Solid Freeform Fabrication 2022: Proceedings of the 33rd Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference
Reviewed Paper

INFLUENCE OF THE DIFFERENT MATRIX MATERIALS ON THE THERMAL PROPERTIES OF SHORT CARBON FIBER REINFORCED COMPOSITES MANUFACTURED BY FUSED FILAMENT FABRICATION

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Abstract

A considerable amount of literature has been published on the thermal properties of the short carbon fiber reinforced composites (SCFRC). However, no study has focused on the effect of the various matrix materials on the thermal properties of the SCFRC. The aim of this study is to investigate the thermal propertiesof neat and composite PETG, PC/PBT, ABS, and Nylon filled with short carbon fibers. In order to do this, thermal conductivity and thermal diffusivity of the samples were measured. Thermogravimetric and differential scanning calorimetry analyses were performed to study degradation, glass transition temperature, and specific heat value. The findings of the study are essential in reporting the relationships between the SCFRCs and commonly used polymer materials.

Keywords: Fiber Reinforced Additive Manufacturing, Short Carbon Fiber, Fused Filament Fabrication, Thermal Properties, Thermal Characterization

Introduction

Additive manufacturing (AM), also known as 3D Printing, is a manufacturing process where the material is often added layer-wise compared to subtractive manufacturing like traditional machining. Fused Filament Fabrication (FFF) is one of the AM methods. It uses a heated extruder and nozzle to extrude polymers for the deposition of new material [1]. But FFF faces different thermal challenges; thermal gradients created during the printing process cause thermal stresses, distorting the ready parts [2, 3]. There is a lack of literature about the thermal properties [4, 5, 6] of various materials used in FFF, ranging from neat polymers such as acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polybutylene terephthalate (PBT), a mixture of PC and PBT (PC/PBT), nylon, polyethylene terephthalate glycol (PETG) to polymers mixed with continuous and short carbon fibers (CF). The addition of filler materials to the polymers affects their thermal properties. Elkholy et al. [7] examined the influence of different fillers (aluminum, copper, brass, and carbon fiber) on the thermal conductivity of the polylactic acid (PLA) in various directions. It was revealed that thermal conductivity increases incredibly with adding the fillers, particularly 26% in the z-direction and 162% in the y-direction compared with the pure PLA. Another study conducted by Pibulchinda et al. [8] investigates the deformation

of the virtually printed short CF and glass fiber (GF) reinforced polyamide (PA) with three different fiber orientations. The authors used UU geometry for the study. They found two primary deformation mechanisms whose main reasons were thermal expansion and stiffness of the material [9]. Shemelya et al. researched the thermal conductivity of ABS compounded with silver micro-spheres, silver flakes, graphite flakes, and carbon fibers. According to the measurement results, graphite increased the thermal conductivity most across and along the printing direction, 28% and 134%, respectively. Ankit et al. [10] performed thermal conductivity and specific heat value analysis of short CF reinforced PC with fiber concentrations of 3%, 5%, and 10% by volume. He found out that both thermal properties increase with an increase in fiber percentage.

Some studies focused on the thermal characterization of the filler reinforced polymers. Billah et al. [4] did a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis of the short CF, GF reinforced ABS, as well as ABS itself. They determined that CF decreased the ABS's degradation onset temperature (DOT) by 16 ℃; however, GF did not affect it at all. DSC analysis showed that carbon fibers increased the glass transition temperature (T_g) more than glass fiber due to increased chain mobility. Quintana et al. [11] conducted TGA and DSC analysis on neat ABS, PC, PETG, short CF ABS, CF PC, and GF PETG. For ABS, the DOT was the same as the inclusion of short CF, but PC and PETG experienced a 30 ℃ and 12 ℃ drop in DOT with the inclusion of CF and GF, respectively. According to the DSC results, however, CF increased the T_g of ABS by 2℃, but in PC and PETG, the fibers decreased the T_g of the neat polymer. Ankit et al. [10] did TGA, creep, and DMA experiments on short CF reinforced PC with a fiber content of 3%, 5%, and 10 % by volume fraction. According to the experimental results, thermal degradation temperature, loss, and storage modulus, and creep resistance increase at high temperatures with increasing amounts of short CF percentage. Mohammadizadeh et al. [12, 13] carried out TGA, DMA, and creep analyses on Nylon with different continuous fibers such as CF, GF, and Kevlar. They concluded that fibers delay the onset degradation temperature, reduce creep, and improve thermal properties. Adeniran et al. [14] investigated the effect of matrix materials in ABS and PA composites reinforced with 15% carbon content. Their study concentrated on mechanical influence, excluding the DSC analysis. The CF-PA showed better thermal stability performance than CF-ABS.

The previous publications focused on the influence of the different filler (fiber) types on the same matrix material. Then they determined either the best thermal properties or TGA/DSC analysis with the variation of fiber concentration/type. To the author's best knowledge, nobody did research on the complete thermal characterization of the composites by varying matrix materials keeping the carbon fiber content the same. Therefore, this study focuses on the thermal characterization of the short CF reinforced composites by varying the matrix material.

Materials and methods

Material selection

The materials used in this study are the neat polymers-ABS, Nylon, PC/PBT, PETG, and their short carbon concentrations by 10% weight. All materials were obtained by Push Plastic, Springdale, Arkansas.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was done with the Discovery Simultaneous Differential Scanning Calorimeter/Thermogravimetric Analyzer – SDT 650 (TA Instruments, New Castle, Delaware, USA). The main experiment parameters are shown in table 1 and carried out according to the ASTM Standard E1131. Experiment results were recorded and analyzed in the TRIOS software of the manufacturer company.

Table 1. TGA experiment details

Mass of samples (mg)	**Temperature ramp rate (℃/min)**	**Maximum temperature (℃)**	**Balance flow rate (ml/ min)**	**Sample flow rate (ml/ min)**	**Pan size ($microliter$)**	**Pan material**
8 to 15	10	600 to 800	40	60	90	Alumina

Differential scanning calorimetry analysis

Samples were prepared according to ASTM D3418-21 and placed on the DSC 250 (TA Instruments, New Castle, Delaware, USA). Each was weighed on Mettler Toledo Analytical Balance (resolution 0.1 mg). The mass range of the samples was 7 to 12 mg. To prevent the contamination of the machine, test specimens were sealed with T-zero pans and lids. The specimens were firstly equilibrated at 25 C for 5 minutes, then heated up to 300 C (according to the results of the TGA to prevent the degradation) with a temperature ramp rate of 5 C/min and then kept isothermal at 300 C for 5 minutes. Afterward, the cooling process started at 5 C/min till 25 C, completing the heating-cooling cycle. This cycle is repeated three times to eliminate the moisture effects in the experimental procedure.

Thermal conductivity measurements

KD2 Pro Thermal Properties Analyzer (Decagon Devices, Inc., Pullman, Washington) was used to measure the thermal conductivity of the materials. The samples were printed by a Stacker 3D S2 printer (STACKER, LLC, Minneapolis, Minnesota) according to the printing settings recommended by the company. The dimensions of the samples are shown in figure 1. The holes are used for inserting the needle sensors of the KD2 Pro, where one sensor is used for heating and the other for measuring the temperature variation with respect to time. The diameter of the holes is 1.3 mm, the spacing between them is 6 mm, and the depth into the specimen is 30 mm. To increase the accuracy of the thermal conductivity measurements, thermal grease was used, and to prevent any heat losses from the tip of the needles, the length of the samples was 3d printed as 45 mm with extra 15 mm insulation layer. The thermal conductivity was measured in 2 directions along and across the fibers, as shown in figure 2.

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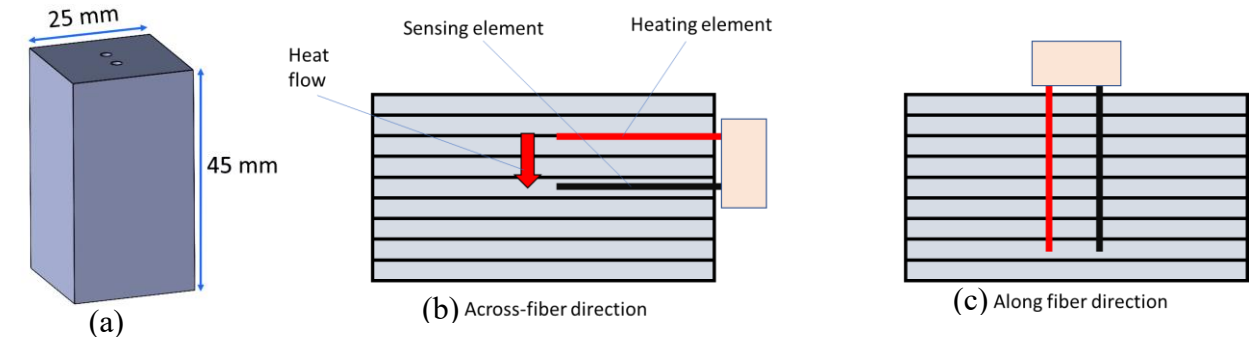

Figure 1. Thermal conductivity measurement setup, (a) CAD dimensions of the sample, (b) experimental setup for measuring the conductivity across the fiber direction, (c) and along the fiber direction.

Scanning Electron Microscopy (SEM) analysis

SEM imaging was performed by Hitachi SU7000 Ultra-High Resolution FE Scanning Electron Microscope equipped with EDAX Octane Elect Detector and APEX software. SEM imaging will alow to compute the fiber dimensions and see the orientations/alignment in the matrix material.

Results and discussions

Analysis of TGA results

TGA analysis was performed to understand the thermal degradation behavior of polymers and composites. Figure 2 indicates the TGA results. All materials except PC/PBT show single-stage degradation behavior. The remaining mass percent at the critical temperature for CF Nylon and CF ABS is about 10%, as stated by the manufacturer. However, for the CF PETG, it is 13.78%,

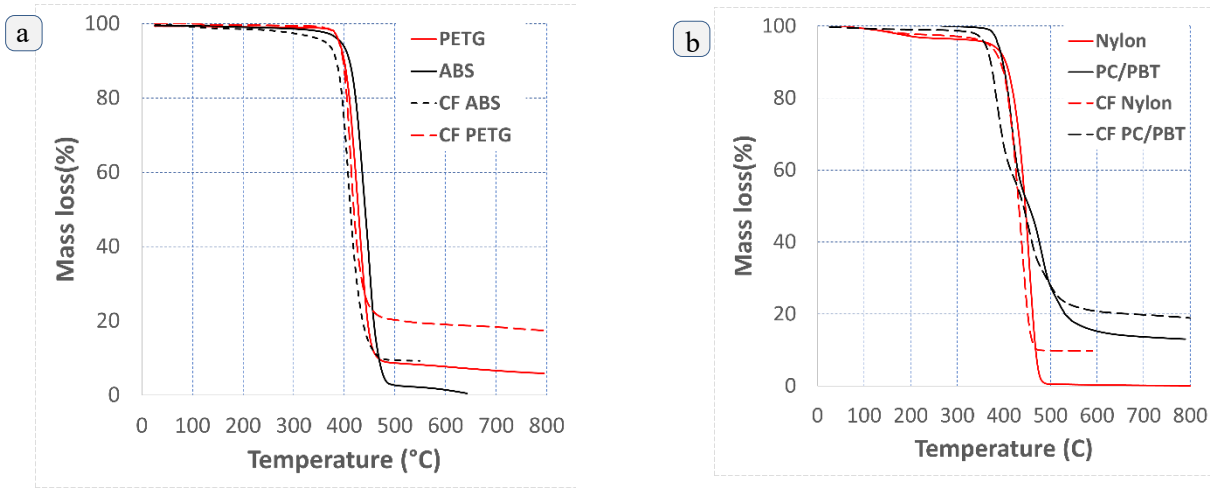

Figure 2. TGA results of a) PETG, ABS and CF versions b) Nylon, PC/PBT and CF versions

and CF PC/PBT is 17.83%. For the neat polymers, ABS and Nylon degraded completely. Still, for PETG and PC/PBT, the remaining mass percent is 5.83% and 13%, respectively.

The addition of carbon fiber decreased the onset degradation temperature as shown in table 2. The least affected matrix materials are PETG and ABS. But the PC/PBT experienced a 12 ℃ drop in glass-transition temperature, and Nylon encountered a 30 ℃ drop in its onset degradation point.

Table 2 TGA results with the remaining mass at the end of the experiment

Name of the material	Degradation temperature (℃)	Remaining mass percent (%)
ABS	402.31	0.5
CF ABS	393.15	8.23
PETG	405	5.83
CF PETG	398.35	13.781
PC/PBT	382.2 and 450	13
CF PC/PBT	381.58 and 426	17.83
Nylon	411.86	0
CF Nylon	381.58	9.7

Analysis of DSC results

Like the TGA experiment, the glass transition (T_g) and melting point (T_m) decreased with the addition of the carbon fibers. In case of ABS, this decrease is minimum (3 ℃) but for PETG the decrease is about 9℃ which is the maximum among the experimented materials. Nylon has semi-crystalline structure and thus, both glass transition and melting temperature have been shown. The results are given in table 3.

Table 3 Glass transition temperatures after DSC

Name of the material	Glass transition/Melting temperature (℃)
ABS	105.5
CF ABS	102.46
Nylon	47.27
CF Nylon	45.70
Nylon ($T_{melting}$)	178.7
CF Nylon ($T_{melting}$)	174.92
PETG	77.87
CF PETG	68.99
PC/PBT	110.48
CF PC/PBT	104.45

Since thermal conductivity has been calculated very close to 33 ℃, the average specific heat values of the polymers and their short CF composites are also calculated at that temperature. This will allow using one prescribed temperature value to evaluate the thermal diffusivity.

Table 4. Specific heat values and change is shown in percentage

Name of the material	Specific heat value ($\frac{J}{gC}$) at 33 ℃
ABS	1.074
CF ABS	0.984 (8.37%)
Nylon	1.152
CF Nylon	1.11 (3.65%)
PETG	0.888
CF PETG	0.882 (0.68%)
PC/PBT	0.846
CF PC/PBT	0.882 (4.25%)

In all cases, except PC/PBT, carbon fiber decreases the specific heat value because CF has much higher thermal conductivity than plastic material. Therefore, more heat is required to increase the temperature by one 1 ℃ due to the higher energy dissipation.

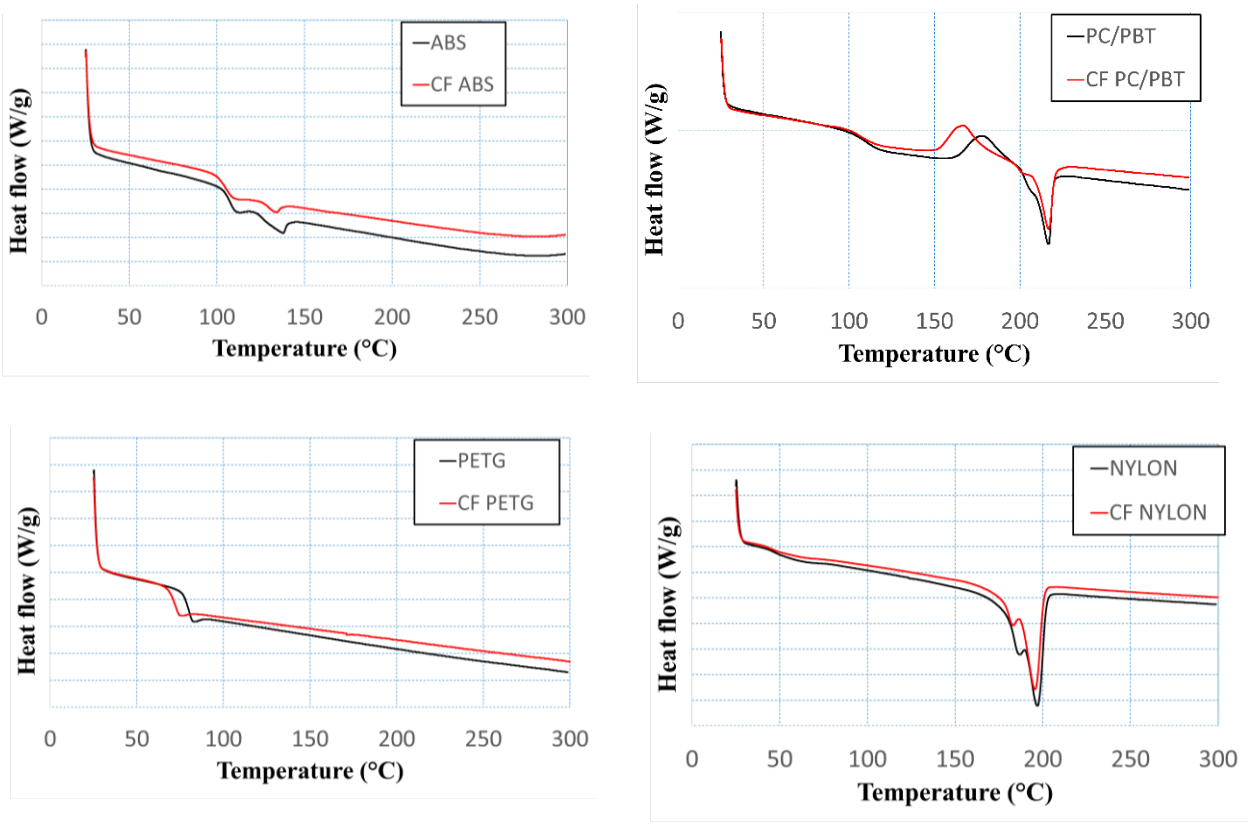

Figure 3 DSC curves of the polymers and their short carbon fiber composites. The name of the material is shown on the top right of the curve.

In the PC/PBT case, the inclusion of the CF does not decrease the specific heat value however increases, but later CF starts to influence by reducing the specific heat value (for example,

at 90 ℃, it drops from 1.146 $\frac{J}{g\,C}$ to 1.134 $\frac{J}{g\,C}$). This effect of CF is stronger for the temperature ramp rate of 5 $℃/min$.

Thermal conductivity and diffusivity measurements

Two print buildup directions were chosen to show the effect of fiber orientation on the samples' thermal properties. For each direction, thermal conductivity values were calculated in the temperature range of 25 to 33 ℃. The small temperature range will not cause any significant errors since properties can be assumed as constant in that range. The tables above show that across-fiber properties are lower than the along-fiber direction. The measurement results are shown in Table 5, and an increase in thermal conductivity is shown in percentage compared with the neat polymers. The results show that the heat conductivity across the fibers is less than the along with them. The increase in thermal conductivity across and along the fibers is maximum with a value of 78 % and 42%, respectively. On the other hand, the thermal conductivity increase is minimum for CF-PC/PBT in an out-of-plane direction (about 14 %). This analysis may need a further investigation of the microstructure analysis to understand the bonding between fibers and matrix materials.

Table 5. Thermal conductivity results in percentage change

Name of the composite	**Along the fibers ($\frac{W}{m^2℃}$)**	**Across the fibers ($\frac{W}{m^2℃}$)**
CF-ABS	0.221 (78%)	0.176 (42%)
CF-PETG	0.263 (51%)	0.195 (34%)
CF-PC/PBT	0.258 (53%)	0.197 (14%)
CF-Nylon	0.293 (52 %)	0.260(16%)

The thermal diffusivity of the samples is also measured using the specific heat value results from the DSC using the formula below

$$\alpha = \frac{k}{c_p \rho}$$ where ρ is the density of the material

To find the material's density, the filament section's mass has been measured and divided by the volume of that given section. CF-ABS had the maximum increase in its thermal diffusivity value in the amount of 93% in the fiber direction and 54% across the fiber direction. The reason is that the fiber alignment helps transfer heat by more solid contacts and, therefore, decreases the thermal resistance created by the plastic matrix material.

Table 6. Thermal diffusivity values with percent change

Name of the composite	**Along the fibers ($10^{-7}\ m^2/sec$)**	**Across the fibers ($10^{-7}\ m^2/sec$)**
CF-ABS	2.64 (93%)	2.10 (54%)
CF-PETG	3.07 (54%)	2.28 (14%)
CF-PC/PBT	3.15 (46%)	2.40 (11%)
CF-Nylon	2.88 (59 %)	2.55 (41%)

SEM imaging

The size of the short carbon fiber is indicated in figure 5. It has a diameter of 9.92 micrometers and a length of 146 micrometers. According to the SEM image, the fibers are mostly aligned in the extrusion direction.

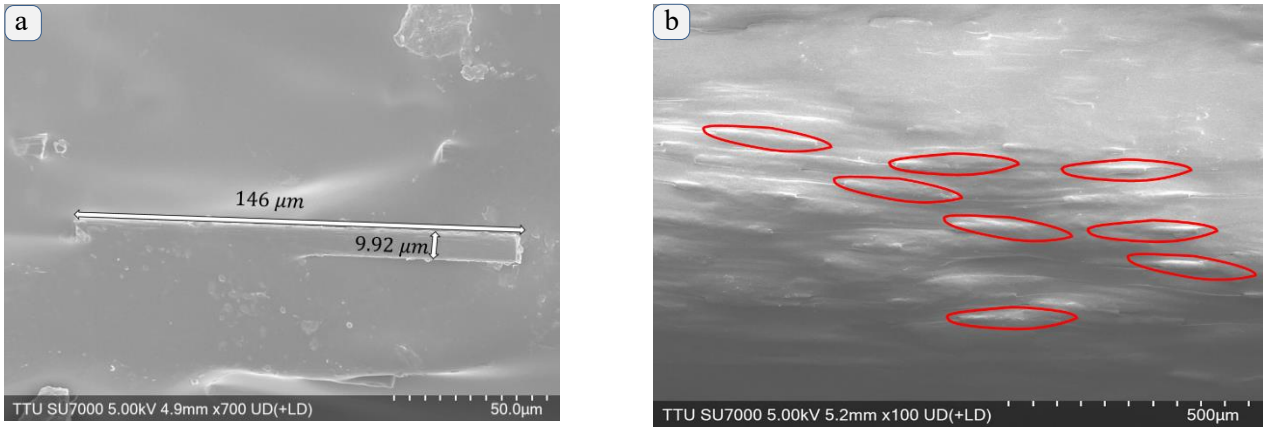

Figure 4. Microstructural analysis using SEM, (a) Size of the short carbon fiber, (b) alignment of the fibers with horizontal print direction

Conclusion

The influence of the different matrix materials with the same short CF concentration has been investigated, and its partial thermal characterization (TGA and DSC) results are shown. The values have been compared with the neat polymers to find the optimum matrix material from the selected experimental ones. It can be concluded that

- The onset degradation temperature of Nylon decreased the most with the addition of CFs.
- According to the DSC results, the glass transition temperature of all polymers dropped, and PETG had the maximum drop of 9 ℃.
- The highest increase in specific heat value, thermal conductivity, and thermal diffusivity occurred with ABS after the addition of CFs, which shows the better bonding between them and greater solid connection of the fibers with each other.

- Print direction aligns the fiber on the analyzed surface due to shear flow in the extruder which is also proven by the SEM imaging. Computer tomography scans are required to observe the internal material structure and fiber orientations.

For future work, thermal simulations are required to predict and compare the values with the experiments. Also, more microstructural analysis is necessary to see the interaction between fiber and matrix materials.

Acknowledgments

This project has been funded by the Carnegie Fellowship of the College of Engineering. The authors greatly appreciate this funding.

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