches 40.

While big spinning die provided possibility to solve the exiting problem, it also brought new difficulties. When small die was used, the extruded melt can be introduced into a roller immersed in water and then veered 90 degree to travel horizontally along the water trough and collected on a take-up roll. This process does not work now because the weighty strand is prone to sink onto the trough bottom at the turning point. It becomes very difficult to control the spinning and drawing processes. To overcome this difficulty, the water trough was replaced by a water bath (plastic pail) placed beneath the spinning die. A 8 mm hole was drilled on the bottom of pail to allow the strand pass through the bath. Attached to the hole was a rubber pad with diameter of 50 mm which let strand pass through without serious leak of water. Being quenched and exiting the water bath, the strand was taken up by a pair of nip rollers. By adjusting the rotating speed of the rollers, the strand can be drawn at desired ratios. Figure 1(B) shows the described cooling and taking up devices.

The practice showed that the new spinning system ran well and the strand properties varied dramatically if different spinning and cooling conditions were used. Figure 2 illustrates the influence of quenching position (or water bath position) on tensile mechanical properties of strand. As shown in the figure, although the apparent draw ratio of the strands is about the same, the strand with quench position farther from the spinneret gets much better mechanical properties. Therefore, the strands were all collected using the favorable quenching position, that is, about 380 mm from the spinneret unless specifically noted.

To qualitatively explain why this happened, the change of strand surface temperature and strand diameter along the spinning line were schematically plotted in Figure 1 (B). As well known, change of strand diameter at two point reflects the apparent draw ratio of the strand within this range. Whether the drawing leads to the molecular orientation depends on the competition of rate of molecular extension and molecular relaxation. In other words, if there is no substantial difference in the extension or drawing rate, the temperature of the strand has decisive impact on effectiveness of the drawing. It was noted that, whether the water bath was placed near to or far from the spinneret, the strand diameter changes mostly before the strand enters the water bath. In case that the water bath was placed near to the spinneret, the strand temperature was still high (above the melting point of the TLCP) when the strand reached the water level. It means that most of the strand drawing was performed while the TLCP molecules had very short relaxation times and, therefore, had little contribution to the TLCP molecular orientation. In contrast, when the water bath was placed far from the spinneret, the strand had been cooled to the temperature well below the melting point of the TLCP before the strand entered the water bath. A considerable part of strand drawing was performed when the rate of TLCP molecular extension exceeds the rate of the TLCP molecular relaxation and did improve the orientation of the TLCP molecules. As a consequence, the strand generated under this situation has higher tensile mechanical properties.

Figure 3 illustrates the dependence of tensile properties on draw ratio of the strand. As the draw ratio increases, the tensile modulus of both HX3000/PP and HX6000/PP strands increases. However, the modulus of HX6000/PP strand appears to be more sensitive to the draw ratio and has potential to rise further if the draw ratio exceeds 40. Also shown in Figure 3 is the effect of draw ratio on the tensile strength of the strands. Unlike the tensile modulus, no significant influence is observed for both systems. In fact, the use of high draw ratio can not only increase the modulus of the strand, but also decrease the size (diameter) of the TLCP fibril. This kind of strand can be used in the injection molding to produce pre-generated material with higher modulus and smoother surface.

The new spinning system can also be used for generating strands with different TLCP/matrix systems, such as HX3000/PET, or with different TLCP loading levels. Figure 4 showed the tensile mechanical properties of strand as a function of TLCP contents (to avoid the impact of draw ratio, all these strands have draw ratio around 25). The modulus for both HX3000/PP and HX6000/PP increases as TLCP content increases, with HX3000/PP having higher modulus at the same composition. This is expected because as pure TLCP, HX3000 has modulus significantly higher than HX6000. But for tensile strength, however, HX3000/PP strand was similar to or lower than HX6000/PP strand. Especially, for strand containing more than 50 wt-% TLCP, the strength kept rising for HX6000/PP but declined for HX3000/PP. Upon the comprehensive consideration, HX3000/PP system with TLCP loading around 50 wt-% was chosen as a material for scaling up. The strand was then chopped and blended with low molecular weight polypropylene (pure matrix) to dilute the system into desired composition, say 30 wt-% for example. Our research showed that, compared with as received strand containing 30 wt-% TLCP, this blending system can be injection molded to produce composite materials with higher mechanical properties. The detail of the work will be reported elsewhere. The comparison of final products also showed that HX3000/PP system has mechanical property better than HX6000/PP. For example, being diluted to 30 wt-% TLCP, the composite material from HX3000/PP has tensile modulus 12% higher than HX6000/PP and the same strength as the HX6000/PP.

The temperature of spinning pack (including the mixing head and die) also has a great influence on the strand properties. For HX3000/PP and HX6000/PP systems, the temperature at 325°C to 340°C was found appropriate. If higher temperature was used, polypropylene would degrade too fast and the viscosity of the melt would become too low to ensure the stable spinning. On the other hand, if lower temperature was used, strand with thicker TLCP fibrils and poor mechanical properties was obtained

Conclusions

A novel spinning and cooling process were developed to generate TLCP/PP composite strand with high TLCP molecular orientation and suitable for injection molding. The mechanical properties of the strand can be optimized by using appropriate spinning (especially mixer) temperature, increasing draw ratio and the distance between spinneret and water bath (or quenching position). The strands generated can be chopped and applied in injection molding to produce wholly thermoplastic composite materials with superior mechanical and surface properties.

Acknowledgments

We gratefully acknowledge support of this work from DaimlerChrysler Inc.

References

1. R. A. Weiss, W. Huh, and L. Nicolais, *Polym Eng. Sci.*, 27, 684, (1987).
2. K. G. Blizard and D. G. Baird, *Polym. Eng. Sci.*, 27, 653, (1987).
3. A. I. Isayev and M. Modic, *Polymer Composites*, 8, 158, (1987).
4. D. Dutta and R. A. Weiss, *Polymer Composites*, 13, 394, (1992).
5. A. A. Handlos and D.G. Baird, *J.Macro. Mat. Sci., Reviews in Macro. Chem. and Physics*, C35(2), 183(1995).
6. E. A. Sabol, A. A. Handlos, and D. G. Baird, *Polymer Composites*, 16, 330, (1995).
7. D.G. Baird and A.M. Sukhadia, U.S. Patent 5,225,488 (1993).
8. R. K. Krishnaswamy and D. G. Baird, *Polymer Composites*, 18, 526, (1997).
9. M. A. McLeod and D. G. Baird, *Polymer Composites*, 20, 3 (1999).

Key Words

Liquid Crystalline Polymer, Polymer Composite, Strand Spinning, Dual Extrusion system

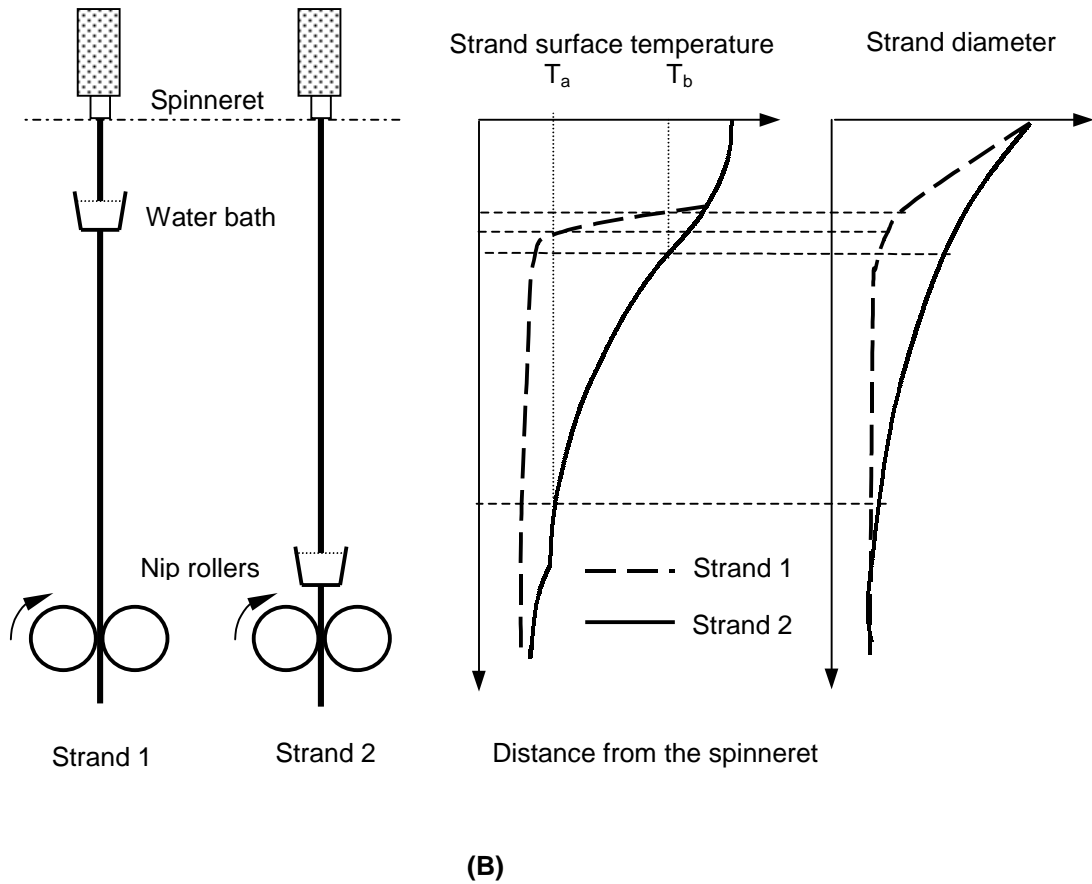
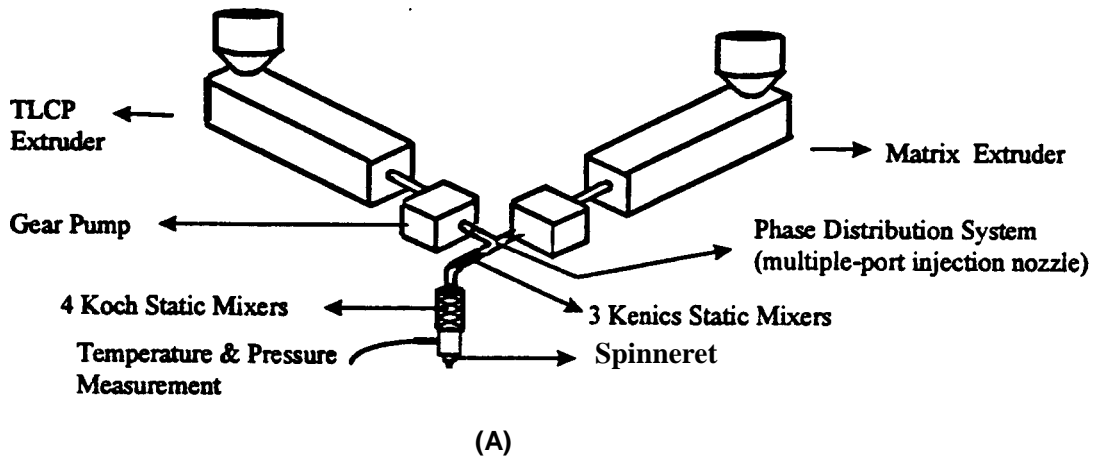


Figure 1. Schematic diagram for the dual extrusion spinning system (A) and cooling and taking up devices (B). Strand 1 and strand 2 represent strand going through water bath placed close to and far from the spinneret, respectively

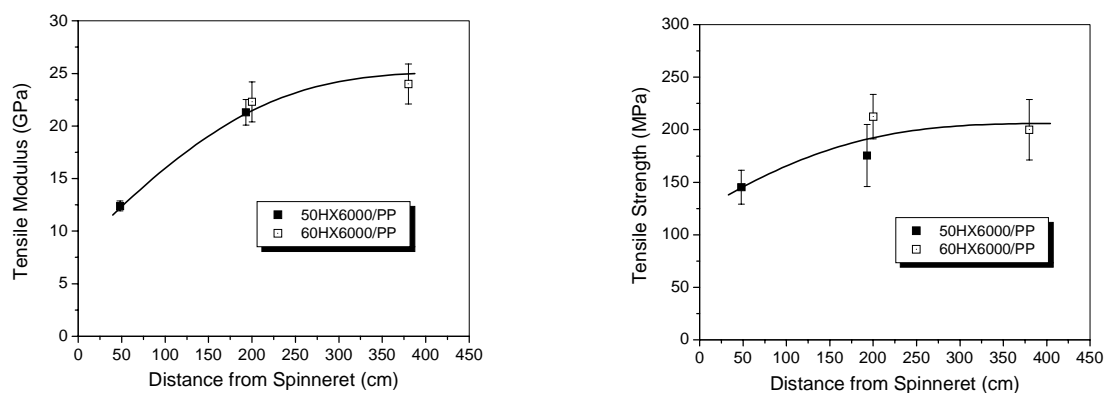


Figure 2. Tensile properties of TLCP/PP composite strands as a function of water bath position

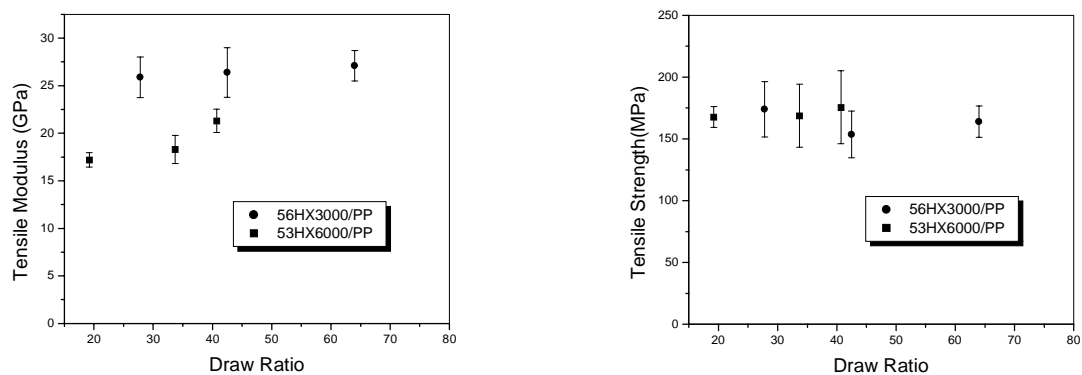


Figure 3. Tensile properties versus draw ratio for TLCP/PP composite strands

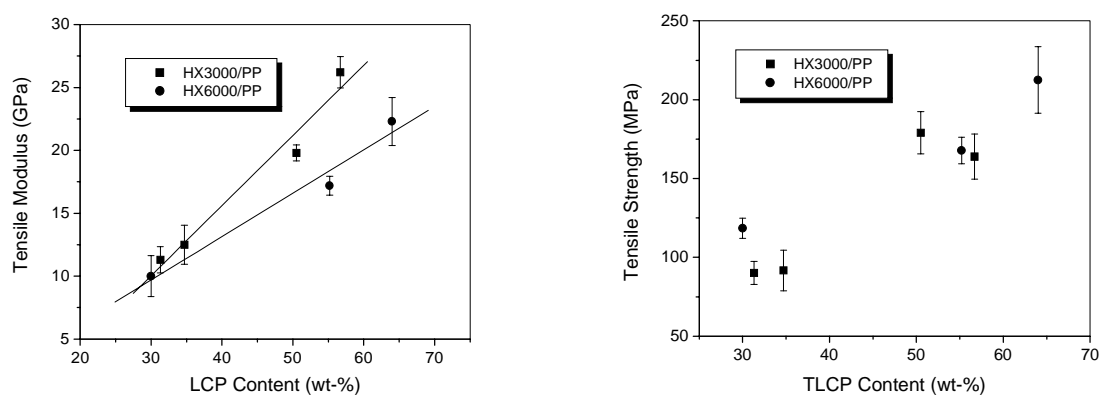


Figure 4. Tensile properties of TLCP/PP composite strands as a function of composition