Thermal Analysis of Thermoplastic Materials Filled with Chopped Fiber for Large Area 3D Printing

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Abstract

At room temperature, material extrusion, in the context of large area fabrication, requires thermally stable materials and, as a result, fillers are included to tailor the thermal behavior. This research investigated the thermophysical properties of neat ABS and short carbon fiber (CF) reinforced ABS. Thermogravimetric analysis, differential scanning calorimetry, and thermomechanical analysis were carried out to determine the thermophysical properties. The addition of CF (20 wt. %) to an ABS matrix caused the glass transition temperature to change slightly (110 °C to 105 °C). Also, the CF within the ABS matrix reduced the thermal stability by decreasing the degradation on set temperature by (323 °C to 253 °C). Thermal deformation analysis showed that large area pellet extruded AM machine produces highly anisotropic materials. Thermomechanical analysis results showed that the coefficient of thermal expansion (CTE) reduced 4 times in the perpendicular to the extruded direction. The dataset and knowledge from the thermal analysis can be useful to design optimized printing parameters for highly filled thermoplastics used in large area 3D printing machines.

1. Introduction

Thermoplastic material extrusion is one of the most popular AM methods because of the wide range of thermoplastic and composite materials available in feedstock. Neat thermoplastics, such as acrylonitrile butadiene styrene (ABS), polylactide acid (PLA), polycarbonate (PC), polyamide (PA), polyetherimide (PEI), and polyphenylsulfone (PPSU) etc., are the most commonly used thermoplastic feedstock materials in material extrusion AM. The impact of the printing parameters on mechanical properties is characterized by a combination of variables including printing orientation, extrusion nozzle diameter, temperature etc. However, inherent properties, such as porosity, within the printed part cause inferior mechanical strength. After realizing the lack of strength and limitations of mechanical properties of neat thermoplastics, composite materials were developed. Ning et al., 2015 [1] described composite fabrication by melt mixing ABS pellets and carbon fibers (CF) up to 15 wt.%. Mechanical characterization showed that tensile strength improved by 75% for the 5 wt.% CF. It was noted that mechanical strength starts to reduce with the further increases of CF content in the ABS material. Increased amounts of fiber content reduced the toughness, yield strength, and ductility. Dul et al., 2016 [2] reported the method and fabrication of 3D printable graphene-based ABS nanocomposite. Upon addition of 4 wt.% graphene nanoparticles (GnP), mechanical strength was improved by 30% compared to the neat ABS. Further addition of the GnP reduced the mechanical strength severely which was attributed to the poor dispersion of nano particles in the matrix materials. Tekinalp et al., 2014 [3], attempted to introduce a large amount (up to 40 wt.%) of short carbon fiber to the ABS material for 3D printing filament fabrication. Tensile and modulus results showed a 115% and 700% strength increase, respectively, compared to the neat specimen. Although they made the composite with 40 wt.% of CF, it was not possible to extrude the composite due to nozzle clogging. In the above mentioned literatures, it was found that the mixing of reinforcing fibers or particles are a promising way to improve the mechanical strength to a certain level.

The inclusion of reinforcing agents is not only important to mechanical properties but also contributes to modifying thermal properties. Love et al., 2014 [4], described the importance of including short fiber such as carbon fiber (CF) to the neat plastic materials used in large area AM by highlighting three important aspects: production rate, physical size of the part, and mechanical strength. Besides the improvement of mechanical strength and stiffness, the thermal conductivity (0.177 W/m·K for neat ABS compared to 0.397 W/m·K of CF reinforced composite) of the composite improved due to the addition of fibers. Note that, the scope of that work was also limited to a maximum of 13 wt.%. CF loading to avoid the nozzle clogging and the detrimental effects on of the mechanical properties. The improvement of thermal conductivity reduced the need of a thermal oven; which in turn reduced the propensity for part distortion by reducing the CTE [5]. However, some fundamental material properties were not investigated leaving the following questions unanswered: how are the material's thermophysical properties changed with the addition of fibers and what impact do they have when determining the successful printing window in the context of large area AM?

The development of process parameters is paramount for filled materials in the field of large-scale printing. This paper investigated the thermophysical properties of commercially available highly filled materials such as short CF reinforced ABS that is commonly used in large-scale printing. To compare and understand the results of filled material, neat ABS materials were also tested. Thermal analysis was carried out with the thermogravimetric analysis and differential scanning calorimetry instruments to produce the necessary information to determine material transition, degradation, and melting. Temperature controlled mechanical analysis was carried out with the thermomechanical analysis machine to understand the temperature dependent material properties. Authors believe that the combination of all these characterizations methods will produce a significant amount of data and generate enough information to develop a shorter processing window for filled materials as well as determine printing parameters.

2. Experimental

2.1. Materials

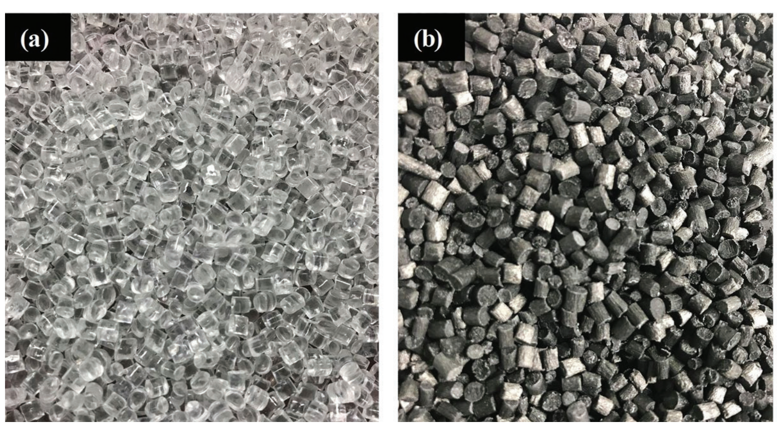

Figure 1. ABS and ABS based composite pellets (a) neat ABS and (b) ABS 20 wt.% CF

Two different types of materials were used in this study as shown in Figure 1. Neat and colorless ABS for 3D printing application was obtained from 3DXTECH Grand Rapids, MI, USA materials and ABS with 20 wt. % CF from Techmer PM, LLC. Clinton, TN, USA.

2.2 Characterization

2.2.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) were performed with a TGA 55 (TA Instruments, New Castle, DE, USA). The instrument was calibrated for temperature, heat flow, and weight according to the manufacturer's suggestions. The goal of the TGA tests was to identify the degradation onset temperature. Note that, in this study the degradation onset temperature (DOT) was defined as the temperature at which 1% weight loss occurred. Moreover, the TGA tests can determine the wt. % of the filler/fiber in the matrix materials so long as the filler does not degrade at the test temperatures and ambient gas. TGA scans were performed from room temperature (25°C) to 800 °C at a heating rate of 10 °C/min according to the ASTM Standard E1131 [6]. The sample purge was 60 ml/min and balance purge was 40 ml/min using nitrogen gas delivered at 20 psi. Samples, in the weight range of 3 to 5 mg, were placed in a high temperature platinum pan and degraded as a function of temperature; their mass loss was recorded by the TGA 55's TRIOS software. The experimental data was then used to plot weight percentage loss with respect to the temperature.

2.2.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) tests were performed to characterize glass transition, crystallinity, melting, and enthalpy of the test specimens, which were subjected to different thermal histories through 3D printing and cooling. DSC tests were performed on the as-received pellets and extruded materials of ABS and ABS 20 wt. % CF. Sample masses ranged within 2 to 3 mg when harvested from pellets and 3D printed beads. Test were performed using a DSC 250 (TA Instruments, New Castle, DE, USA) in accordance to ASTM D3418 [7]. Aluminum Tzero containers were used to seal the test specimens, ensuring the test environment was not contaminated due to the heating and cooling sequences. Initially, temperature was equilibrated at 25 °C, then held isothermally for 5 minutes. Afterwards, the temperature was then ramped at a rate of 5 °C/min from 25 °C to 200 °C. The test temperature of 200°C was chosen based on the TGA analysis to avoid sample degradation within the DSC test chamber. TRIOS software was used to record the time, temperature, heat capacity, and heat flow at a sampling rate of 10 Hz.

2.2.3 Thermomechanical Analysis

A TMA Q400 (TA Instruments, New Castle, DE, USA) was used according to the ASTM E831 standard [8]. The coefficient of thermal expansion (CTE) was measured in dilatometric mode with a small load of 0.02 N over the temperature range of 25 °C to 120 °C while using a heating rate of 5 °C/min. The test temperature was limited to 120 °C as higher temperature testing could melt the test specimen and contaminate the quartz probe. The test specimens were cut to sample size with dimensions of length and width being between 3 and 5 mm, thus the surface area was limited to 25 mm^2 and thickness of 3–6 mm.

Due to the fibers being orientated along the extrusion direction, thermal expansion and contraction was anisotropic and dependent on fiber directions. Hence, the tests were conducted in two directions: longitudinal (fiber direction) and the transverse direction. The tests specimens were

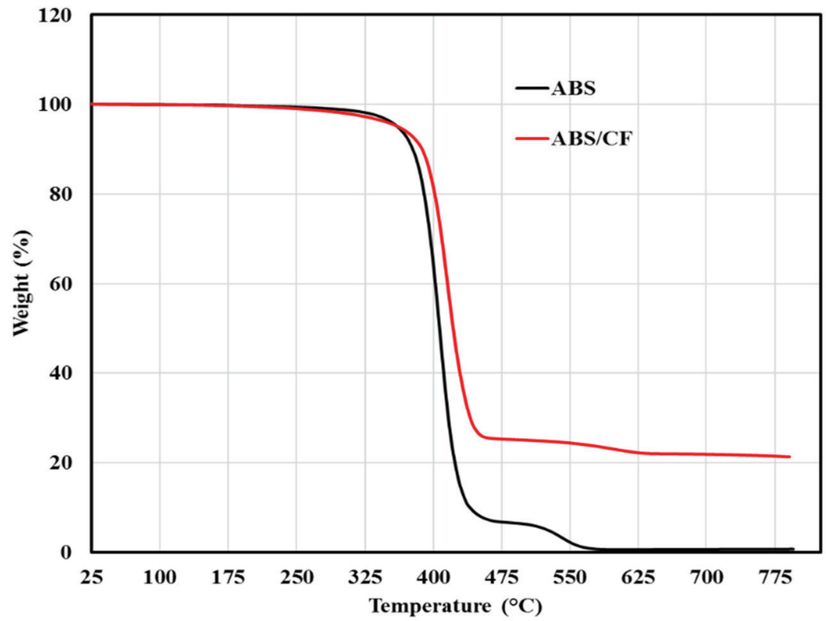

Figure 2. Thermogravimetric analysis of neat ABS and CF reinforced materials

harvested from BAAM printed beads and five specimens were used in each direction. Note that, each test specimen was used for one single test to obtain consistent results and test reliability.

Results

3.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out to investigate the effects of the fiber content on the thermal behavior of ABS based composites. Figure 2 shows the TGA curve of ABS and ABS with 20 wt. % CF. In case of the neat ABS, degradation occurs in two steps; fiber reinforced ABS also exhibit this behavior i.e. where two major stages of weight loss are observed. The first stage started in the range of 300 °C and ended at about 450 °C, corresponding to the structural decomposition of the ABS polymer. The second stage started around 450 °C and ended at around 480 °C, which indicates the combustion of residual material. In materials extrusion AM it is important for a material to become thermally stable to obtain the desired dimensions of the printed object.

The introduction of chopped CF into the ABS material reduced the thermal stability. To determine the thermal stability of the composite, decomposition onset temperature (DOT, defined as the 1% reduction of the weight) was identified from each test. In the case of 20 wt. % CF, DOT was found at 253 °C while the neat ABS had a DOT of 323 °C. Mixing chopped carbon fiber with ABS matrixes increased the thermal mobility of the composite material. As CF was introduced into the neat ABS, the reduction of DOT implied that the thermal energy dissipated by the composite has a path to conduct. Carbon fiber is superior to ABS in its ability to conduct thermal energy (thermal conductivity of CF is 1800W/m·K while the ABS has 0.18 W/m·K) thus the thermal gradient within matrix and fiber becomes higher, making the composite thermally

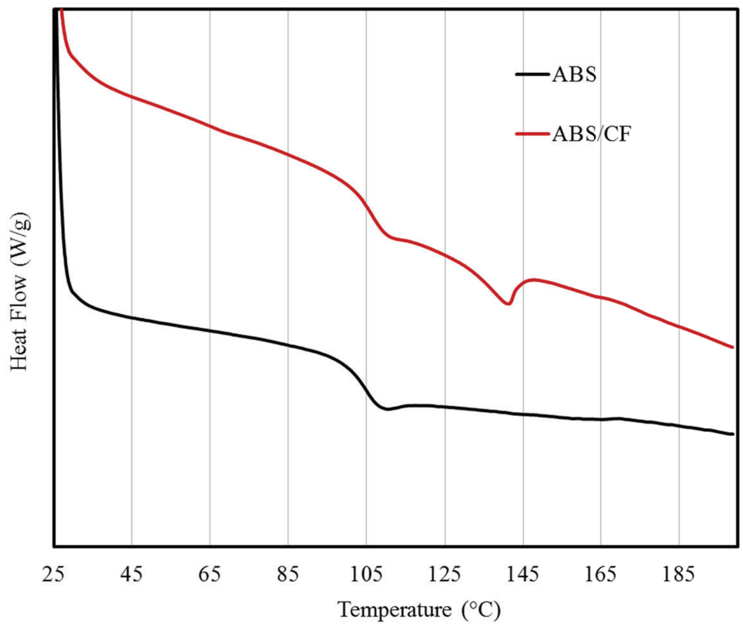

Figure 3. DSC thermograms of ABS and ABS based composite

unstable. Moreover, the thermal gradient within the composite helps to extrude the specimen at a relatively low temperature and extrusion force.

3.2 Differential Scanning Calorimetry

DSC tests were performed to investigate the thermal properties such as glass transition (Tg) temperature. Figure 3 shows the thermograms of DSC tests for ABS and ABS based short 20 wt. % CF reinforced composite. In the case of neat ABS, there was a transition in the thermogram at 110 °C which is known as the glass transition temperature. It represents the transition from the glassy phase to the rubbery phase. As the ABS is amorphous, there is no definite melting temperature. The endothermic peak around 140 °C rather, represents the melting of processed materials that were used to mix SAN and butadiene copolymer. Reed et al. [9] confirmed that the mixing of mold lubricant during ABS production remains within the ABS matrix. Moreover, some unknown chemicals are used by the manufacturer to reduce the viscosity and narrow down the extrusion/compression parameters. Thus, the melting temperature of 140 °C can be attributed to the melting of processing materials that are used during composite production.

The addition of CF to the ABS matrix had a slight impact on the polymer chain mobility. The Tg of 20 wt. % CF based ABS was found at 105 °C which was lower than the neat ABS at 110°C. Increased chain mobility due to the conductive fibers within the matrix material reduces the glass temperature. In other words, the chopped fibers contributed to the enhancing of the thermal mobility of the polymer chain; thus, at relatively lower temperature matrix, materials transformed from the glassy to the rubbery phase.

3.3 Thermomechanical Analysis (TMA)

In material extrusion AM, sudden temperature changes happen during and after the extrusion. Sudden changes of temperature can cause thermal expansion or contraction which is

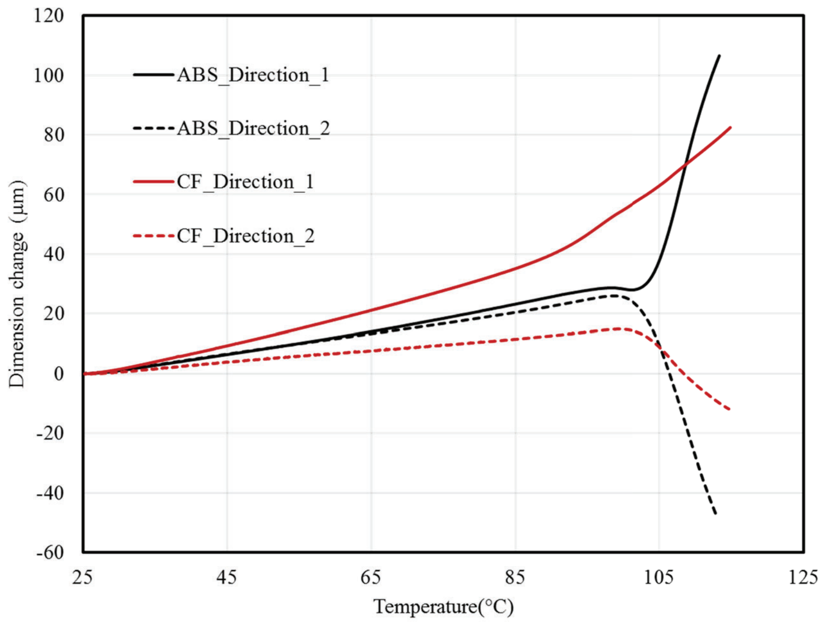

Figure 4. TMA thermogram of ABS and CF reinforced ABS

known as thermal deformation. It is desirable to reduce the CTE value of 3D printing materials to avoid the occurrence of thermal stress. Figure 4 shows the TMA thermogram of neat ABS and CF reinforced ABS. Two distinct regions in the graph are noticed before and after the transition. The linear CTE value was calculated before the transition. In general, ABS/CF has a lower thermal expansion compared to neat ABS. As the temperature increased, changes in the dimensions of the specimen also increased. However, after the transition region, the ABS/CF composite showed relatively larger expansion than the ABS in direction 1. In the direction 1 both composites have relatively large amounts of CTE values as listed in table 1. Lower values of CTE in ABS/CF can be attributed due to the thermal conductivity and CF shear along the extrusion direction Love et. al., 2014 [4].

Table 1. Linear thermal expansion as a function of direction for ABS based materials

Test direction	ABS (μm/m·°C)	ABS/CF (μm/m·°C)
Direction 1	94.66 ± 7.50	130.54 ± 6.5
Direction 2	92.92 ± 8.03	22.30 ± 6.93

4. Conclusion and future work

Neat and short CF reinforced ABS composite were characterized to understand their thermophysical properties. This paper depicts the technique used to thermally analyze CF reinforced ABS to determine the contribution of the fibers . Due to the superiority of the CF's thermal conductivity, the thermal instability of the ABS composite was noticed at relatively lower temperatures compared to neat ABS. Also, the chain mobility started within the composite matrix

(ABS) phase at a relatively lower temperature. Thermal expansion and shape retention are important criterion in material extrusion AM processes. As the material experiences several thermal events during heating, deposition, and cooling phases, a lower value of CTE reduces the probability of printing failure. While CF was added to the ABS filament, CTE was reduced 4 times the total amount which indicates the applicability of the composite in large scale 3D printing. In the future, dynamic mechanical analysis and rheological analysis needs to be performed to determine the printing parameters as well as how to the shorten the processing window.

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