Effects of Processing Conditions on Prototypes Reinforced with TLCPs for Fused Deposition Modeling

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Polypropylene (PP) composite strands, reinforced with thermotropic liquid crystalline polymers (TLCPs), were generated using a novel dual extrusion process which allowed for the use of a TLCP with a significantly higher melting temperature than that of the PP. Pregenerated TLCP/PP microcomposite strands were reprocessed using a second novel process to produce a well-controlled monofilament composite for use in a FDM 1600 rapid prototyping system in order to build complex geometries. Uniaxial parts were built to determine the effect of differing material compositions and processing temperatures, in order to develop an operating window for the optimal mechanical properties. By adjusting the lay down pattern of orientable materials, the final mechanical properties of the part could be engineered independent of the material. To understand the effect of the reprocessing steps on the pregenerated microcomposites, the final mechanical properties of the monofilament composite were compared with those of the pregenerated strands.

1.0 Introduction

At present, only a few polymeric materials with limited mechanical properties are used in fused deposition modeling (FDM) rapid prototyping systems. Many of the prototypes fabricated can only serve as geometric replicas of the proposed production part because of the inherently poor mechanical properties. The materials that are commercially available for the FDM 1600 rapid prototyping system are acrylonitrile butadiene styrene copolymer (ABS), a nylon copolymer, and investment casting wax. Of the three commercially available materials, ABS has the highest tensile modulus and strength, and the properties of prototypes fabricated using ABS have been determined to be 1.5 GPa and 22 MPa, respectively [1]. Therefore, there is interest in developing materials that can be used to fabricate prototypes with higher mechanical properties which give the parts greater functionality.

Thermotropic liquid crystalline polymers (TLCPs) are a novel class of materials that have potential for use in FDM applications for several reasons. First, it has been shown that TLCPs have excellent tensile properties with moduli ranging from 50 GPa to 100 GPa for neat fibers. It has also been shown that due to their excellent tensile properties and due to their fibril forming nature, TLCPs have been used to reinforce thermoplastics [2 - 4]. The diameter of the reinforcing TLCP fibrils are typically one order of magnitude smaller compared to typical glass and carbon fiber. However, it may be not possible to extrude glass and carbon fibers through the die head and still maintain high aspect ratio fiber (i. e. L/D > 100) due to the small diameter capillary die used in order to fabricate dimensionally precise prototypes.

The final mechanical properties of TLCP based composites, where the reinforcing fibrilar morphology is developed during the processing step on an in situ basis, are directly dependent upon the processing conditions [4 - 7]. Shear and extensional flow fields during processing serve to deform dispersed TLCP droplets into reinforcing fibrils and impart molecular orientation to the fibril, which results in increased tensile properties in the direction of the flow field. This preferred orientation, of both the molecules and the fibrils, results in anisotropic mechanical properties. It is generally known that extensional flow fields develop higher aspect ratio fibrils and greater molecular orientation, and hence extensional flow yields higher tensile properties than strong shear flow. For example, 20 wt% Vectra A, a commercial TLCP marketed and sold by Hoechst Celanese, was used to reinforce polypropylene (PP), and composites that were generated via fiber spinning and injection molding had tensile moduli of 9.6 GPa and 2.6 GPa, respectively [5, 8, 9]. Therefore, in order to obtain the optimal reinforcement, strong extensional forces, such as those present in fiber spinning, are necessary. The purpose of this work is to fabricate TLCP reinforced composite prototypes in such a fashion as to capitalize on the full potential of the reinforcement.

2.0 Experimental

2.1 Materials

The TLCP used was Vectra A950 (Hoechst Celanese). It is a random copolyester based on hydrobenzoic acid (73% mole) and 2-hydroxy-6-napthoic acid (27% mole). It has a glass transition temperature of 108°C and a melting point of 283°C [10]. However, Vectra A needs to be heated to 320°C to melt out all of the residual crystallites [11]. The matrix material used was the 4018 grade of Amoco polypropylene (PP). It has a melting point of 160°C and a melt flow index (MF) of 13.5 [12].

2.2 Spinning of TLCP/PP Composite Strands

A novel dual extrusion process was used to blend the TLCP and PP forming a self reinforced composite fiber in order to obtain optimal mechanical properties in the composite [13 - 15]. In this extrusion process, the thermoplastic and TLCP are plasticated in separate extruders so that independent thermal histories are imposed to the two materials. TLCP is heated to sufficiently high temperatures to fully melt all of the crystallites. For example, the melting point of Vectra A is 283°C, but it needs to be heated to 320°C in order to fully melt all the residual crystallites [11]. Vectra A is then supercooled to the temperature at which the matrix is processed, and using a multiple-port injection nozzle is then injected into the matrix stream which results in continuous TLCP streams encapsulated within the matrix. The melt is passed through a series of static mixers which serve to divide the TLCP streams, before being extruded through a capillary die and drawn in the spinline to high draw ratios in order to achieve high levels of molecular orientation in the TLCP fibrils.

There are several advantages of the dual extrusion process over generating TLCP fibrils in situ during FDM. Processing the TLCP in a separate extruder minimizes degradation of the matrix because the matrix is not exposed to the high temperatures that are necessary to fully melt the TLCP. The TLCP is supercooled before being injected into the matrix minimizing the degradation of the matrix. The dual extrusion process does not rely on droplet deformation because the multiple-port injection nozzle introduces continuous TLCP streams into the matrix, resulting in high aspect ratio fibrils. Finally, the composite strands can be post-processed above the melting point of the matrix and below the melting point of the TLCP using a variety of conventional processing techniques (e. g. FDM) which allow for the retention of the TLCP reinforcing fibrils generated during the dual extrusion process in the final part [1, 8, 9, 14 - 23].

3.0 Discussion and Results

3.1 Novel Process for Generation of Composite Feed Stock for FDM

In order to develop new materials for use in the FDM 1600 rapid prototyping system that could be used to fabricate prototypes with greater mechanical properties and greater functionality than those presently available, self-reinforced thermoplastic composite strands were generated using a novel dual extrusion process. Vectra A, a TLCP know for its exceptional mechanical properties, was used as the reinforcing phase, and PP served as the matrix. Vectra A/PP strands were spun with 20 wt% and 40 wt% TLCP concentrations, and the moduli of the strands were 9.55 GPa and 22.8 GPa, respectively. Further results concerning the properties of these strands are given elsewhere [8, 9].

Strands from the dual extrusion process were then post-processed to form monofilaments with a well controlled diameter for use in the FDM 1600 rapid prototyping system. In this process, the continuous TLCP reinforcement was granulated into short TLCP fibrils having lengths less than 6 mm and diameters ranging from 1 to 5 μm. The tensile moduli of the 20 wt% and 40 wt% monofilaments were 1.9 GPa and 2.2 GPa, respectively, and the strengths were 25.6 MPa and 21.1 MPa, respectively. The properties compare favorable to those of pure PP where the tensile modulus and strength are 0.98 GPa and 23.2 MPa, respectively [15]. The Vectra A reinforcement resulted in an increase in modulus of approximately 100% over those neat PP, while having similar strengths. The tensile properties of the monofilaments were significantly lower than those of the strands from the dual extrusion process. Previous work has shown that these lower properties were probably due to a reduction in aspect ratio, poor fibril distribution, and poor fibril alignment [20 - 22].

3.2 Plaque Fabrication via FDM

Vectra A/PP monofilaments were used as feed stock to fabricate plaques via FDM, and the effects of fabrication temperature on the tensile properties of the final part were examined. Monofilaments with 20 wt% and 40 wt% Vectra A were used to build parts with a lay-down pattern aligned uniaxially in the machine direction. In Figure 1, the tensile modulus is shown as a function of fabrication temperature for both the 20 wt% and 40 wt% Vectra A composite parts. Plaques with 20 wt% Vectra A reinforcement were fabricated at processing temperatures of 190°C, 240°C, and 290°C. The moduli of these plaques were essentially independent of processing temperatures and were approximately 1.6 GPa, even above the melting point of the reinforcement. The 40 wt% Vectra A monofilaments were processed at 240°C and 290°C, and the moduli of the plaques were 2.7 GPa and 2.4 GPa, respectively. Thus, the moduli of the fabricated plaques decreased somewhat when processed above the melting point of the reinforcement. Parts were not fabricated at 190°C because the FDM 1600 rapid prototyping system was unable to generate the pressure required to extrude the composite.

In Figure 2, the tensile strength is shown as a function of fabrication temperature. The strengths of both the 20 wt% and 40 wt% Vectra A reinforced plaques decreased by approximately one third when processed at 290°C as compared to the strengths of the plaques when processed below the melting point of Vectra A. The strength of the 20 wt% Vectra A plaques decreased from approximately 33 MPa when fabricated below the melting point of the Vectra A to 21 MPa when fabricated above the melting point. Similarly, the strength of the 40 wt% Vectra A plaques decreased from 37 MPa when post-processed at 240°C to 25 MPa when extruded above the melting point of the TLCP. When processed below the melting point of Vectra A, the composite relies on the reinforcement generated in the dual extrusion process. However, when Vectra A/PP composites are processed above the melting point of the TLCP, the reinforcing fibrils are melted and orientation is lost within the TLCP phase. In the melt state, the fibrils form into droplets, and there are minimal extensional forces present in the FDM 1600 rapid prototyping system to develop the fibrilar morphology required for the optimal tensile properties. Thus, tensile properties of Vectra/PP prototypes, where reinforcement was generated in the dual extrusion process, were somewhat better than those where the reinforcement was generated during prototype fabrication.

The mechanical properties of the Vectra A/PP monofilament feed stock were compared to those of the plaques fabricated via the FDM 1600 rapid prototyping system. The modulus of the 40 wt% Vectra A monofilament was measured to be 2.2 GPa. Plaques fabricated uniaxially in the machine direction at 240°C had a modulus of 2.7 GPa. Similarly, the strength of the composite increased from 21 MPa to 37 MPa in the fabricated plaque. The modulus of the 20 wt% Vectra A monofilaments and plaques was similar before and after fabrication and was approximately 1.8 GPa. The strength of the 20 wt% Vectra A monofilaments increased from 26 MPa to 33 MPa after being fabricated into a plaque. The increase in mechanical properties of the 40 wt% Vectra A composite was probably due to a change in alignment of the reinforcing fibrils as a result of the flow kinematics of the FDM 1600 extruder. It has been shown elsewhere that the tensile properties of post-processed long fiber composite strands are very sensitive to the flow kinematics of the die [8, 9]. It was shown that a critical L/D was necessary in order to obtain the optimal mechanical properties and that the extrusion rate, and die diameter can effect the tensile properties of the extrudate. Vectra A/PP (28/72 wt%) composite strands from the dual extrusion process were post-processed into monofilaments, and the maximum tensile modulus and strength were 4.0 GPa and 45 MPa. Thus, higher properties can be obtained with lower Vectra A concentrations under the proper post-processing conditions [8, 9].

Plaques were fabricated from composite monofilaments using three different lay-down patterns: uniaxial in the machine direction, uniaxial in the transverse direction, and a 0-90 lay-down pattern. The plaques were fabricated from the Vectra A/PP (40/60 wt%) composite monofilaments at 240°C which was the processing temperature that resulted in the greatest tensile properties for plaques fabricated uniaxially in the machine direction. In Figure 3, the mechanical properties are shown as a function of lay-down pattern. The abscissa is defined as the volume percent of material laid in the machine direction. Thus, plaques fabricated entirely in the transverse direction had 0 vol% laid in the machine direction, and parts with 0-90 lay-down patterns had 50 vol% laid in the machine direction, and parts built uniaxially in the machine direction had 100 vol% of the material laid in the machine direction. It is shown that both the tensile modulus and strength increased monotonically with the volume percent laid-down in the machine direction. For parts fabricated uniaxially in the transverse direction and parts fabricated uniaxially in the machine direction, the modulus increased from 1.3 GPa to 2.7 GPa, and the strength increased from 10 MPa to 37 MPa. This dependence of mechanical properties on the lay-down pattern was due to anisotropic reinforcement of the matrix by the TLCP fibrils as was observed in Figure 4, and this reinforcement was aligned in the direction in which the roads were laid. This was why the greatest mechanical properties were observed in the plaques fabricated uniaxially in the machine direction. Plaques fabricated uniaxially in the transverse direction had the lowest properties because the reinforcement was aligned orthogonal to the machine direction. Thus, the bulk properties of these plaques were highly dependent on the tensile properties of the matrix. Also, the mechanical properties of a part built in the transverse direction were probably somewhat lower due to weld lines perpendicular to the machine direction. As predicted by composite theory, there was a monotonic increase in mechanical properties with increasing volume fraction laid-down in the machine direction [24]. Therefore, using composite theory, the mechanical properties of the final part can be engineered to match the requirements of the proposed prototype by adjusting the lay-down pattern.

4.0 Conclusions

Plaques were fabricated from Vectra A/PP composites and neat Vectra A monofilaments via FDM. The tensile modulus of Vectra A/PP (40/60 wt%) composite plaques were approximately 100% greater than those of ABS prototypes and approximately 150% greater than those of pure PP, and these properties could probably be increased if long fiber reinforced composite monofilaments were used as feed stock.

Due to the anisotropic mechanical properties present in TLCPs and TLCP composites, the lay-down pattern affected the properties of the final part. It was found that the tensile properties of Vectra A/PP composites increased monotonically with roads laid in the machine direction. Thus, the final mechanical properties of a prototype can be tailored to a specific application by adjusting the lay-down pattern, increasing the functionality of the prototype.

5.0 Acknowledgments

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1 R. W. Gray IV, D. G. Baird, J. H. Bøhn, *Rap. Proto. J.*, in preparation (1997).
2 A. I. Isayev, in Liquid-Crystalline Polymer Systems Technological Advances, ed. A. I. Isayev, T. Kyu, and S. Z. D. Cheng, American Chemical Society, Washington D. C. 1996.
3 D. G. Baird, in Polymeric Materials Encyclopedia, ed. J. C. Salamone, CRC Press, Boca Raton 1996.
4 A. A. Handlos and D. G. Baird, *J. Macromol. Sci.-Rev. in Macromol. Chem. and Phy.*, C35, 183 (1995).
5 K. G. Blizard and D. G. Baird, *Polym. Eng. and Sci.*, 27, 653 (1987).
6 G. G. Viola, D. G. Baird, and G. L. Wilkes, *Polym. Eng. and Sci.*, 25, 888 (1985).
7 A. Kohli, N. Chung, and R. A. Weiss, *Polym. Eng. and Sci.*, 29, 573 (1985).
8 R. W. Gray IV, M. S. Thesis, Virginia Polytechnic Institute and State University (1997).
9 R. W. Gray IV, D. G. Baird, and J. H. Bøhn, *Polym. Comp.*, in preparation (1997).
10 M. Y. Cao and B. Wunderlich, *J. Polym. Sci.: Polym. Phy. Ed.*, 23, 521 (1985).
11 S. M. Guskey and H. H. Winter, *J. Rheol.*, 35, 1191 (1991).
12 Amoco Polypropylene Homopolymers Bulletin PP-8n, Amoco Polymers, Inc. (1996).
13 D. G. Baird and A. Sukhadia, U.S. Patent 5,225,488 (1993).
14 E. A. Sabol, M. S. Thesis, Virginia Polytechnic Institute and State University (1994).
15 E. A. Sabol, A. A. Handlos, and D. G. Baird, *Polym. Comp.*, 16, 330 (1995).
16 C. R. Robertson, M. S. Thesis, Virginia Polytechnic Institute and State University (1995).
17 C. G. Robertson and D. G. Baird, *Intern. Polym. Proc.*, in press (1996).
18 R. K. Krishnaswamy and D.G. Baird, *Polym. Comp.*, in press (1997).
19 C. G. Robertson, J. P. de Souza, and D. G. Baird, Recent Advances in Liquid Crystalline Polymers, A. I. Isayev, T. Kyu, and S. Z. D. Cheng eds., ACS Books, Washington D. C. (1996).
20 A. A. Handlos and D. G. Baird, *Intern. Polym. Proc.*, XI, 82 (1996).
21 A. A. Handlos and D. G. Baird, *Polym. Comp.*, 17, 73 (1996).
22 A. A. Handlos and D. G. Baird, *Polym. Eng. and Sci.*, 36, 378 (1996).
23 R. K. Krishnaswamy, J. Xue, and D. G. Baird, *SAMPE J.*, in preparation (1997).
24 J. C. Halpin, *Polym. Eng. and Sci.*, 16, 344 (1976).

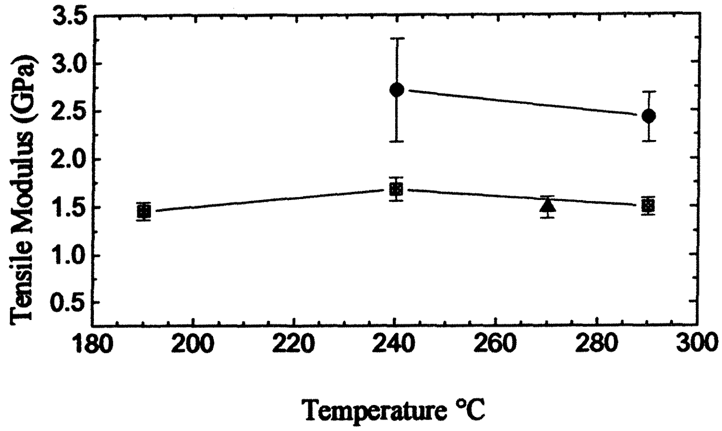

Figure 1 : Tensile modulus of Vectra A/PP (20/80 wt%) (—●—) and (40/60 wt%) (—■—) and ABS (—▲—) plaques built uniaxially in the machine direction as a function fabrication temperature.

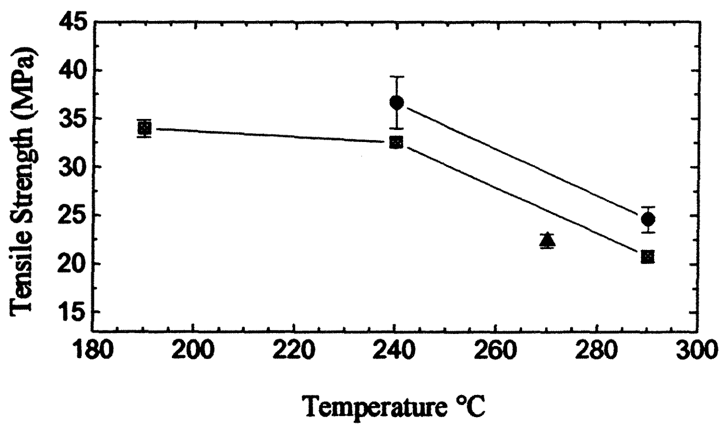

Figure 2 : Tensile strength of Vectra A/PP (20/80 wt%) (—●—) and (40/60 wt%) (—■—) and ABS (—▲—) plaques built uniaxially in the machine direction as a function fabrication temperature.

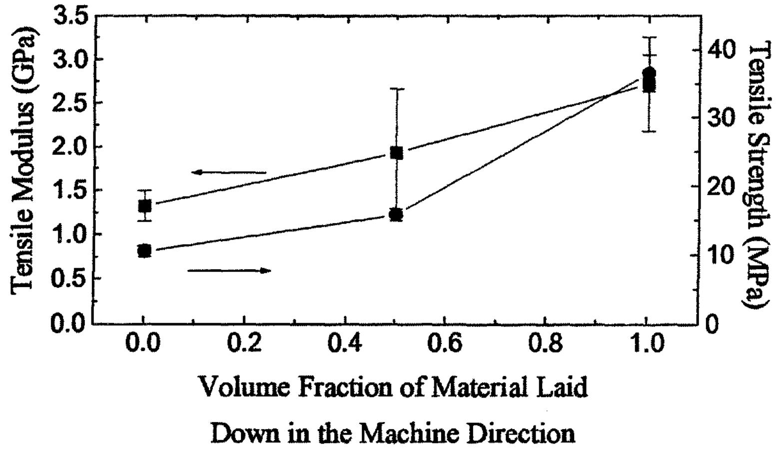

Figure 3: Tensile modulus (—■—) and strength (—●—) of Vectra A/PP (40/60 wt %) composite plaques fabricated via FDM as a function of volume fraction laid in the machine direction processed at 240°C.

Figure 4 : Micrographs of the cross-section of Vectra A/PP (40/60 wt%) composite prototypes fabricated via FDM at 240°C.