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Influence of the matrix material on the thermal properties of the short carbon fiber reinforced polymer composites manufactured by material extrusion

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the printed parts.

ARTICLE INFO ABSTRACT Keywords: In the past decades, additive manufacturing field has moved from prototyping to industrial applications. In this Material extrusion regard, the development of the new materials and their characterization is gaining importance. Most of the Fused filament fabrication previous studies focused on the effect of fiber concentration and orientation on the material properties. However, Thermal properties the influence of the matrix material on composite thermal properties is not considered extensively. Therefore, the Thermal characterization aim of this study is to investigate the thermal properties of the short carbon fiber reinforced polymer composites Short carbon fiber by varying the matrix material. The techniques included the Thermogravimetric Analysis (TGA), Differential Fiber-reinforced composites Scanning Calorimetry Analysis (DSC), Thermo-mechanical Analysis (TMA) and Laser Flash Analysis (LFA). According to the results, matrix material has high impact on the thermal conductivity and coefficient of thermal

1. Introduction

Additive Manufacturing (AM) is the preparation of parts in a layerby-layer fashion with advantages of low cost, less material weight, and minimization of wastes. In addition, tools, molds, and fixtures are not often used in AM machines, therefore does not need large working space, [1–3]. AM, also known as 3D printing, has primarily focused on prototyping in the past decades and nowadays, it is transitioning into end use functional parts. Fused Filament Fabrication (FFF) or Fused Deposition Modeling (FDM) is one of the most widely used AM methods due its lower cost, ease of operation and reproducibility [4,5].

FFF uses a range of materials such as metals, ceramics, thermoplastics, composites [6,7]. Commonly used ones are thermoplastics and fiber reinforced versions [8]. The composite materials have better mechanical and thermal properties than their neat polymer counterparts due to their lightweight, high dimensional stability, increased strength/stiffness values and resistance to corrosion [9–13]. To use these pros, continuous and short fibers are widely used in AM. Material extrusion with a continuous fiber is an open research topic [11], due to many challenges including the need for a modified nozzle to accommodate the fiber [14], limitations in manufacturing parts with complex geometry [11] and difficulties in ensuring good wetting between the matrix and the fiber [15].Thus, this research concentrates on the short carbon fiber reinforced composites and enhancement of their printability.

expansion, whereas the variation of the glass transition temperature and specific heat capacity is not changing significantly compared to the neat polymer. The study can be used as a design guideline to increase the quality of

Main challenges during FFF process are the residual stresses created during the printing process, distortion (warping, delamination etc.) of the parts and anisotropic thermal/mechanical properties due to addition of fibers [12,16,17]. In addition, the available thermal characterization data for FFF are limited and mostly reliant on trial-and-error approach [9,14,18,19]. Therefore, for load-bearing and high-temperature applications of this FFF technology, careful material characterization is required as presented in Fig. 1. According to the Figure, in (FFF), two critical temperature values are the glass transition temperature (T_g) and degradation temperature (T_{deg}). When polymers are below T_g , they lack bonding between layers but maintain a stable structure. However, once T_g is surpassed, the polymers begin to bond, but there is a risk of structural instability due to low viscosity. As the temperature approaches T_{deg} , the polymer starts to decompose, making it unsuitable for

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Fig. 1. Process window criteria for FFF printing (inspired by [20]).



Fig. 2. Thermal characterization roadmap.

use in additive manufacturing. Thus, it is essential to thermally characterize these materials and prevent the printed parts from experiencing structural instability during and after the printing process.

The chart in Fig. 2 shows the roadmap for the study which is complimentary to Fig. 1. Differential Scanning Calorimetry (DSC) allows to find the minimum processing/printing temperature and Thermogravimetric Analysis (TGA) measures the maximum temperature for the filaments. Thermomechanical (TMA) and Laser Flash Analysis (LFA) determine the thermal properties of the printed parts.

The well-known FFF materials are Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC), Polybutylene Terephthalate (PBT), mixture of PC and PBT (PC/PBT), Polyamide (Nylon), Polyethylene Terephthalate Glycol (PETG), Polylactic Acid (PLA) and their composite counterparts. Billah et al. did study on the thermal characterization of the materials used for Large Area Additive Manufacturing. The authors used 20 % weight short carbon fiber (SCF), 20 % weight short glass fiber

(SGF) reinforced ABS, as well as pristine ABS for TGA, DSC, TMA, and Dynamic Mechanical Analysis (DMA) studies. According to the results, the fibers don't show consistent behavior for chain mobility and sometimes it may even increase the thermal properties opposite to the expectation [19]. A similar study was done by Quintana et al. for again Large Area Additive Manufacturing materials of ABS, SCF ABS 20 % weight, PC, SCF PC 25 % weight, PETG, SGF PETG 30 % weight. The research team also developed Gaussian functions to fit the coefficient of thermal expansion curve versus temperature [21]. Gavali et al. studied the TGA and DSC behavior of PLA versus SCF PLA by varying the SCF weight % as 12, 15 and 20 [22]. Liao et al. studied the crystallization, degradation and thermal conductivity change of PA material with SCF inclusion of 2, 4, 6, 8 and 10 % weight. According to their findings, carbon fiber increases crystallization and degradation temperature. Likewise, Bhandari et al. did DSC study on PLA versus 20 % weight SCF PLA, PETG vs 20 % weight SCF PETG and studied the influence of

Table 1

Printing parameters for the experiments.

Parameter name	Value								
Print speed (mm/s)	10 mm/s for LFA	10 mm/s for LFA and 20 mm/s for TMA							
Layer height (mm)	0.1 mm	0.1 mm							
Layer width (mm)	0.2 mm								
Nozzle diameter (mm)	0.4 mm	SCF ABS	Nylon	SCF Nylon	PC/PBT	SCF PC/PBT	PETG	SCF PETG	
	245	240	240	240	220	220	240	240	
Bed temperature for LFA (°C)	85	70	75	75	70	70	75	75	
	255	255	275	275	275	275	250	250	
Bed temperature for TMA (°C)	110	110	80	80	100	100	90	90	

Table 2

TGA experiment parameters.

Mass of samples (mg)	Temperature ramp rate (° <i>C/ min</i>)	Maximum temperature (° <i>C</i>)	Balance flow rate (<i>ml</i> / min)	Sample flow rate (<i>ml</i> / min)	Pan size (<i>microliter</i>)	Pan material
8 to 15	10	600 to 800	40	60	90	Alumina

annealing temperature with and without inclusion of the fibers [23]. Love et al. measured the coefficient of thermal expansion and thermal conductivity of ABS and short SCF ABS 13 % weight. The researchers found out that both properties are positively influenced in the fiber direction but across the fiber direction, the values are either close to the neat polymer value or less [24]. Hassen et al. investigated the thermal conductivity and specific heat variation of the BAAM materials of SCF ABS 20 % weight, Polyphenylene Sulfide (PPS) SCF 25 % weight and Polyphenylsulfone (PPSU) SCF 50 % weight using Transient Plane Source Technique. According to the measurements, all materials followed linear behavior in the range of 20–180 °C. The alignment of the CF which gave rise to anisotropy was also considered, and the variation of the properties were compared with neat polymers [25].

Some studies focused on the mechanical behavior of thermoplastic composites due to matrix influence. Adeniran et al. investigated the influence of the matrix material on the mechanical performance of the composite parts. The study was extensive including tensile, compressive, and flexural behavior of the matrix materials. The research team used SCF PA and SCF ABS with 15 % weight and included a limited study of DSC analysis on the parts, specifically degree of crystallinity and phase change behavior [26]. Another study has been done by Albert et al. to investigate the effect of the matrix material on the impact behavior of the composites of ABS, PLA, PC, PA and PETG reinforced with 15 % weight short SCF (only PA had 25 % weight SCF). They varied the raster angle and build direction as well resulting in 15 different samples to be printed and molded. The study did not include the thermal analysis of the parts [27].

According to the reviewed literature, the previous studies are either focused on the influence of the variation of fiber types/concentrations or mechanical impact of the matrix material on the composites. Therefore, the main goal of this study is to present a detailed analysis of the matrix material effect on the thermal properties of the composites. Furthermore, the extensive study done on the short carbon fiber reinforced composites will provide an input library for the thermal simulation of the FFF.

2. Materials and methods

2.1. Materials

The material analyzed for the research is ABS, PETG, Nylon and PC/ PBT with and without short carbon fibers. The selected materials are widely used in FFF as said before and, these matrix materials are amorphous (ABS, PETG, PC) and semi-crystalline (Nylon, PBT) allowing to see the impact of the chain morphology. To have consistency in the analysis, the SCF used in all materials are the same grade and in the same amount of 10 % weight. SCF concentration has been selected 10 % because this is the widely used material in FFF and, it is close to the threshold limit of ductile to brittleness transitions [28].The filaments were supplied by Push Plastic, Springdale, Arkansas. In addition, the same polymers were extruded in neat and composite case. Before the analysis, the polymers were dried for at least 48 h in relevant temperature and dry environment. For printing the samples, Prusa i3 MK3S+ (Prusa Research, Prague, Czech Republic) was used with its slicing software PrusaSlicer. The printing parameters are shown in Table 1 and based on trials to get high quality part. Trial-and-error approach in addition to following the manufacturer's recommendations were employed to determine the appropriate 3D printing settings. The LFA samples used in the study were particularly susceptible to distortion due to their small size, hence lower temperature settings have been tuned for LFA samples.

2.2. Thermogravimetric analysis

TGA is used to measure the degradation temperature of polymers and residual mass variation with respect to temperature. Because as said before, above the degradation temperature, the polymer structure decomposes, and it is not possible to print it. In addition to determine the correct amount of fiber content the material should be burnt till all the polymeric structure and other degradable additives are eliminated. 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 2 and carried out according to the ASTM Standard E1131 [29]. Experiment results were recorded and analyzed in the TRIOS software of the manufacturer company. The samples were cylindrical form with a diameter of 1.75 mm.

2.3. Differential scanning calorimetry (DSC) analysis

Glass transition temperature, melting temperature (semi-crystalline polymers), degree of crystallinity and specific heat value are some of the important parameters measured with DSC. Samples were prepared according to ASTM D3418–21 [30] 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 cylindrical samples was 7 to 12 mg with a diameter of 1.75 mm. 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 min, then heated up to 300 °C (according to the results of the TGA to prevent the degradation) with a temperature ramp rate of 10 °C/ min and then kept isothermal at 300 °C for 5 min. Afterward, the cooling



Fig. 3. Thermal conductivity measurement setup A) experimental setup for measuring the conductivity across the fiber direction, B) and along the fiber direction.



Fig. 4. TGA results of A) PETG, ABS and SCF versions, B) Nylon, PC/PBT and SCF versions.

process started till the temperature drops to 25 $^{\circ}$ C, completing the heating-cooling cycle. This cycle is repeated three times to eliminate the moisture and previous process history effects in the experimental procedure.

For specific heat capacity measurements, Modulated DSC (MDSC) method introduced in 1990's [31] has been used. The parameters were 120 s modulation period, 1 °C amplitude and 2 °C/min ramp rate. The test was initially calibrated for the sapphire disk with a mass of 26.083 mg. The cell calibration constant (K_{cell}) was calculated as

$$K_{cell}(T) = \frac{c_{p_{sapphire}literature}}{c_{p_{sapphire}, experimental}}$$
(1)

Then $K_{cell}(T)$ has been used to measure the heat capacity of the samples as

$$c_{P_{sample}} = c_{P_{sample,measured}} K_{cell} \tag{2}$$

2.4. Thermo-mechanical analysis (TMA)

It is another measurement method used for quantifying the thermal strain of polymeric samples. The sample is loaded with some force (it can be tension, compression etc.) in a temperature-controlled environment which provides the deformation as a function of temperature and time. Then the equation of linear strain which is the ratio of change in length to initial length at constrained temperature values provides the variation of the strain of the material versus temperature under fixed loading. For this study, TMA Q400 (TA instruments, New Castle, DE, USA) was used in accordance with ASTM standard E831 [32]. The temperature ramp rate is 5 °C/min with a probe force of 20 mN in dilatometric mode. Six cyclic runs for each test sample were carried out where the first run is used to relieve the residual stress in the specimen. All the test runs except the last one is carried out till glass transition temperature. The last cycle was carried out until 20 °C more than the glass transition temperature, since after glass-transition temperature properties start to show inconsistent behavior and they are mostly non-linear. In addition, above glass transition temperature, polymer matrix carry low load only having about 1 % of Young's modulus at room temperature [33]. Initial temperature for samples is 20 °C which is the room temperature. Samples were printed in cubic form of each dimension as 7.5 mm. The coefficient of thermal expansion (CTE) was measured along the printing (fiber, bead) direction and across the fiber/bead/printing direction.

2.5. Laser flash analysis (LFA)

LFA was used to measure the thermal diffusivity (α) of the samples. The equipment is Netzsch LFA457 (Selb, Bayern, Germany). During testing, argon purge gas with a flow rate of 80 mL/min was supplied to create an inert environment. The α value was recorded at 5 discrete temperature values (\sim 25 ° C, \sim 53 ° C, \sim 75 ° C, \sim 102 ° C, \sim 120 ° C) and for each temperature values, 3 measurements were taken with a temperature increment of about \sim 1 ° C. Then the average temperature and average thermal diffusivity values were calculated. The tests were in accordance with ASTM E1461 standards [34]. Samples were tested across and along the fiber (printing direction) as shown in Fig. 3.

Table 3

Degradation temperatures and terminal masses of the samples.

Name of the material	Degradation temperature (°C)	Remaining mass percent (%)
ABS	405.95	0.5
CF ABS	404.06	9.201
PETG	405	5.83
CF PETG	398.5	13.781
PC/PBT	382.2 and 450	13
CF PC/PBT	381.58 and 426	17.83
Nylon	423.55	0
CF Nylon	420.44	9.7

Cowan correction factor is used in this research [35];

$$K_{Cowan} = C_1 + C_2(T_{ratioi}) + C_3(T_{ratioi})^2 + C_4(T_{ratioi})^3 + C_5(T_{ratioi})^4 + C_6(T_{ratioi})^5 + C_7(T_{ratioi})^6 + C_8(T_{ratioi})^7$$
(3)

where C_i are the empirical coefficients given in [35] and T_{ratio} is the $\frac{T(x,L)}{T_{max}}$ values calculated at $it_{1/2}$.

Finally, the flash method for determining the thermal diffusivity with Cowan correction becomes

$$alpha_{Cowan} = \frac{\alpha K_{Cowan}}{0.138785} \tag{4}$$

The specimens were printed in circular form with a diameter of 12.7 mm and thickness of 0.9 mm. Two print buildup directions were chosen to show the effect of fiber orientation on the samples' thermal properties.

3. Results

3.1. Thermogravimetric behavior of the materials

TGA curves are shown in Fig. 4. According to the curve, only PC/PBT shows two stage degradation since SCF PC/PBT includes two matrix materials of PC and PBT. Two separate degradation temperatures indicate that the matrix materials are not miscible, and phases remain separate. The first degradation temperature is associated with the decomposition of PBT and the second one is with PC. Random scission of PBT main chains results in formation of volatile products and low molecular weight species during the pyrolysis process in the composite and therefore, creates the earlier weight loss of PBT [36]. The rest of the materials have a single stage degradation. The remaining mass percent at terminal temperature of SCF ABS and SCF Nylon are as specified by

l'able 4						
Measured	CTE	values	for	the	mater	riale

Name of the composite	Along the bead $(10^{-6} 1/ \circ C)$	Across the bead $(10^{-6} 1 / \circ C)$	Arithmetic mean $(10^{-6} 1 / ° C)$
ABS	97.73	101.15	99.44
PETG	80.60	81.65	81.13
PC/PBT	81.79	83.55	82.67
Nylon	97.58	99.63	98.61
SCF-ABS	38.99 (-60 %)	128.83 (30 %)	
SCF-PETG	26.92 (-67 %)	90.36 (11 %)	
SCF-PC/PBT	30.59 (-63 %)	111.78 (35 %)	
SCF-Nylon	30.15 (-69 %)	123.35 (25 %)	



Fig. 5. Variation of the thermal strain with temperature, A) x dir. SCF ABS and PETG, B) x dir. SCF PC/PBT and Nylon C) z dir. SCF ABS and PETG, D)z dir. SCF PC/PBT and Nylon.



Fig. 6. DSC curves of the polymers and their short carbon fiber composites A) SCF ABS, B) SCF PC/PBT, C) SCF PETG, D) SCF Nylon.

Table 5Phase transition temperature for the specimens.

Name of the material	Glass transition/peak melting temperature (°C) by DSC	Glass transition/peak melting temperature (°C) by MDSC
ABS	105.5	104.03
CF ABS	102.4	102.10
Nylon	47.27	49.63
CF Nylon	45.70	48.68
Nylon	186.37/196.81	187.43/196.06
(I _{melting}) CF Nylon (T _{melting})	182.72/195.68	185.79/196.35
PETG	77.87	75.83
CF PETG	70.10	74.90
PC/PBT	110.48	106.21
CF PC/PBT	104.45	105.66

the manufacturer. Furthermore, the ABS and Nylon degrade completely. In the case of SCF PETG and SCF PC/PBT, the residual mass at the end of the experiment is more than the specified. The same behavior was observed by Quintana et al. for GF PETG 36 % weight measured compared to 30 % weight specified by the manufacturer [21]. In addition, the same research group had PETG residual mass of more than 5 % at the end of the decomposition. The main reason for this is the additives used by the manufacturer also highlighted by [19]. The same behavior was observed for PC and SCF PC by Quintana et al., Ankit et al. [21,37].

The variation of the degradation (decomposition) temperature is shown in Table 3. In this study, degradation temperature is taken as the temperature value where the mass loss happens by 1 %, but since Nylon is highly hygroscopic, its mass at 200 °C was taken as reference. According to the table, the CF PC/PBT firstly degrades at around 382 °C and then 450 °C. Addition of the carbon fiber did not influence the first

degradation but the effect of the fibers is more pronounced in the second decomposition temperature by about 24 °C. The action mechanism of SCF in polymer matrixes is still a question, since it may either block the chain motion or enhance it [38]. If the SCF enhances the chain motion, it creates a less thermally stable composite and therefore enhances the deterioration characteristics of the material. In this case, the fibers enhance the chain segmental motion in PC more than PBT. In PBT, fibers act as a physical barrier at lower temperatures due to lack of reactive groups on the fiber surface and hinder the transfer of decomposed products out of the matrix [39,40]. In addition, the onset degradation behavior of PC was also attributed to the active sites in polymer-fiber interface by Sharma et al. which is not present in PBT-CF interface [41]. The experiments show that the matrix variation did not have significant influence on the degradation temperature and the change is on the order of ~ 10 °C. The maximum drop in decomposition temperature occurs with PETG matrix, and it is only about 7 °C. Change in the case of ABS matrix is as low as 0.11 °C which shows that the thermal stability is not even affected in composite case. In all matrix variations, the thermal stability drops, and early degradation occurs which is not favorable condition in FFF. One of the reasons for the early decomposition may be the presence of volatiles within the matrix [42]. Moreover, the matrix materials have lower thermal conductivity than the fibers, therefore act as an insulation between the small fibers. This way the matrix materials are blocking segmental motion of the polymer chains and preventing uniform temperature distribution within the matrix [43]. For FFF, generally, as a factor of safety, the printing temperature must be way below the degradation temperature and this analysis gives the maximum safe temperature to be used while printing the samples.

3.2. Thermomechanical analysis of the materials

Due to anisotropic nature of the carbon fibers, the coefficient of



Fig. 7. Variation of specific heat capacity versus temperature, A) SCF Nylon, B) SCF ABS, C) SCF PETG, D) SCF PC/PBT.

thermal expansion values along the fiber direction with all matrix materials is more than the transverse value, but the ratio of them is dependent on the temperature and grade of the carbon fiber used [44]. The influence of the matrix material is more dramatic in thermal strain measurement results as shown in Fig. 5.

The CTE values are also calculated for each composite material by taking the slope of the curve till glass transition temperature and listed in Table 4. The x direction is defined as the longitudinal/bead/fiber or printing direction and z direction is transverse or perpendicular to the x direction. The thermal strain changes can be analyzed before and after glass transition temperature for neat as well as composite materials. Till glass transition temperature, all of them follow linear behavior due to solid glassy state where polymer segmental motion is to a large extent blocked. The behavior of the CTE changes sharply after the T_g . The behavior of the materials after T_g depend on enthalpic recovery of the polymers and effect of SCF. During 3D printing process the molecular chains are oriented in a particular direction. When the specific layer is finished, it cools down rapidly without having enough time for thermodynamic equilibrium. As a result, thermal stress builds up [45]. After T_{g} , this stress is released resulting in shape transformation. x-direction samples with the aid of aligned carbon fibers cause the material to undergo shrinking deformation after T_{g} .

ABS matrix expands 23 % more in composite case than the neat version which is slightly higher than the PC/PBT composite. PETG matrix shows the minimum deformation with almost no change compared to pristine version which is favorable condition for FFF. CTE value increases with the amount of the adhesion force between fillers and matrix material as illustrated by Shubin et al. [46]. According to Yuan et al., transverse CTE is governed by the amount of interface bonding with the maximum stress located in the interface [47]. The experiment results show that PETG matrix has better adhesion with SCF

compared to other matrix materials resulting in lower CTE values.

The opposite case is observed in printing direction. If the interfacial bonding is strong, the matrix material shrinks/expands as allowed by the fiber. Furthermore, in fiber direction, the thermal stress is shared by fiber and matrix depending on the interfacial bonding, therefore, the CTE values drop. During extrusion process, as will be shown in thermal conductivity results, different voids are created. The amount of adhesion force is also correlated with the voids present in the composite material and higher values of voids decrease the adhesion [48]. However, the direct relation between porosity of the material and thermal expansion coefficient is not monotonic. According to Ghabezloo's paper there is no general trend for the behavior of porous materials to show the variation of the CTE [49]. In fiber direction, ABS and PC/PBT again show minimum change with SCF as 75 % and 72 %, respectively. PETG and Nylon matrix contracts in bead direction about the same amount of 77 % by the influence of SCF. The different morphology of Nylon due to semicrystallinity nature makes the CTE analysis very complex, since strain response has components of thermal (reversible) strain as well as permanent strain due to crystallization. Furthermore, crystalline structure is function of temperature as well, thus thermal strain development is poorly understood [50,51].

According to the TMA results, to have the minimum deformation and thus, high print quality, the PETG matrix demonstrates better behavior than other samples with the addition of the SCF, hence preferred for FFF.

3.3. Differential scanning calorimetry measurements

The DSC curves are illustrated in Fig. 6. ABS and CF ABS firstly show glass transition process and then endothermic peak due to melting of processed materials. PC/PBT and CF PC/PBT undergo three distinct processes of glass transition, cold crystallization (due to PBT) and



Fig. 8. Thermal diffusivity values, A) SCF ABS, B) SCF Nylon, C) SCF PETG, D) SCF PC/PBT.

Table 6The density measurements for the materials.

Name of the material	Volume in m^3 (D = 1.75 mm, L = 365 mm)	Weight (g)	Density (kg/ m ³)
CF PC/PBT	8.78E-07	0.9883	1125.72
CF PETG	8.78E-07	1.0718	1220.83
CF ABS	8.78E-07	0.9302	1059.54
CF NYLON	8.78E-07	0.9740	1109.43
PETG	8.78E-07	1.1023	1255.57
NYLON	8.78E-07	0.9697	1104.53
PC/PBT	8.78E-07	1.0145	1155.56
ABS	8.78E-07	0.8957	1020.24

melting (due to PBT), whereas PETG and CF PETG first transitions from glassy to rubbery state with an immediate follow-up of enthalpic recovery. Finally, the semi-crystalline material of Nylon and CF Nylon has the glass transition process and then, due its structural changes, melting process with 2 endothermic peaks.

According to the curves, the glass transition (amorphous samples) and melting temperature (semi-crystalline morphology) of the samples can be determined. In FFF, the printing temperature is at least 120 °C higher than the glass transition temperature ensuring continuous stream of the polymer and allowing better bonding between beads and layers [52]. PC/PBT has semi-crystalline component PBT in it and therefore it shows endothermic peak around 216 °C. To determine whether the polymer blend is semi-crystalline or amorphous, its degree of

crystallinity has been calculated in the following formula:

$$\chi = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_0} \tag{5}$$

where ΔH_m and ΔH_{cc} enthalpy change during melting and cold crystallization respectively. The enthalpy changes during melting of 100 % crystalline PBT (ΔH_0) is taken as 145 J/g [53]. For PC/PBT, χ becomes 0.72 % and SCF PC/PBT 0.08 % and both are very close to 0 meaning that PC restricts the polymer segmental motion and therefore, the mixture is amorphous. Degree of crystallinity is also calculated for Nylon and SCF Nylon as 21.26 % and 16.1 %.

Mid-point of the slopes to the baselines has been used to calculate the glass transition temperature. The results are listed in Table 5. For comparing the values from DSC, the MDSC T_g values were also shown which was calculated from reversing heat flow curve. For our measurements, in all cases, the composite materials had a drop in glass transition values and similar values were also obtained by TMA experiments. As seen, the DSC and MDSC values are in good range except PETG matrix and PC/PBT matrix. T_g variation is slightly more in DSC than MDSC.

experiments. Thus, to make sure that this behavior by DSC results is not due to the heating rate, the same weight samples were run under 5 °C/min resulting in similar values. Each technique has its own pros and cons which is beyond the scope of the paper, but generally MDSC is more sensitive to the T_g due to the frequency effect included to detect the time dependent macro-molecular motion. In addition, the errors can be caused by the aging of the materials since each experiment was carried



Fig. 9. Thermal conductivity values, A) SCF ABS, B) SCF Nylon, C) SCF PETG, D) SCF PC/PBT.

 Table 7

 Kruskal-Wallis test summary for thermal conductivity measurements.

Parameter name	H-value	df	P-Value
Along fiber direction Across the fiber direction	13.88 1.3831	3 3	0.003073 0.7095

at different times and selection of different ramp rates for MDSC and DSC, constraints on the sample mass selection to prevent the contamination of the equipment, freezing of the chain mobility by the MDSC periods [54]. Moreover, according to the reviewed literature, there is no consensus on the interaction of matrix material with the SCF to determine the final T_g . For example, Ajinjeru et al. state that the fibers don't influence the glass transition temperature, however according to Quintana et al. the fibers can increase or decrease the T_g since it heavily depends on the interaction of the fibers and matrix material [21,52]. It can be seen from Table 5 that the composite materials after addition of SCF does not have high change in the glass transition temperature. The maximum drop is less than 8 °C (CF PETG in DSC results) and 2 °C in ABS and CF ABS results. Glass-transition temperature also denotes the processing temperature of the material in industrial and daily applications. In this case, a good candidate is Nylon and ABS matrixes since they are insensitive to the SCF inclusion.

Finally, specific heat capacity values were calculated using conventional MDSC. The curves are presented in Fig. 7. Variation of the matrix material here also did not have high impact on the specific heat capacity values. PC/PBT matrix is not affected by the SCF however the PETG and Nylon matrixes had a slight drop in specific heat capacity which can be calculated with rule of mixtures summarized in coming paragraphs. Interestingly, ABS matrix had an increase in specific heat capacity with SCF inclusion. The variation of specific heat capacity with matrix material and SCF interaction is not fully understood according to the reviewed literature. According to Billah et al., specific heat capacity of CF ABS 20 % weight can increase 4 times which is contradictory to rule of mixtures, however same matrix material with SCF 20 % weight inclusion follows rule of mixtures tested by Hassen et al. [19,25]. Rule of mixture for different matrix and SCF combinations also validated by [55,56] but conversely, not confirmed by [57]. The authors tie the increase of specific heat capacity as some possible reasons of higher thermal conductivity of the carbon fibers and thus, higher heat dissipation, complex interaction between.

fibers and matrix material, fiber size and distribution inside the resin. In addition, Weidenfeller et al. show that the interconnectivity between particles/fibers inside the matrix play a significant rule for the determination of the composite specific heat value [58]. Additionally, the rule of mixtures doesn't consider the interaction between the fibers and polymers as well as the molecular structure of the polymer. Following the above discussions, the specific heat values by 10 % weight concentration of the fibers were calculated for all cases by using rule of mixture.

$$c_{p_{composite,mixrule}} = f_w c_{p_{fiber}} + (1 - f_w)^* c_{p_{matrix}}$$
(6)

And the relative error as percentage in absolute value

$$e_{rel} = abs\left(\frac{c_{p_{composite,mixrule}} - c_{p_{MDSC}}}{c_{p_{MDSC}}}\right) * 100\tag{7}$$

According to the selected discrete values, the relative error is 6.88 % for CF ABS at 100 °C, but it should be noted that the amount of error increases during the phase transitions. In the case of CF Nylon, this error during the melting process becomes as high as 18 % which is the maximum of all the data points of the composites. As noted by other researchers, the mixture rule can only predict if there is no interaction between fiber and polymers and no structural changes in polymer



Fig. 10. Optical images of the composite samples, A) SCF PETG, B) SCF PC/PBT, C) SCF ABS, D) SCF Nylon.

morphology.

The change in specific heat capacity has also been calculated as

$$change = \frac{c_{p_{composite}} - c_{p_{neat}}}{c_{p_{neat}}} 100$$
(8)

The changes are maximum in Nylon and PETG matrixes while negative value shows the drop of the specific heat capacity of the composites. In the case of PC/PBT and ABS, the specific heat values are the least affected with a peak value of around 3 %. Higher specific heat means more heat can be added to the system while extruding but if the thermal conductivity is low, then this heat cannot be dissipated and leads to a residual stress due to large thermal gradients. Therefore, measurement of the thermal conductivity is also important.

3.4. Flash diffusivity measurements

For the thermal simulation of the parts, increasing thermal diffusivity value, helps to cool the part more rapidly, more heat transfer from the bed plate to the interior of the parts and also, decreases the time to reach glass transition for the higher layers away from the bed [59]. According to the flash method results in Fig. 8, the thermal diffusivity of the samples along the fiber direction increased by addition of short carbon fibers. For comparison at room temperature, the maximum increase in thermal diffusivity is seen in PETG matrix with about 3.5 times and minimum change is in Nylon matrix with 1.8 times. ABS and PC/PBT matrixes follow similar values of 2.43 and 2.26 times increase in

thermal diffusivity, respectively. Interestingly, the carbon fiber decreased the thermal diffusivity values across the printing direction and this behavior was.

also experienced by Love et al. for CF ABS 13 % weight concentration, Shemelya et al. for ABS Silver 1.4 % volume concentration [24,60]. In addition, flash diffusivity values have a second order phase transition close to glass transition temperature due to change of state from glassy to rubbery state. The values are similar to DSC and MDSC results but with slight differences since these are tested on Additively Manufactured parts and also, TMA measures the mechanical response of the material. All materials show linear behavior till glass transition temperature and thermal diffusivity values drop with increasing temperature values.

Thermal conductivity is commonly used and referenced thermal property and thus, it can be determined by using

$$k = \alpha \rho c_p \tag{9}$$

which requires prior knowledge of the density, specific heat capacity and thermal diffusivity. The only unknown density values were calculated using Mottler Toledo balance XSR204 with 0.1 mg resolution. Each sample has the same dimensions and therefore the same volume. Accordingly, the density values were determined by the ratio of the weight to volume. The details of the experiment are shown in Table 6 below. As experienced from the density values, the matrix materials have similar density values, and the influence of CF is negligible. Since lighter weights are desired as an advantage of CF, maximum change is in PC/PBT case by 2.58 % drop in mass. The density of CF ABS is minimum



Fig. 11. Fracture surface for 3D printed sample.

however it is 3.85 % more than the pristine material due to the higher Molecular Weight of the included carbon fiber.

The thermal conductivity chart shown in Fig. 9 follows the linear behavior till softening temperature and then changes the trend afterwards. The specific heat value increases with temperature whereas thermal diffusivity decreases resulting in the competing behavior of those thermal properties. Overall, the thermal conductivity increases with temperature. As also noted by Amico et al., the thermal conductivity increase is more than the specific heat capacity and density by inclusion of the chopped carbon fibers. According to the figure, taking the values at room temperature as reference, PETG matrix has experienced the most dramatic rise in thermal conductivity by almost 3 times along the fiber direction. It is followed by ABS, PC/PBT and Nylon matrices with the increase as 2.7, 2.2 and 1.6 times, respectively. Similar to thermal diffusivity chart, the thermal conductivity across the fiber direction does not show any significant variation. To test the validity of the thermal conductivity values, the results are compared with the previously published articles. A great degree of anisotropy is seen in printing and across the printing direction. Weidenfeller et al. show the interconnectivity among the higher conducting phases (here carbon fibers) as the main cause of the anisotropy [58], Hassen et al. list the reasons as the voids created during compounding as well as printing process [25]. The neat materials are averaged to isotropic behavior due to very small variation in bead and across the bead direction [25,61,62].

Statistical analysis has also been performed on thermal conductivity results to see the influence of SCF orientation with hypotheses as follows.

Null hypothesis. Variation of matrix material in composites doesn't have significant influence on thermal properties.

Alternate hypothesis. Variation of matrix material in composites has statistical influence on thermal properties.

The statistical analysis conducted in this study involved the use of R

programming language. Prior to conducting the ANOVA, the normality of the data was assessed using the Shapiro-Wilk normality test, which yielded a *p*-value of 0.0016. Additionally, the assumption of equal variances was found to be violated. As a result, a non-parametric test, specifically the Kruskal-Wallis method, was chosen to analyze the data instead of ANOVA. The composite materials were tested in both the along and across carbon fiber (CF) directions, and the results are presented in the Table 7. It can be observed that the p-value for the variation in matrix properties along the fiber direction is less than 0.05. This indicates strong evidence against the null hypothesis and suggests a significant difference between the groups. Similar results were obtained for the experiments conducted across the fiber direction.

3.5. Microstructural analysis

To make sure that the fibers are aligned in the printing direction, specimens were polished in the printing plane and then their optical images were taken. Buehular Consumables were used along with different size sandpapers. For each sample, three different cross-sections were analyzed to make sure that fiber orientation is homogeneous. In addition, the size of each fiber is measured using ImageJ software.

According to software results and as seen in Fig. 10, the fibers don't have the same size but averaged on the length of approximately 100 μm except CF Nylon and diameter of about 6.5 μm . The fibers of CF Nylon are more chopped than the others with an average length of 60 μm . To make sure that these are not caused by the printing process, samples from original filaments were cut and analyzed under optical microscopy which showed the similar result meaning that the fibers were broken during extrusion of the pelletized raw material into filament form. As seen from the figure, the fibers are mostly aligned in the printing direction due to shear stress created by the flow except the centerline. At the centerline the shear stress is zero and close to the centerline of the profile, the fibers are more randomly oriented.

The thermal conductivity of the composites is affected by the pores as

mentioned above. These pores or voids can be categorized as intra-beads that are formed due to entrainment of air during extrusion process. These pores are dependent on extrusion temperature, and they are randomly aligned. In this research, all specimens have similar extrusion temperature range. Thus, they are not influenced by these pores in a significantly different manner. The second type of voids, also called, inter-bead pores, are preferentially aligned. They can be between the beads of the same layer and also, of the different layers. These second group of pores are often macro-sized and create thermal resistance. Thus, materials with highest thermal conductivity, in this case SCF PETG will have less inter-bead voids (Fig. 11).

4. Conclusion

In this study, the influence of matrix materials on the thermal properties of thermoplastic composites has been investigated. Same matrix materials have been used in neat as well as composite case, furthermore, the carbon fibers used in all the specimens are of the same grade and same concentration (10 %). The TGA results show that the matrix materials don't have significance in the variation of the degradation temperature. Residual mass amount in CF Nylon and CF ABS are the same as claimed by the compounder, but CF PETG and CF PC/PBT have masses at terminal temperature more than specified due to the number of additives used. According to the DSC experiments, the glass transition temperature changes 6 °C for PC/PBT and 7 °C for PETG matrix composite. The variation in specific heat capacity with Nylon and PETG matrixes is close to 8 %.

Main changes happen in the thermal diffusivity, thermal conductivity, and coefficient of the thermal expansion of the materials. PETG matrix almost quadruples the heat diffusivity value whereas Nylon has the minimum increase of 1.83 times. Across the fibers, thermal diffusivity follows the neat polymer values. For CTE measurements, again PETG matrix sees the maximum drop of 67 % and this drop favors FFF in terms of less residual stress and deformation.

The findings of this paper may be used as an accurate material database for predicting the thermal history of the Additively Manufactured parts and as a result, accurate thermal history coupled with mechanical simulations can give more insight into the final deformation of the parts.

CRediT authorship contribution statement

Conceptualization, O.H., S.H. and I.F.; methodology, O.H.; software, O.H.; validation, O.H.; investigation, O.H.; resources, I.F. and S.H.; writing—original draft preparation, O.H., writing—review and editing, S.H. and I.F.; supervision, I.F.; project administration, I.F.; funding acquisition, I.F. All authors have read and agreed to the published version of the manuscript.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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