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DEVELOPMENT OF HIGH-TEMPERATURE THERMOPLASTIC COMPOSITES REINFORCED WITH RECYCLED CARBON FIBERS AND THERMAL BLACK PARTICLES FOR FUSED FILAMENT FABRICATION

Arslan, D.[1,2], Mihai, M.[2], Therriault, D.[1] , Levesque, M.[1]

[1]Laboratory for Multiscale Mechanics (LM^2), Department of Mechanical Engineering, Polytechnique Montreal, Montreal, QC H3T 1J4, Canada

[2]Advance Manufacturing, Automotive and Surface Transportation Research Center, National Research Council Canada, 75 de Mortagne, Boucherville, QC J4B 6Y4, Canada

*Corresponding author (dogan.arslan@polymtl.ca)

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ABSTRACT

This study investigates the development of novel formulations for high-temperature thermoplastic polymer composites by modifying amorphous polyetherimide (PEI) and semicrystalline polyphenylene sulfide (PPS) matrices with the incorporation of recycled carbon fiber (rCF) and thermal black (TB) particles and processing them into filaments for Fused Filament Fabrication (FFF). rCF and TB particles were used for their sustainable and eco-friendly characteristic respectively. Different formulations of composites are manufactured using a combination of rCF and TB in which rCF content is gradually replaced by TB to investigate the effect of a second filler on the properties. The effect of rCF and TB contents on the mechanical properties of composites was investigated for FFF 3D printed specimens. Moreover, scanning electron microscopy (SEM) and X-ray micro-tomography were carried out to observe possible formation of porosity for the composite filament and FFF 3D printed specimens. The morphology of the composites showed that there is good level of adhesion between successive layer of printed parts. The differential scanning calorimetry (DSC) characterization results showed that the incorporation of TB affects the crystallization kinetics of the semicrystalline PPS matrix which could provide better layer adhesion of the printed parts. The obtained results will allow us to understand the developed composites behavior and optimize the FFF printing parameters for better mechanical performance of the printed parts for aerospace applications.

1 INTRODUCTION

Fused Filament Fabrication (FFF) is an open-source 3D printing technology for processing thermoplastic feedstocks to manufacture complex 3D structures [1, 2]. High-temperature and high-performance thermoplastic polymers have superior thermal and mechanical properties, when compared to commodity polymers such as polypropylene (PP), polyethylene (PE), or polystyrene (PS) [3]. Polyetherimide (PEI) has a high tensile strength (up to 110 MPa for some grades) with inherent flame retardancy, chemical and UV resistance, and high service temperature (up to 175 ^{o}C for selected grades) [3]. Moreover, melt flow properties of different grades of PEI enable them to be melt processed through extrusion, injection molding or FFF 3D printing [4]. Polyphenylene sulphide (PPS) is a semi crystalline thermoplastic polymer consisting of an aromatic ring connected to a sulphide atom that forms the basic unit of polymerization [1, 2]. There has been a high interest in PPS due to its high tensile strength (90 MPa), tensile modulus (3500 MPa), thermal stability (up to 500 °C) and electrical properties. PPS is inherently flame-retardant owing to its distinctive chemical configuration and its innate capacity to undergo charring upon exposure to an open flame [1]. Commercially available filaments of PEI and PPS composites are limited to a few manufacturers and are expensive, up to 10-fold, when compared to their conventional pellets form. Moreover, commercially available carbon fiber-reinforced PEI and PPS filament feedstocks are currently limited up to 15 wt.% of carbon fiber contents and the mechanical properties of resulted 3D printed parts do not meet the requirements for aerospace applications.

This study investigates the development of novel formulations of high-temperature thermoplastic composites featuring significantly improved specific stiffness and strength and also FFF process optimization for the developed composites.

2 METHODOLOGY

2.1 Materials

ULTEM 1040A, a low viscosity PEI grade was purchased from SABIC Americas (USA). PPS Fortron 0214P1 grade in pellet form was purchased from Celanese (Celanese Corporation, Fortron Industries LLC., Wilmington, NC., USA). re-Evo® HSC (Phenix 0.25) recycled short carbon fibers used in this study were purchased from Carbon Conversion (Lake City, SC, USA). Thermal Black Thermax® N990 (TB N990) particles were supplied by Cancarb Limited (Medicine Hat, AB, Canada).

2.2 Composite Processing Methods and Characterization

Polymer pellets were compounded with rCF and TB by using a Bühler clamshell co-rotating twin-screw extruder (Bühler Group, Gupfenstrasse 5, Uzwil 9240, Switzerland). The composites were then extruded into filaments by using a Noztek Xcalibur filament extrusion line. Simplify 3D software (Simplify3D, USA) was used to slice the 3D models to 3D print mechanical specimens for tensile mechanical testing. AON-M2 (AON3D, Montreal, QC, CA) 3D printer equipped with a heated bed and chamber was used to print test specimens. Moreover, tensile mechanical specimens were injection molded (IM) with neat polymer matrices for the sake of the comparison. The formulation of composites and 3D printing parameters are given in Table 1.

Scanning electron microscopy (SEM) was used to observe fractured surface of composite filaments and impact testing specimens. X-ray micro tomography (μ-CT) was carried out to observe porosity of composite filaments. The scans were analyzed with the open-source segmentation tool for quantifying the porosity distribution [5]. Tensile properties of the FFF printed composites were carried out according to ASTM D638 standard.

Table 1: Formulation of developed composites and their optimized FFF parameters.

Formulation (wt.%/ wt.%/ wt.%) (Matrix/rCF/TB)	FFF parameters for PEI composites	FFF parameters for PPS composites
	Nozzle temperature: 400 °C	Nozzle temperature: 350 °C
PEI (0/0/0), PPS (0/0/0)	Bed temperature: 180 °C	Bed temperature: 160 °C
PEI/rCF/ TB (80/20/0), PPS/rCF/ TB (80/20/0)	Chamber temperature: 130 °C	Chamber temperature: 100 °C
PEI/rCF/TB (80/15/05), PPS/rCF/TB (80/15/05)	Printing speed: 20 mm/s	Printing speed: 20 mm/s
PEI/rCF/TB (80/10/10), PPS/rCF/TB (80/10/10)	Layer height: 0.2 mm	Layer height: 0.2 mm
PEI/rCF /TB (80/0/20), PPS/rCF /TB (80/0/20)	Raster angle: +45°/−45°	Raster angle: +45°/−45°
	Infill ratio: 100%	Infill ratio: 100%

3 RESULTS AND DISCUSSION

3.1 Microstructural Characterization

Figures 1. (a.1-d.1) and (a.2-d.2) show the SEM morphology of fracture surfaces of PEI and PPS composite filaments, respectively. Their diameter was controlled during the extrusion for a constant diameter of 1.75 +\- 0.05 mm and for a constant ovality, which were confirmed by SEM. The rCF incorporation leads to porosity formation up to 17 vol.% which could be due to a possibly degradation of their sizing materials during the high-temperature processing. The porosity content was determined with micro-CT and decreased with the gradual replacement of rCF by TB particles. Further, Figure 1. (d.1 and d.2) shows that the porosity was almost fully eliminated (~ 1 vol. %) at 20 wt.% TB containing composites. The porosity reduction in the 3D printed material is one important care to take to significantly improve the printing quality and the mechanical performance of the printed parts.

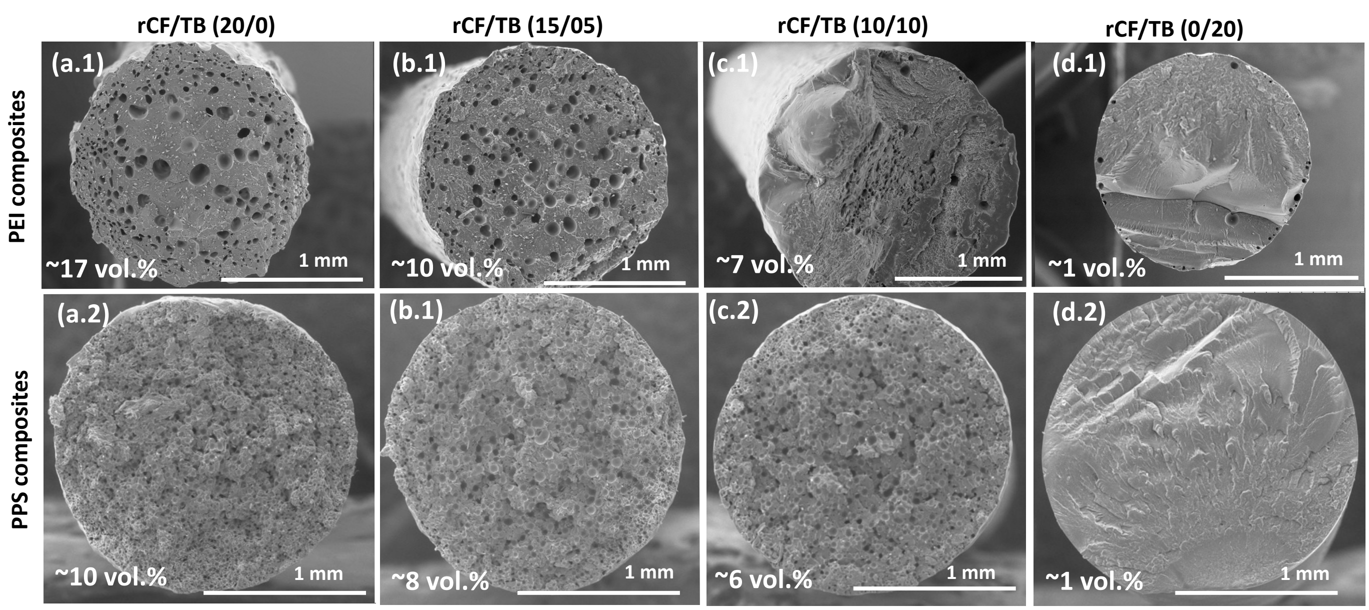

Figure 1. SEM of fracture surface of custom-made filament (1.75 mm): (a.1-d.1) PEI composites and (a.2-d.2) PPS composites.

Figure 2 presents SEM images depicting the fracture surfaces of impact-tested specimens for both PEI and PPS composites containing rCF/TB (20/0) and rCF/TB (10/10) at different magnifications. These fractured surfaces were analyzed to observe the fiber-matrix adhesion and the rCF and TB distributions through the matrix. In Figure 2. (a.1-a.2), fiber breakage, fiber pull-outs and unwetted fiber surfaces are clearly seen that would indicate a low-medium level of adhesion between the rCF and the matrix for PEI and PPS reinforced with 20 wt.% rCF composites. Figure 2. (b.1-b2) shows SEM images of the hybrid composites of PEI and PPS reinforced with 10 wt.% rCF and 10 wt.% of TB. The incorporation of TB seemed to enhance fiber-matrix adhesion since the rCF surfaces were covered by the matrix and the TB particles as well. A similar phenomenon was observed before when TB was used as filler in different thermoplastic matrices, such as polypropylene (PP), polyamide 6 (PA6), polyphenylene sulfide (PPS), and acrylonitrile butadiene styrene (ABS) [6]. The similar surface characteristic of rCF and TB due to their carbon structure that provide carbon-carbon interaction may improve the affinity of the matrix and the carbon fibers.

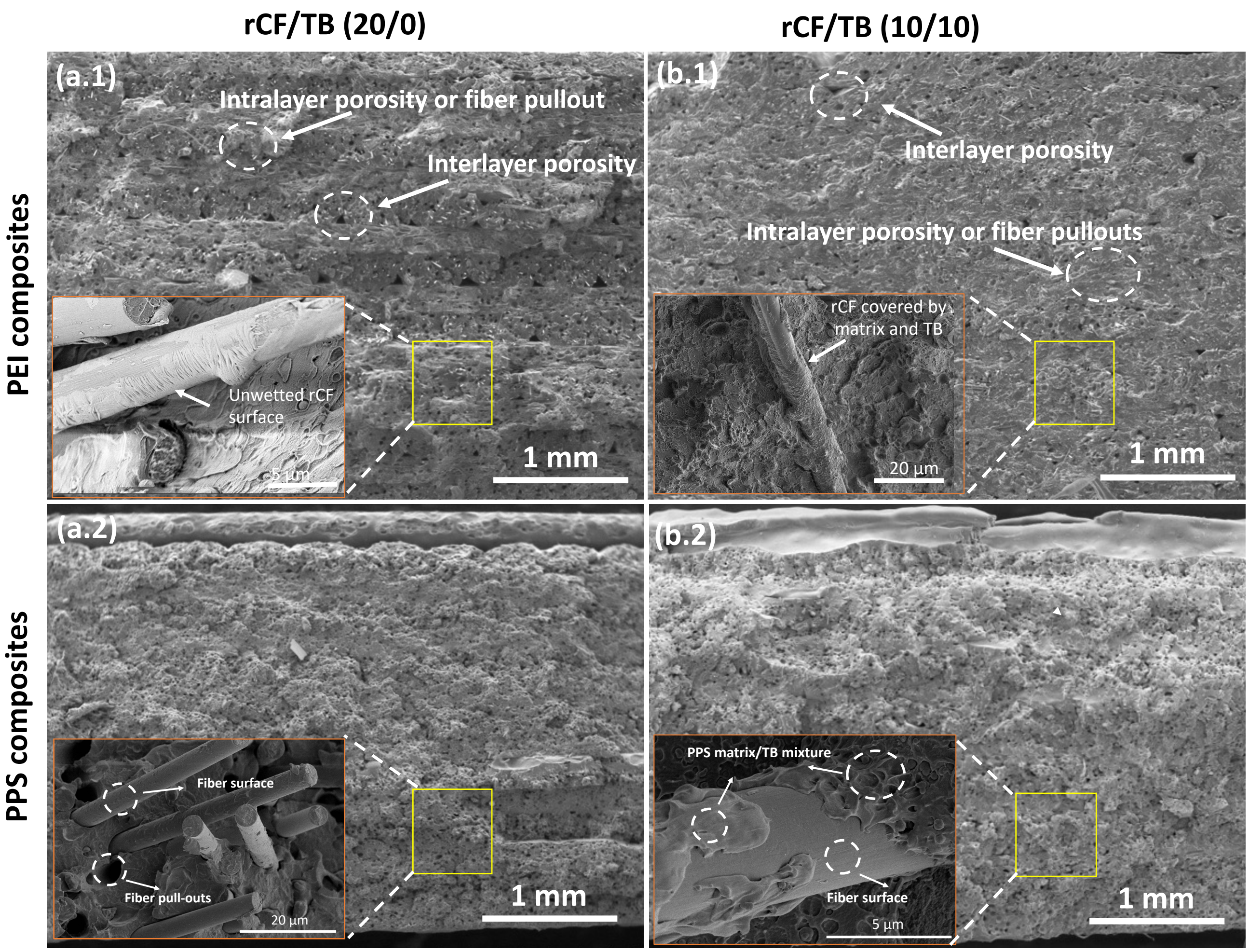

Figure 2. SEM images of fracture surface of impact tested specimens:
(a.1-b.1) PEI/rCF/TB (80/20/0) and PEI/rCF/TB (80/10/10), (a.2-b.2) PPS/rCF/TB (80/20/0) and PPS/rCF/TB (80/10/10).

3.2 Crystallization behavior of PPS composites

Figure 3.a illustrates FFF printing conditions of PPS composites in which heat loss (convection/conduction) is a significant factor that directly affects the crystallinity of printed parts. The microstructure of PPS composites directly affects layer adhesion and bond formation mechanism during FFF printing. The steps of the bond formation mechanism between the extruded filaments starts with contact of filaments followed by the formation of neck through molecular diffusion of amorphous region between layers (Figure 3.a-b). Figure 3.c shows that incorporation of rCF and TB particles with combination of increasing isothermal temperatures seem to defer the crystallization which can provide longer time for adhesion between deposited layers during FFF printing. According to DSC analysis results, it would be possible to fine-tune the crystallization kinetic of PPS composites to further enhance the mechanical performance of the final 3D printed parts.

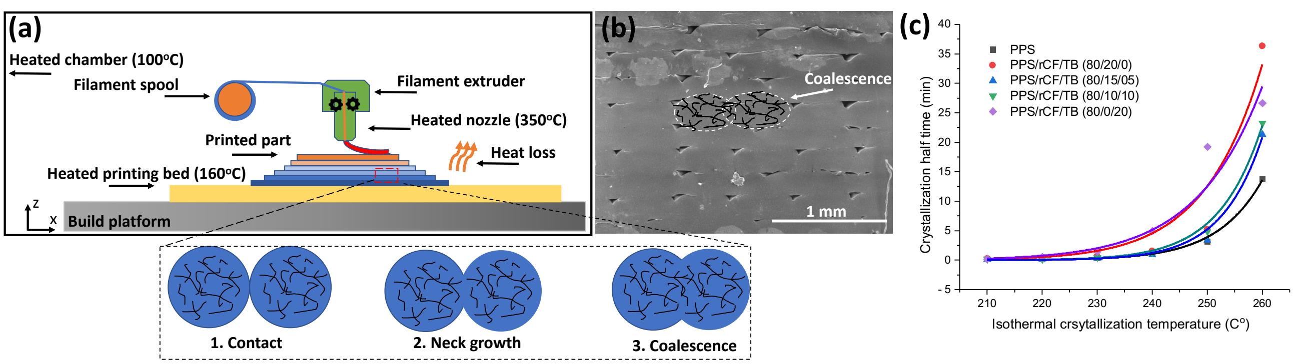

Figure 3. (a) Schematics for layer deposition during FFF printing, (b) SEM images of fracture surface of PPS/rCF /TB (80/0/20), (c) Graph of crystallization half time with respect to isothermal temperatures.

3.3 Mechanical properties of FFF printed composites

Figure 4.a-b presents the tensile modulus and strength of the injection molded (IM) neat PPS and PEI compared to their FFF printed composites, respectively. There is remarkable enhancement on the tensile modulus of the neat matrices at different rCF and TB loadings. The tensile modulus increased from 3500 MPa up to 6000 MPa, and from 3200 MPa up to 4200 MPa for FFF printed PPS and PEI composites, respectively. The tensile strengths were almost preserved, when replacing the rCF by the TB particles for FFF printed PPS and PEI composites. This phenomenon shows that increasing TB content and decreasing rCF content had a limited effect on tensile performance of the hybrid composite system, while replacing rCF by TB particles is a cost-efficient strategy [6]. FFF printed PPS/rCF/TB and PEI/rCF/TB composites seem to present equivalent tensile performance when compared to injection molded neat matrices. The incorporation of rCF and TB compensated the reduction in tensile performece resulting from the 3D printing process.

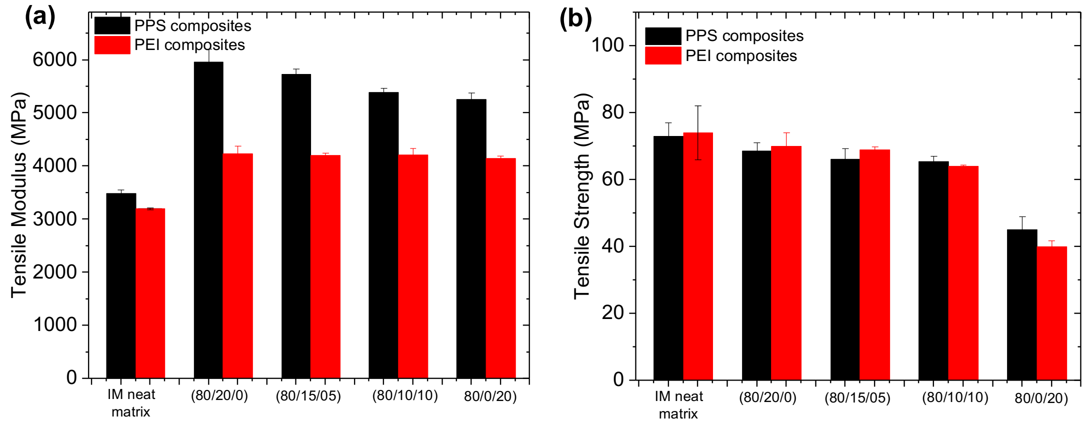

Figure 4. Tensile mechanical performance of FFF printed PPS and PEI composites and of IM neat matrices: (a) tensile modulus, and (b) tensile strength.

4 CONCLUSION

In this study, microstructural, crystallization kinetic, and mechanical properties of the PEI and PPS polymers reinforced with rCF and TB were studied for FFF 3D printed parts. Microstructural analysis has shown that the developed advanced composite filaments have a consistent dimensional accuracy and low level of porosity content of ~17 vol.% and ~10 vol.% for PEI and PPS matrices containing 20 wt.% rCF. rCF and TB particles revealed an uniform dispersion and distribution throughout the PPS and PEI matrices. Moreover, the incorporation of TB particles seems to improve fiber-matrix adhesion possibly due to similar surface characteristic of rCF and TB particles. Tensile strength and modulus of the matrices were significantly enhanced by the incorporation of 20 wt.% of rCF and the mechanical properties were kept relatively similar with the replacement of rCF by TB particles. Moreover, the tensile properties of FFF 3D printed advanced composites were found to be comparable at the injection molded specimens of neat matrices.

5 REFERENCES

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