

# RECYCLABLE COMPOSITES BASED ON POLYMERS REINFORCED WITH THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

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## Abstract

In this work, wholly thermoplastic composites were generated using a dual extrusion technique for processing by means of various polymer processing technologies. These composites were generated by continuously injecting thermotropic liquid crystalline polymers (TLCP's) of higher melting point into matrix polymers of lower melting point. The use of the TLCP's allowed *in situ* fibril generation, thereby avoiding fiber breakage, very common when processing traditional fiber filled composites, e.g. carbon fiber reinforced composites. A wide range of thermoplastics were reinforced in this work, such as acrylonitrile butadiene styrene (ABS), polyphenylene sulfide (PPS) and a lower melting TLCP. On post processing the composites using injection molding, compression molding and Fused Filament Fabrication (FFF), a form of additive manufacturing (AM), a significant improvement in the mechanical properties was obtained. The composites generated are highly recyclable by either direct reprocessing after grinding or by a TLCP reclamation process developed earlier.

## Background and Requirements

Growing pressure on the automotive industry to cut greenhouse gas emissions [1], improve recyclability of the composites [2], and achieve the ambitious goal of doubling fuel economy [3] requires that the solutions that are adopted be multipronged. Industry requires switching to composites that are highly recyclable without compromising the mechanical properties. Moreover, with the introduction of novel processing methods such as additive manufacturing (AM), the composites need to be compatible with the AM processes for faster adoption of the AM technologies [4]. This is to harness the advantages of AM to achieve the goals of the automotive industry, mentioned earlier, faster than can be achieved by conventional processing technologies.

In the quest for light weighting, the automotive industry constantly relies on composites. Traditionally, composites are generated by reinforcing using solid fibers such as carbon and glass fiber. One major disadvantage of using these composites is poor recyclability. For example, in the work carried out by Kuram et al. [5], reprocessing of the glass-fiber reinforced composites by repeated injection molding until five processing cycles showed a decrement of 33.5 % in tensile strength and 23.5 % in flexural strength compared to the virgin blend. The processing technologies, such as injection molding and extrusion, are known for fiber breakage with each processing cycle. Improvement in recyclability can be achieved by switching to *in situ* composites. In these composites, polymeric fibrils are generated during the processing stage which avoids the fiber breakage problems in addition to allowing regeneration of the fibrils on subsequent recycling cycles. The utilization of polymeric reinforcement eliminates the drop in the aspect ratio of the fibrils, which on contrary is very common on using traditional fibers.

In this work, generation and reprocessing of *in situ* composites has been described. The matrix polymers were reinforced using TLCP's, composed of rod-like aromatic monomers, which under extensional flow kinematics lead to excellent one-dimensional mechanical properties [6]. In addition, the TLCP's are wholly thermoplastics and have lower density. Two recycling schemes

are viable for TLCP composites: direct reprocessing after grinding and reclamation of the TLCP's from the composites. *In situ* composites based on TLCP-reinforced thermoplastics have the advantage of regeneration of reinforced fibrils during melt processing steps under elongational flow. Sasaki et al. [7] used a twin-screw extruder to prepare polypropylene-TLCP strands and then pelletized and re-extruded until the 10th cycle. The results showed no loss in tensile strength with the reprocessing cycles. This illustrates the greater ability of TLCP's to endure multiple processing cycles than carbon or glass reinforced composites.

For TLCP composites with non-overlapping processing temperature, direct reprocess may not be feasible without significantly deteriorating properties of the composites. The reclamation process developed in our laboratory by Collier et al. [8] successfully realized the separation of the TLCP from the polypropylene matrix with 96.0 wt.% purity. On re-injection molding, composites showed no discernible difference in mechanical properties compared to the virgin blends. Reactive extrusion was incorporated in this process to degrade the polypropylene and enhance the phase separation. The extrudate was dissolved in a mineral oil bath for selective dissolution of the polypropylene. TLCP was filtered out of solution and reprocessed. The material cost of producing the reclaimed TLCP was found to be three times lower than the cost of pure TLCP. This process is potentially suitable for use in other TLCP-reinforced thermoplastics as well.

One major problem in using TLCP's is that the processing temperature of TLCP's is higher compared to most matrix polymers which may prevent blending in a single extruder [9]. This problem can be solved by utilizing super-cooling behavior of the TLCP's in technology developed in our lab, called dual extrusion technology [10]. The dual extrusion technology leads to nearly continuous injection of the TLCP in the matrix polymer, thereby generating nearly continuously reinforced composites. In this technology, discussed elsewhere in detail [11], the TLCP's and the matrix polymers are plasticated in two different extruders. TLCP is then injected into the matrix polymer using a multiport injection nozzle, following which the blend is passed through static mixers which subdivides the TLCP stream into finer streams. The extrudate is drawn at high draw ratio and subsequently cooled in a water bath to lock down the fibril orientation. The selection of temperatures is determined using rheological tests discussed in detail elsewhere [9]. The generated filaments can then be post processed as solid filled systems by only melting the matrix polymer and keeping the reinforcing polymer solid. Different post-processing technologies, such as injection molding, compression molding and Fused Filament Fabrication have been utilized to process the TLCP reinforced composites generated using dual extrusion technology.

This paper will discuss two subtypes of the composites generated in our laboratory by using TLCP as a reinforcement in the dual extrusion technology. In the first type, thermoplastics such as acrylonitrile butadiene styrene (ABS), polyphenylene sulfide (PPS) and polypropylene (PP) were reinforced with the TLCP's. These composites will henceforth be termed as thermoplastic-TLCP *in situ* composites (TTICs). TLCP/ABS and TLCP/PPS composite strands generated using dual extrusion technology were post processed in fused filament fabrication (FFF), a form of additive manufacturing (AM). In FFF, polymeric filaments are used to fabricate objects layer upon layer [12]. The TLCP/PP strands generated using the dual extrusion technology were injection molded. The second subtype of the composites generated in our lab are called as two TLCP *in situ* composites (TPICs). In TPICs, a lower melting TLCP is reinforced by a higher melting TLCP using the dual extrusion system. TPIC strands generated were injection molded.

## Materials

ABS used in this work, MAGNUM 555, was generously supplied by Trinseo. The PPS used was generously supplied by Solvay and melts at 285 °C. The TLCP's used, HX3000 and HX8000, were supplied by DuPont and are believed to be synthesized from different ratios of terephthalic

acid (TA), 4-hydroxybenzoic acid (HBA), hydroquinone (HQ) and hydroquinone derivatives (HQ-derivatives). The melting temperatures of HX3000 and HX8000 are 280 and 330 °C, respectively, determined using dynamic scanning calorimetry. Vectra A950, henceforth referred to as Vectra A, was provided by Hoechst Celanese. Vectra A is a random copolyester based on 73% hydrobenzoic acid and 27% 2-hydroxy-6-naphthoic acid. It has a glass transition temperature of 108°C and a melting point of 283°C [6]. Polypropylene used was the 4018 grade provided by Amoco.

## Experimental

The dual extrusion system consisted of two Killion KL-100 single screw extruders with Maddock screws of 25.4 mm diameter and length-to-diameter ratio of 30. Two Zenith gear pumps (model number: 6135419-001 and flow/revolution: 1.725 cm<sup>3</sup>/rev) were used to meter the reinforcing TLCP and the corresponding matrix polymer. A 28-hole injection nozzle was used to inject the TLCP phase into the matrix phase. The melt was then passed through a 4-element KOCH mixer and a 4-element Kinecs mixer. The die used had a diameter of 3 mm and length-to-diameter ratio of 20.

The key step in the fabrication of our wholly thermoplastic composites is the selection of TLCP's. The selected TLCP's should have a melting temperature above that of the matrix polymer to avoid melting the TLCP on reprocessing in various polymer processing technologies discussed earlier. In addition, the temperature selected for processing in FFF needs to be such that relaxation in orientation of the TLCP's is minimum to avoid loss in mechanical properties. Selected processing temperatures should also avoid degradation of the matrix polymers.

HX8000/ABS and HX3000/PPS were processed in the dual extrusion system using the temperatures shown in Figure 1. Detailed discussion of generation, morphology and postprocessing of HX8000/ABS and HX3000/PPS has been carried out elsewhere [13, 14, 15].

56 wt.% Vectra A/PP strands were generated using dual extrusion technology by plasticating Vectra A and PP at 325°C and 245°C, respectively. TPICs were generated by using HX8000 as matrix and HX3000 as reinforcement. HX8000 and HX3000 were plasticated at 320 and 360 °C, respectively, to generate 50.0 wt.% HX8000/HX3000 TPIC strands.

Postprocessing of the 40.0 wt.% HX8000/ABS and 67.0 wt.% HX3000/PPS strands were carried out by printing rectangular specimens (80mm x 8mm x 2mm) using a RoVa3D printer using the print parameters shown in Table I. Extrusion multiplier is the relation between the extrusion rate and scan speed. The nozzle diameter was chosen to avoid clogging of the nozzle. The specimens were printed without severing such that the roads were aligned parallel to each other along the length of the specimen.

56.0 wt.% HX3000/PP and 50.0 wt.% HX8000/HX3000 TPICs were injection molded using a BOY 35E machine. End-gated rectangular plaques were produced using both, 56.0 wt.% HX3000/PP and 50.0 wt.% HX8000/HX3000 pelletized strands. For HX3000/PP, zone temperatures used were 190, 250, 250 and 280 °C. The mold temperature was 60°C. For HX8000/HX3000 TPIC, zone temperatures were 300, 310, 310, and 310 °C. The mold temperatures were set to 210 °C. 56.0 wt.% HX3000/PP was also used to compression mold square plaques of dimension (76.2mm x 76.2mm x 2mm) by laying 76.2mm long strands parallel to each other and molding at 290, 300, 310 and 330 °C. Tensile testing strips were cut in the alignment direction to assess improvement in the mechanical properties.

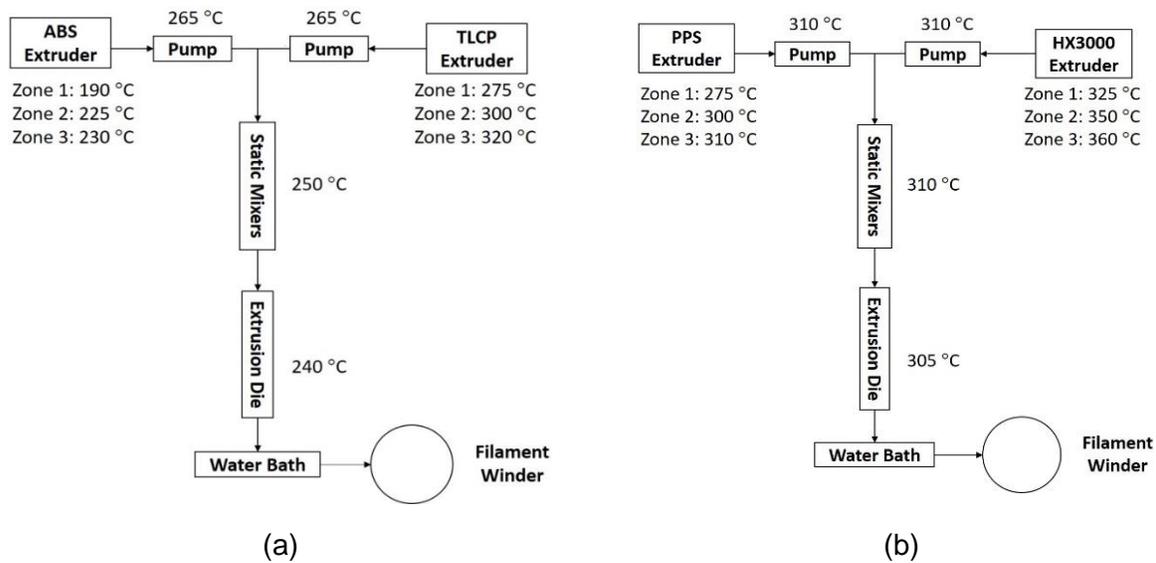


Figure 1: Temperature schematic used to carry out to generate strands using dual extrusion technology consisting of (a) HX8000/ABS and (b) HX3000/PPS.

Table I. Print parameters used in FFF to print specimens.

Printing Parameters	Settings
Layer Width	0.65 mm
Layer Height	0.65 mm
Scan Speed (X,Y & Z)	1200 mm/min
Extrusion Multiplier	1
Nozzle Diameter	1 mm

## Results

This section has been arranged to show improvement in tensile properties of the strands generated using dual extrusion technology. It also demonstrates processability of these composite strands using various processing technologies. The tensile properties of the post-processed parts have also been shown. Table II shows the tensile properties of the composite strands generated using dual extrusion technology. A significant improvement in the mechanical properties can be seen compared to those of the pure matrices shown in the table. The rectangular parts printed using 40.0% HX8000/ABS and 67.0 wt.% HX3000/PPS can be seen in Figure 2. Tensile properties of the 3d printed parts, printed using 40.0 wt.% HX8000/ABS and 67.0 wt.% HX3000/PPS composite filaments are shown in Figure 3 and Figure 4, respectively. Drastic improvement in the properties can be seen, which is very promising in FFF. All of these properties are in the alignment direction.

Table II: Tensile property of the composite strands generated using dual extrusion technology and that of the pure matrix strands generated using single screw extruder.

Strands	Composition (Wt. %)	Strength (MPa)	Modulus (GPa)
HX8000/ABS	40.0	169.2±4.0	39.9±3.7
HX3000/PPS	67.0	155.0±24.2	40.4±7.5
HX3000/PP	56.0	147.9±13.1	55.2±8.4
ABS	Pure	39.3±3.3	2.3±0.4
PPS <sup>1</sup>	Pure	80.0	3.5
PP [6]	Pure	23.2±3.9	1.0±0.2

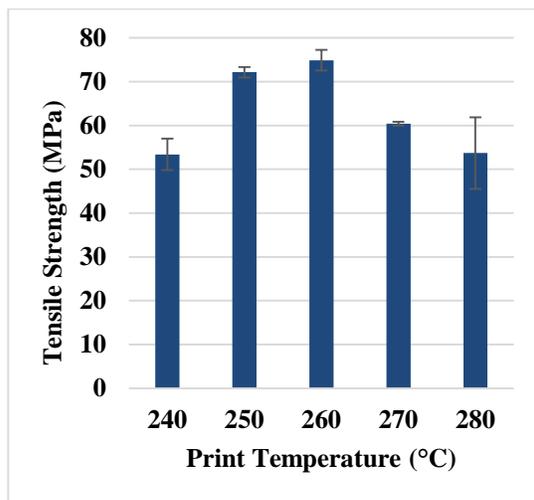


(a)

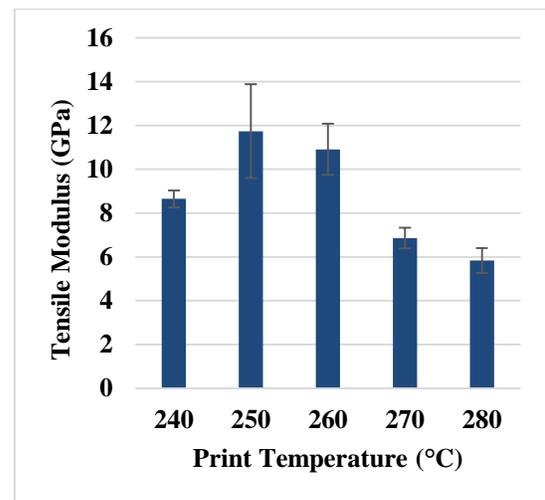


(b)

Figure 2: Rectangular specimens printed using (a) 40.0 wt.% HX8000/ABS and (b) 67.0 wt.% HX3000/PPS for tensile testing. All roads are aligned in the length direction



(a)



(b)

Figure 3: Tensile (a) strength and (b) modulus of the rectangular specimens printed using 40.0 wt.% HX8000/ABS composite filaments.

<sup>1</sup> These properties were as received on the processing guide.

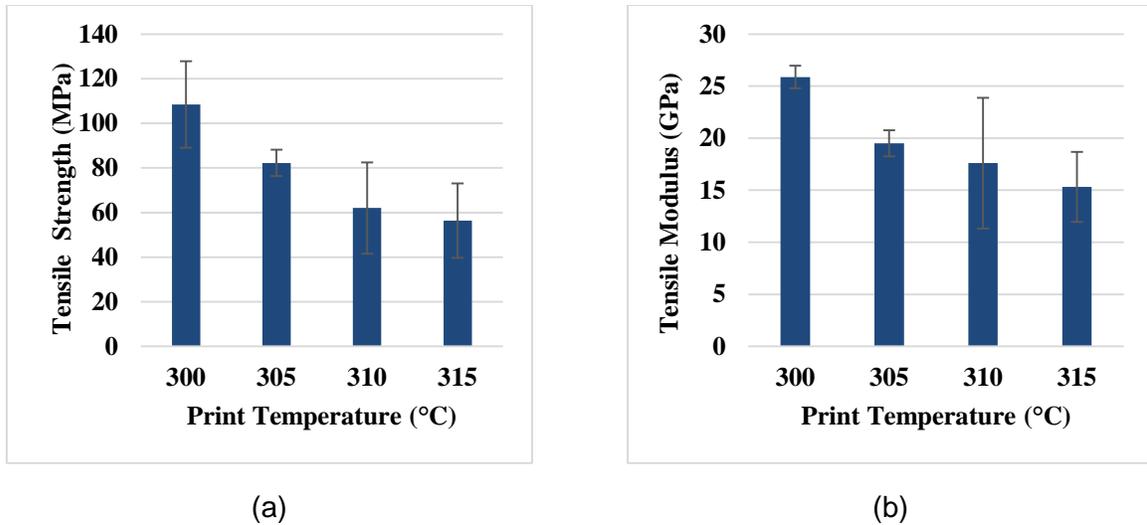


Figure 4: Tensile (a) strength and (b) modulus of the rectangular specimens printed using 67.0 wt.% HX3000/PPS composite filaments.

Now follows the tensile properties obtained on post processing 56.0 wt.% HX3000/PP. Table III shows improvement in tensile properties on compression molding. On the other hand, injection molded plaques, molded using pelletized 56.0 wt.% HX3000/PP strands had tensile properties shown in Table IV in the flow and transverse direction. Tensile properties of the injection molded 50.0 wt.% HX3000/HX8000 TPIC end-gated plaques in the flow and transverse direction have been shown in Table V. End-gated plaques molded using 56.0 wt.% HX3000/PP and 50.0 wt.% HX3000/HX8000 TPIC pelletized strands are shown in Figure 5.

It can be seen that the tensile properties of the postprocessed parts produced using wholly thermoplastic composites are similar to those reinforced using traditional fibers [16] and in some cases even better. Thus these composites have potential to replace traditionally used composites.

Table III: Tensile properties of the compression molded 56.0 wt.% HX3000/PP, molded at 290, 300, 320 and 330 °C. All properties are in the alignment direction.

Molding Temperature (°C)	Tensile Strength (MPa)	Tensile Modulus (GPa)
290	129.3	39.7
300	127.7	30.5
320	129.8	28.6
330	142.2	26.8

Table IV: Tensile properties of the injection molded 56.0 wt.% HX3000/PP end-gated plaques in the flow and transverse directions.

Orientation	Tensile Strength (MPa)	Tensile Modulus (GPa)
Flow Direction	54.0±7.3	5.1±0.2
Transverse Direction	24.5±3.2	2.8±0.2

Table V: Tensile properties of the injection molded 50.0 wt.% HX3000/HX8000 TPIC end-gated plaques in the flow and transverse direction.

Orientation	Tensile Strength (MPa)	Tensile Modulus (GPa)
Flow Direction	68.4±9.4	4.1±1.0
Transverse Direction	36.0±6.9	2.2±0.4



Figure 5: Injection molded end-gated plaques, molded using (a) 56.0 wt.% HX3000/PP and (b) 50.0 wt.% HX3000/HX8000 TPIC pelletized strands.

### Summary and Next Steps

In summary, wholly thermoplastic strands composed of a thermotropic liquid crystalline polymer and a matrix polymer were successfully generated using dual extrusion technology. Our efforts not only reinforced commonly used thermoplastics such as acrylonitrile butadiene styrene (ABS) and polypropylene (PP) but also extended the work to reinforce high performance thermoplastics such as polyphenylene sulfide (PPS). Upon post processing the composite strands using compression molding, injection molding and FFF, significant improvement in the tensile properties were obtained. The properties were similar and in some cases superior to those of the traditional fiber composites.

Future efforts will be to extend the work carried out in the past in our laboratory to study the recyclability of TLCP/ABS and TLCP/PPS composites. In the past, work carried out in our

laboratory was to develop a separation method to separate TLCP and PP. We will now focus on extending the work to separate other wholly thermoplastic composites as well. In addition, the effect of direct reprocessing after grinding will also be studied.

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