EFFECT OF POST-PROCESSING ANNEALING ON CRYSTALLINITY DEVELOPMENT AND MECHANICAL PROPERTIES OF POLYPHENYLENE SULFIDE COMPOSITES PRINTED ON LARGE-FORMAT EXTRUSION DEPOSITION SYSTEM

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ABSTRACT

This work investigates the effect of annealing on structure development and mechanical properties of parts printed on a large-format extrusion additive manufacturing system using short carbon fiber reinforced polyphenylene sulfide (PPS). PPS, being a semi-crystalline polymer, offers the potential to alter the mechanical properties of parts with changes in crystallinity. Annealing PPS at temperatures above the glass transition and below the melting point for long hours can enhance crystallinity in the material, thereby improving the mechanical properties. However, high temperature polymers such as PPS can also undergo reactions (branching and/or crosslinking) when annealed in an oxidative environment, which further influence crystallization. This work reports the effect of annealing on the changes in crystallinity, possibility of chemical reactions taking place, melt rheological properties and thermo-mechanical properties of the chosen PPS grades.

1. INTRODUCTION

Additive manufacturing (AM) of autoclave tooling using composites of high temperature thermoplastics is advantageous to lower both, the lead time as well as manufacturing costs [1]. In addition, the use of semi-crystalline matrix enables the ability to tailor the final mechanical properties of the printed component by varying the degree of crystallinity of the polymer. Typically, for semi-crystalline polymers, increasing the crystalline fraction enhances mechanical performance at higher temperatures, even above the glass transition temperature (T_g) of the polymer for short spans [2]. In the quest to improve the final mechanical properties of the printed components, this work investigates the method of post-processing isothermal annealing treatment for parts printed on a large format extrusion deposition AM platform. Annealing semi-crystalline

polymers for long time periods at temperatures above their T_g and below their melting point (T_m) has been a method used in traditional manufacturing processes to increase the degree of crystallinity in the manufactured parts [2-4]. In this study, the chosen material system is polyphenylene sulfide (PPS) reinforced with short carbon fiber. This composite material is of interest for applications in autoclave tooling and successful large-scale prints on the Big Area Additive Manufacturing (BAAM) system with this material have been demonstrated [1]. Therefore, up on printing components on the BAAM system, isothermal annealing of the entire part at a temperature above T_g and below T_m can potentially improve the mechanical properties of the part by increasing the crystalline fraction. However, there exists another process simultaneously taking place during annealing of PPS in this temperature range. Some grades of PPS can undergo structural changes due to thermal and oxidative reactions in the form of chain branching and/or crosslinking [5-9]. Since large components printed on the BAAM system would have to be annealed in a large oven in air (or oxidative) environment, there exists a possibility of chemical changes taking place during annealing, in addition to the changes in crystallinity. The two processes can influence each other and there is a possibility of the mechanical properties depending more on the dominating process.

Therefore, the primary objective of this work has been to understand the effect of post-processing annealing on crystallinity and structure development of printed PPS/CF components, in turn relating to the changes in mechanical properties. Firstly, mechanical testing has been performed on both annealed and unannealed parts over a range of temperature to determine the effect of annealing on variations in mechanical performance at different temperatures. Next, to determine if any structural changes have occurred, annealed pellets have been subjected to melt rheological analysis (done at temperatures above T_m, thereby melting all the crystals and testing the amorphous fraction) to determine changes in viscosity due to annealing. Typically, there would be an increase in viscosity when there is an increase the molecular weight of the polymer due to branching and/or crosslinking reactions [2, 10]. Following this, the quantitative determination of the changes to the degree of crystallinity due to annealing has been performed using differential scanning calorimetric (DSC) analysis. Finally, optical microscopy has also been performed to determine changes in sample appearance due to possible reactions and if so, the extent of its impact.

2. EXPERIMENTAL

2.1 Materials

The materials used in this study are unreinforced (neat) PPS and PPS reinforced with 50 wt.% carbon fiber (PPS 50CF), both procured from Techmer ES in the form of pellets. Prior to all testing, the neat grade pellets were dried at 120 ^oC for 3 hr and the fiber reinforced grade pellets were dried at 130 ^oC for 4 hr in a vacuum oven.

2.2 Sample Preparation and Characterization Methods

Firstly, PPS 50CF walls were printed on the Big Area Additive Manufacturing (BAAM) system and samples for dynamic mechanical analysis (DMA) were cut-off from the printed walls along the x-direction (axial direction or along the print bed). The samples dimensions were ~ 60 mm x 12 mm x 3 mm. For neat PPS, DMA samples were obtained from injection molded discs. Annealing was carried out in a muffle furnace in air by heating the dried samples to 250 ^oC for 18 hr and the unannealed dried samples were used as control samples.

DMA analysis (temperature ramp) was performed on a Discovery Hybrid Rheometer (DHR-2) system fitted with torsional DMA test geometry (Figure 1a) by heating the sample from 40 ^{o}C to 250 ^{o}C at the rate of 2 ^{o}C/min in nitrogen and at a frequency of 1Hz and 0.05% strain. For melt

rheological analysis, frequency sweep tests were performed on the pellets using the same DHR-2 system fitted with parallel plates fixture (Figure 1b). Tests were performed at 337 ^{o}C in nitrogen at 0.05% strain. Differential Scanning Calorimetry (DSC) analysis of the pellets was performed on TA Instruments Q2000 system, with a heating rate of 10 ^{o}C/min in nitrogen environment and optical microscopy was done on Keyence VHX 5000 microscope.

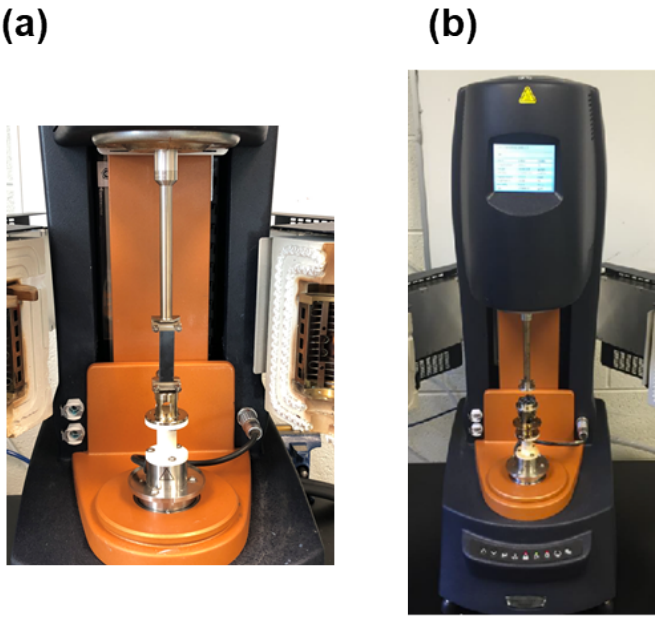

Figure 1. Experimental set-up for (a) DMA analysis and (b) Rheological analysis.

3. RESULTS AND DISCUSSION

Figure 2 (a,b) and Figure 3 (a,b) represent the variation of storage modulus (G') and damping (tan δ) with temperature for neat PPS and PPS 50CF samples respectively. It can be observed that in both cases, annealing increased the modulus, especially at temperatures above T_g (~ 97 ^{o}C) and the extent of this increase has been greater with an increase in temperature (Table 1). This can possibly be due to increased crystallinity in the sample which restrict the movement of amorphous chains even at temperatures above T_g. However, if the material crosslinks sufficiently, there is a possibility of this effect happening due to crosslinking as well. Hence to check for the possibility of any structural changes taking place, melt rheological analysis was performed.

In rheological tests, samples were tested at temperatures well above the melting temperature, thereby melting all the existing crystals and any changes in the viscoelastic properties would primarily be due to structural changes taking place up on annealing. Figure 4 (a,b) indicates the variation of complex viscosity with frequency for neat PPS and PPS 50CF respectively. Clearly, for both the materials, annealing has led to an increase in viscosity by at least an order of magnitude

across all frequencies. This indicates a possible increase in the molecular weight up on annealing due to branching and/or crosslinking reactions taking place.

With both changes in crystallinity as well as structural changes taking place in the chosen materials, there was a need to understand which mechanism possibly dominates the changes in

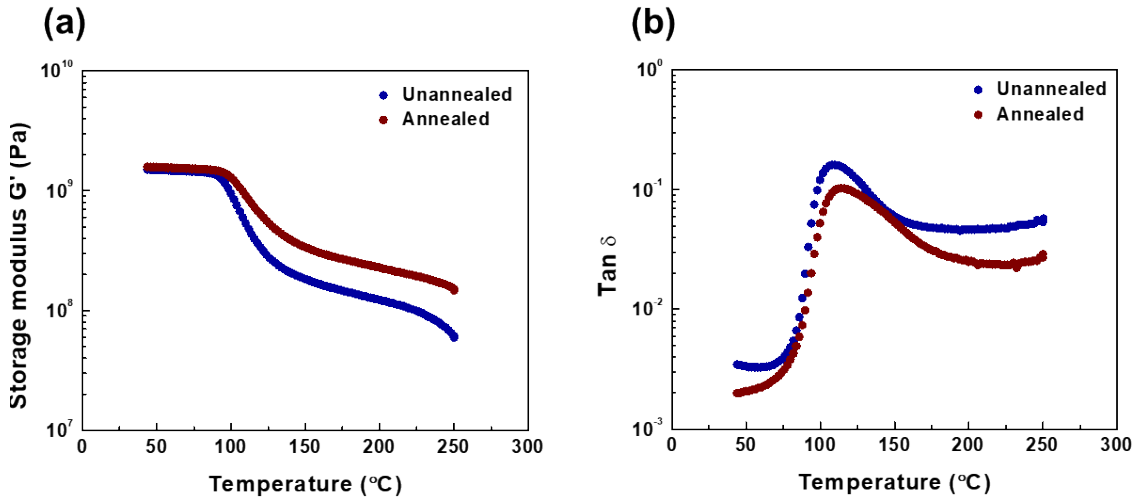

Figure 2. Variation of (a) Storage modulus and (b) Tan delta with temperature for neat PPS.

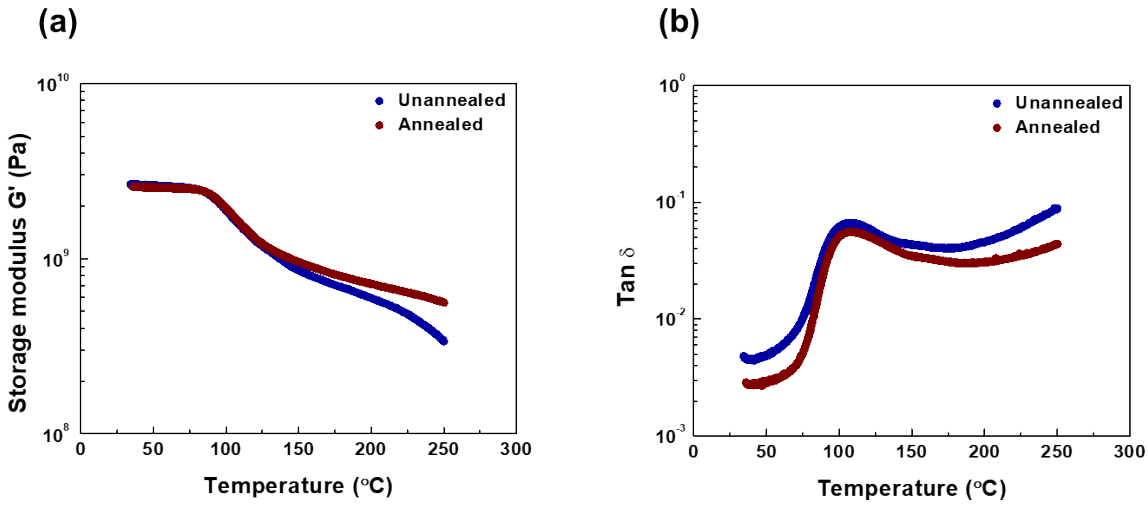

Figure 3. Variation of (a) Storage modulus and (b) Tan delta with temperature for PPS 50CF (printed).

Table 1. Effect of annealing on G' at various temperatures.

Material	G' at 50 °C (GPa)	G' at 175 °C (GPa)	G' at 250 °C (GPa)
Neat PPS- Unannealed	1.491	0.146	0.061
Neat PPS- Annealed	1.572	0.267	0.152
PPS 50CF- Unannealed	2.613	0.706	0.345
PPS 50CF- Annealed	2.544	0.808	0.561

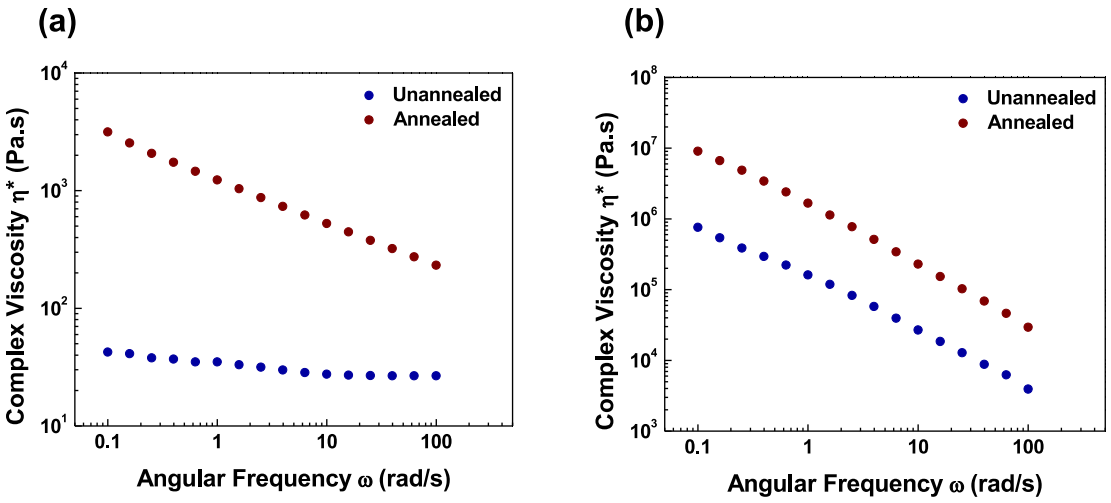

Figure 4. Effect of annealing on melt viscosity of (a) Neat PPS and (b) PPS 50CF.

mechanical properties. The degree of crystallinity of the unannealed and the annealed samples was determined by performing DSC analysis, with results from the first heating cycle as shown in Figure 5. Degree of crystallinity was calculated using Equation 1 for neat PPS and Equation 2 for PPS CF50 (accounting for filler weight fraction W_f) using a ΔH_f^o value of 77.5 J/g for PPS [2, 11].

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^o} \quad \text{(Eq. 1)}$$

$$\chi_c = \frac{\Delta H_f}{(1 - W_f)\Delta H_f^o} \quad \text{(Eq. 2)}$$

For neat PPS, annealing increased the degree of crystallinity from 0.48 to 0.67 and for PPS 50CF, annealing again increased the degree of crystallinity from 0.32 to 0.63. From DSC analysis of as-annealed samples, it is evident that annealing led to an overall increase in the crystalline fraction, thereby influencing the mechanical properties.

To check for the effect of structural changes due to annealing on the mechanical properties, cross-sections of molded neat PPS samples were observed after annealing (Figure 6). These results showed that annealing led to a change in color of neat PPS (from pale white to brown) and this color change was more confined to the surface than being throughout the bulk of the sample. This can be attributed to the oxidative nature of these reactions wherein the structural change could have occurred only in regions with the availability of oxygen. As observed, the colored region is

only about one-third of the total sample thickness. This points in the direction that the changes in crystallinity occurring throughout the bulk of the sample could be the dominant mechanism influencing the mechanical properties and the structural changes taking place could influence crystallization factors such as size of crystals (as observed by the occurrence of multiple peaks and changes in peak broadening in Figure 5).

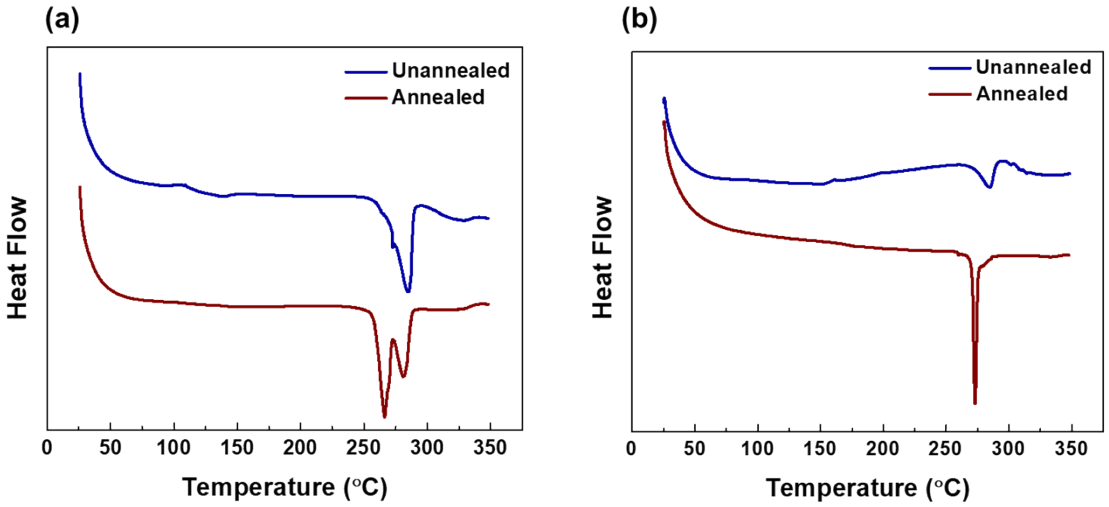

Figure 5. DSC first heating cycle for (a) Neat PPS and (b) PPS 50CF (exothermic-up).

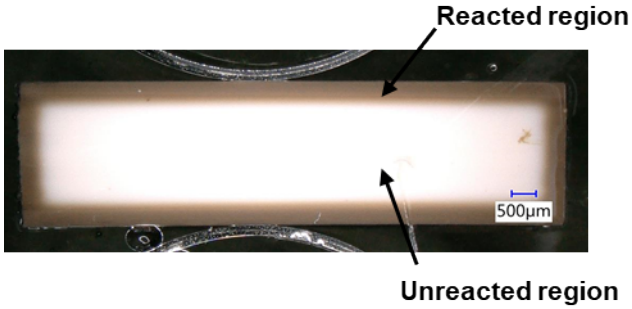

Figure 6. Optical micrograph of annealed neat PPS sample (cross-section).

Therefore, for the chosen materials, isothermal annealing has led to improved mechanical properties (storage modulus in torsion), especially at temperatures above T_g. Annealing influenced both changes in crystallinity as well as the occurrence of structural changes and overall, led to an increase in the degree of crystallinity of the materials, which could be the primary factor influencing better high temperature mechanical performance of the tested materials.

4. CONCLUSIONS

This work investigated post-processing isothermal annealing as a technique to enhance the mechanical properties of components printed on large format extrusion AM system using carbon fiber reinforced composite of PPS. Results indicated annealing to increase the storage modulus of the material (in torsion) especially at temperatures above T_g, and this trend is beneficial for

applications such as autoclave tooling which demand good mechanical properties at elevated temperatures. In addition, the possibility of structural changes taking place in PPS due to thermal and oxidative reactions was studied. Results showed that although these reactions occur, their effect is not prominent throughout the bulk of the sample and the overall increase in the degree of crystallinity throughout the sample could be the primary factor to influence changes in mechanical properties. Future work in this area involves more characterization to better validate the process influencing the mechanical properties dominantly and further understand the influence of structural changes on crystallinity development. In addition, other grades of PPS with varying carbon fiber content will also be explored.

5. ACKNOWLEDGEMENTS

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