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Experimental Study on Influence of Multiwalled Carbon Nanotubes on Thermal Behavior of ABS & PETG Hybrid Polymer Composites

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Abstract

Polymer composites with enhanced thermal conductivity not only exhibit impressive heat transfer capabilities comparable to metals and ceramics but also preserve the inherent benefits of polymers, including their lightweight nature, ease of processing, and cost-effectiveness. These composites find extensive applications in aerospace, electronics, medical devices, and various other industries. Polymer-based composites incorporating multiwalled carbon nanotubes (MWCNTs) were created, and the impact of different concentrations on the thermal stability of the resulting hybrid composite was examined. This study examines the way of behaving of PETG and ABS materials fabricated through 3D printing and built up with differing measures of carbon fibers (CF) and multiwall carbon nanotubes (MWCNT). The study aims to shed light on the ways in which these materials improve polymer properties, focusing particularly on the beneficial effect of reinforcement on thermal behavior. Additionally, the influence of temperature on the thermal properties of hybrid polymer composites is briefly addressed. These findings underscore the significance of both the content and dispersion state of nanoparticles in shaping the thermal characteristics of such composites.

Keywords: *PETG, ABS, Multi walled carbon nano tube, TGA, DSC.*

1. INTRODUCTION

High-performance polymer composites have gained widespread acceptance, particularly in applications with demanding operating conditions that necessitate a combination of high mechanical and thermal properties, low specific weight, and strong resistance to degradation, ensuring both safety and economic efficiency. Among these composites, thermosetting epoxy resins have gained immense popularity. Their success stems from their well-established track record as effective structural polymers, adhesives, surface coatings, and laminates for electronic circuit boards. These epoxy resins find extensive use in various industries, including automotive, aerospace, and others [1].

The utilization of 3D printers has opened avenues for innovation and opportunities, sparking increased interest in swiftly manufacturing intricate objects with enhanced material properties. The most notable expansion of 3D printing has occurred in the consumer and low-performance commercial sectors. Nevertheless, the most significant advancements in 3D printing knowledge are poised to benefit the composites industry by meeting the demands of high-performance manufacturing [2].

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Given their distinctive structures and exceptional mechanical properties, including strength, modulus, and resilience that match or surpass those of existing materials, carbon nanotubes (CNTs) have been strategically employed to augment hierarchical composites. This has emerged as a topic of considerable interest in recent years, driven by the brilliant electrical and thermal properties exhibited by CNTs. [3].

Polyethylene terephthalate glycol is popular for a wide range of consumer and commercial applications due to its ease of vacuum, pressure, and heat bending due to its low forming temperatures. These properties likewise make one of the more broadly involved materials for 3D printing and other heat-forming processes. PETG has acquired popularity for use in present day 3D printers. A polyethylene terephthalate glycol fiber prints effectively and gives incredible layer grip. Low shrinkage rates consider bigger prints than with PLA or ABS, while PETG is areas of strength for additionally, safe, and unscented while printing [4].

ABS (acrylonitrile butadiene styrene) stand out as a widely favored thermoplastic polymer, commonly applied in injection molding applications. This engineering plastic has gained popularity due to its cost-effectiveness in production and ease of machinability, making it a preferred choice for plastic manufacturers [5].

The commonly acknowledged thermal conductivity value for Multi-Walled Carbon Nanotubes (MWCNTs) is around 2000W/(m.K), surpassing that of graphite at 298W/(m.K), despite both materials exhibiting comparable electrical conductivity. However, it is important to note that the thermal conductivity of MWCNTs can vary significantly in the literature due to factors such as the presence of defects, diverse production processes, and variations in measurement methods. These factors underscore the intricate nature of characterizing MWCNTs' thermal conductivity accurately [6].

2. LITERATURE SURVEY

The study successfully showcases the improved thermal properties of Cu-CNTs composite materials in comparison to the pure matrix. Remarkably, a notable enhancement of +7% in thermal properties was observed with just a 1% carbon nanotube content. What sets this research apart is the development of a fabrication method for Cu-CNTs composites that eliminates the need for acid-treated carbon nanotubes. By avoiding the functionalization process, the physical properties of the nanotubes remain unaltered. This innovation not only contributes to the advancement of composite materials but also underscores the significance of preserving the inherent qualities of nanotube reinforcements in the manufacturing process [7].

Thermogravimetric analysis (TGA) serves as a valuable tool for a comprehensive understanding of functionalized carbon nanotubes (CNTs), offering insights into both thermal stability and surface functionalization. Pure CNTs demonstrate outstanding thermal stability at 800°C, with a minimal weight loss of 1.6%, possibly attributed to inherent structural defects. In contrast, functionalized CNTs, specifically carboxylated and aminated variants, exhibit distinct thermal behavior. Carboxylated CNTs display a notable weight loss stage at 220°C-290°C, corresponding to the degradation of carboxyl and hydroxyl groups in MWCNTs-COOH. Even at 800°C, a substantial residual amount of 57.72% is observed [8].

Pure epoxy resin, being a type of polymer, typically exhibits poor thermal conductivity. However, according to principles of thermal conduction, the addition of fillers with higher thermal conductivity can enhance the thermal performance of the epoxy resin. In this context, the exceptional thermal properties of Multi-Walled Carbon Nanotubes (MWCNT) and Graphene Nanoplatelets (GNP) make them promising candidates for improving the thermal conductivity of the epoxy matrix. It's crucial to understand that in polymer composites, heat is predominantly transferred in the form of acoustic phonons.

Several factors come into play in determining the overall thermal conductivity of these composites. These factors include the filler fraction, aspect ratio, surface roughness of the fillers, degree of dispersion, orientation of the fillers, intrinsic crystallinity of the filler material, and the thermal contact resistance at the interface between the filler and the matrix [9].

In the examination of thermal conductivity and diffusivity of PDMS/MWCNT composites, the aspect ratio played a crucial role. The research indicated that Long Multi-Walled Carbon Nanotubes (L-MWCNTs) exhibited superior thermal properties. Subsequently, the focus shifted to the thermal conductivities of PDMS/L-MWCNT composites with varying weight percentages (1 wt%, 2 wt%, 5 wt%, 7 wt%, and 10 wt%) to discern any discernible trends. To enhance the understanding of the observed data, a thermal conductivity prediction model for Carbon Nanotube (CNT) polymer composites was employed. This model, previously presented, was refined to incorporate the impact of filler aspect ratio within the composite. The experimental values derived from the thermal conductivity measurements were then compared with the predictions from this model [10].

The thermal properties of various materials were investigated through comprehensive testing methods. Thermogravimetric analysis (TGA) was conducted using a TGA Q500 thermogravimeter. The samples underwent testing at 800 °C under a nitrogen atmosphere with a combustion rate of 10 °C/min. The resulting thermogravimetric curves allowed for the determination of specific parameters, including the temperature at which a 2% weight loss (T2%) occurred, the temperature at which a 5% weight loss (T5%) occurred, and the maximum degradation temperature (Tmax). The glass transition temperature (Tg) was determined using Differential Scanning Calorimetry (DSC) with a Q1000 calorimeter from TA Instruments (USA). Approximately 9 mg samples were placed in aluminum pans, and a specific program was followed. This program involved cooling the samples to -90 °C, maintaining the constant temperature for 5 minutes, and then heating to (T5% - 10 °C). Subsequently, the samples were cooled again to -90 °C and reheated to (T5% - 10 °C). The heating process was conducted at a rate of 10 °C/min, while the cooling process proceeded at a rate of 5 °C/min. This detailed approach allowed for precise determination of the glass transition temperature [11].

The objective of the study was to analyze specific characteristics of various composite materials through a series of measurements. The equipment underwent recent official calibrations for scale accuracy, temperature, and enthalpy. The analyses included Differential Scanning Calorimetry (DSC) and thermogravimetry under a nitrogen atmosphere at a flow rate of 100 mL/min. Sample masses ranged from 4.5 mg to 8.0 mg. For measurements up to 300°C, uncovered aluminum crucibles with a volume (V) of 75 µL were utilized. For experiments reaching up to 600°C, uncovered Al2O3 crucibles with a volume of 100 µL were employed. The sample cooldown rate was tailored appropriately, eliminating the need for any external cooling apparatus. DSC-TGA measurements were conducted with a uniform heating rate of 10°C/min. The measurements proved to be optimal for capturing the maximum achievable mass decrease while ensuring the preservation of extra carbon content [12].

2.1 Methodology

The approach utilized in the ongoing work contains.

- Determination of matrix and reinforcement materials.
- Picking the weight percentage of matrix and reinforcement materials.
- Selection of Processing technique.
- Selection of Build orientation.
- Treating and samples preparations.

3. EXPERIMENTAL WORK

The highlights of the trial work including the base materials chosen, reinforcements, its weight percentage, processing methods commissioned, and testing considerations are assessed in short in this segment.

3.1 Base Material

ABS: Acrylonitrile butadiene styrene, also known as ABS, has high elasticity and is exceptionally impervious to physical impacts and chemical corrosion, which permits the finished plastic to endure heavy use and adverse environmental conditions. Table 3.2 shows the thermal properties of ABS.

TABLE 3.1. Thermal Properties of ABS

Parameters	Value
Density	1.04g/cm^3
Glass Transition Temperature	105^{0}C
Decomposition Temperature	380^{0}C

PETG: PETG where the ‘G’ stands for glycol has greater strength and durability, as well as being more impact resistant and better suited to higher temperatures. Table 3.1 shows the thermal properties of PETG.

TABLE 3.2. Thermal Properties of PETG

Parameters	Value
Density	1.23g/cm^3
Glass Transition Temperature	85^{0}C
Decomposition Temperature	260^{0}C

Figure 3.1 a show the unrefined substance in type of spool which is white tone with a diameter of 1.75mm. Figure 3.1 b shows the raw material in type of spool which looks perfectly clear with a measurement of 1.75mm diameter.

(a) (b)

FIGURE 3.1. (a)PETG Spool (b) ABS Spool

3.2 Reinforcement Materials

Carbon Fiber: It is a low-density material with a very high strength to weight ratio. This implies that carbon fiber is intense without getting hindered like steel or aluminum. Carbon fiber is five times more durable and twice as rigid as steel. Table 3.3 shows the thermal properties of Carbon fiber. Figure 3.2 shows the fine carbon as a powder.

TABLE 3.3. Thermal Properties of Carbon Fiber

Parameters	Value
Density	1.75g/cm^3
Glass Transition Temperature	250^0C
Decomposition Temperature	250-500^0C

FIGURE 3.2. Carbon Fiber

FIGURE 3.3. MWCNT

Multi Walled Carbon Nano Tubes: One method for considering WNTs is as an assortment of single wall tubes settled inside each other. These concentric walls could number as many as 6 or upwards of 25. Along these lines, MWNTs might have distances as extensive as 30 nm instead of 0.7 to 2.0 nm for regular SWNTs. Table 3.4 shows the thermal properties of MWCNT. Figure 3.3 shows the MWCNT fiber in the powder form.

TABLE 3.4. Thermal Properties of MWCNT

Parameters	Value
Density	1.72g/cm^3
Glass Transition Temperature	70^0C
Decomposition Temperature	3550^0C

3.3 Processing Technique

The polymer material is processed using the 3D printing method. Figure 3.4 demonstrates the fabrication equipment used in the current work.

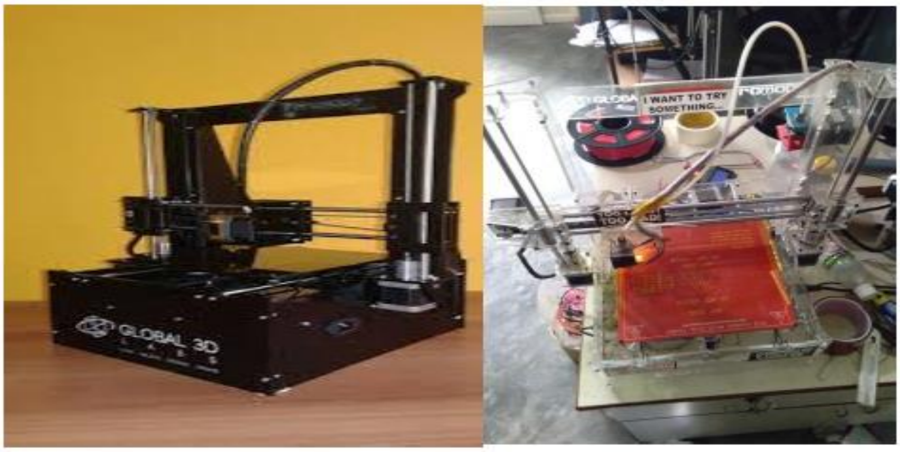


FIGURE 3.4. FDM Apparatus Used

Table 3.5 indicates the proportion of matrix and supplementing materials utilized in polymer composite processing.

TABLE 3.5. Matrix and Reinforcement Details

Sl.No	Matrix Material	Weight Percentage	Reinforcement Material	Weight Percentage
1	ABS	100	-	-
2	PETG	100	-	-
3	ABS	98	Carbon Fibre	2
4	PETG	98	Carbon Fibre	2
5	ABS	96	Carbon Fibre	2
			MWCNT	2
6	PETG	96	Carbon Fibre	2
			MWCNT	2

ABS and PETG composites are handled straightforwardly as filaments. For handling the composite materials, particularly the carbon fiber and MWCNT strands the reinforcements will be as powder which will be mixed in blending chamber in with glue specialist. Later the materials will be compacted in the die and materials will be extruded to acquire it as filaments. These fibers will be constructed in the appropriate direction in response to weight percentage changes.

3.4 Thermal Behavior Study

Thermal properties such as degradation temperature and mass reduction were examined using thermogravimetric analysis using ASTM E1131 standard as well as decomposition temperature study was conducted with the help of differential scanning calorimetry employing ASTM D3418. Table 3.6 illustrates the parameters undertaken for the conduction of examination of properties. The particulars of the apparatus used are shown in Figures 3.5 and 3.6.

TABLE 3.6. Thermal Testing Parameters

Parameters	Value
Atmosphere	Nitrogen
Flow Rate	50 ml/min
Cell	Alumina
Sampling Time	1 sec

FIGURE 3.5. TGA Apparatus

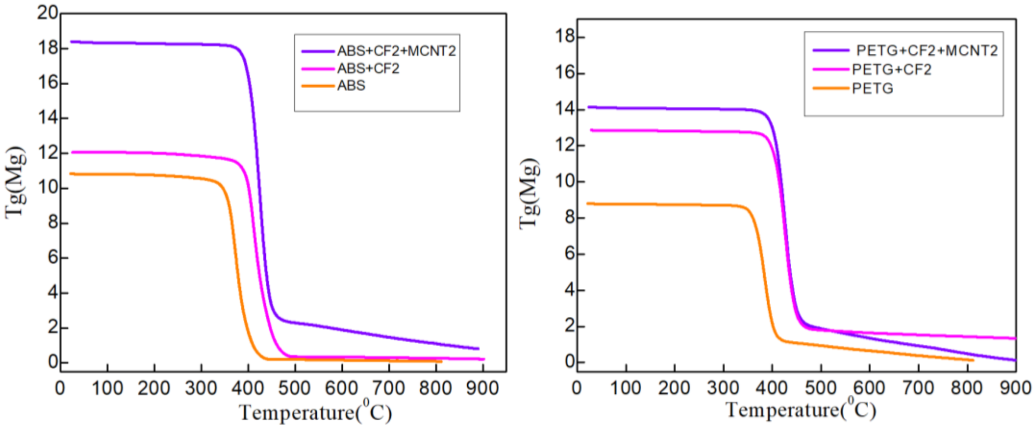
FIGURE 3.6. DSC Apparatus

4. RESULTS & DISCUSSION

Thermal tests, namely thermogravimetric analysis and differential scanning calorimetry are performed on the powdered type of various blend of composites as referenced in Table 3.5. The TGA test is being led for season of something like 5300 seconds while DSC test is performed for close to 3100 seconds with an examining pace of 1 second in an aluminum fixed cell having nitrogen in its climate.

The thermal stability of nanocomposites consisting of varying carbon fiber and MWCNT content were studied using thermal gravimetric analysis and differential scanning calorimetry. The result of the above condition is depicted in detail in the segment below.

4.1 Thermogravimetric Analysis

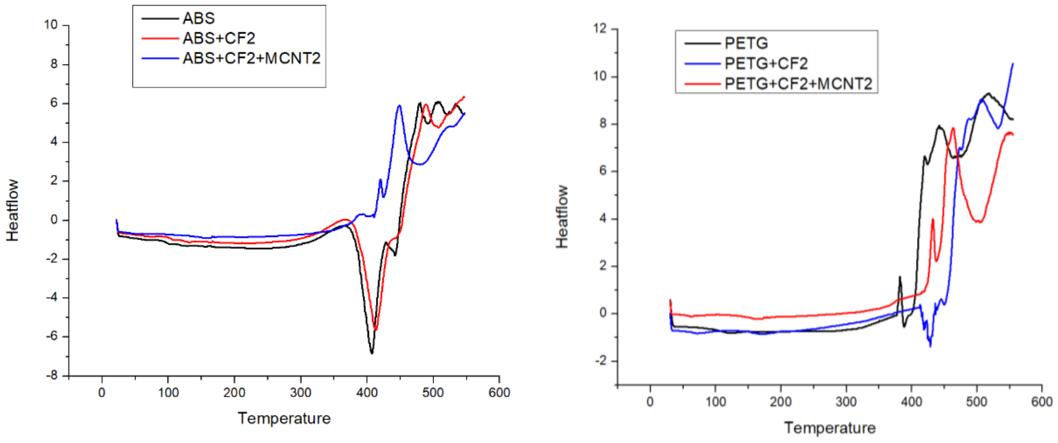


(a) (b)

FIGURE 4.1. Glass transition v/s Temperature

The TGA curves as shown in figures 4.1 (a) and (b) show that both ABS and PETG blend and its nanocomposites observe single-step degradation with a prompt mass loss in the temperature range of 336 - 466°C with respect to ABS and 349-452°C concerning PETG. The figure (a) indicates an evident increase in thermal resistance with higher material reinforcement. The Thermogravimetric Analysis (TGA) of ABS demonstrated a significant 91.26% mass reduction at 336.61°C. In the case of ABS+CF2, a mass drop of 89.58% was observed at 381.59°C. Additionally, the TGA curve for ABS+CF2+MWCNT2 exhibited a notable 82.75% reduction in mass at 379.77°C. This underscores the trend of enhanced thermal stability with increased material reinforcement in the composite. TGA curve for PETG as shown in figure (b) showed 79.59% of mass drop at 349.18°C. Also, at 387.04°C, the PETG+CF2 TGA curve revealed a mass drop of 81.02 percent. Further at 382.93°C, the TGA curve for ABS+CF2+MWCNT2 displayed a substantial 79.69 percent reduction in mass. Regardless of the reinforcement of the materials among PETG mix composites, because of the lower crosslink densities in the nanophased framework, it showed no huge improvement in mass loss conversely, with the ABS blend which showed critical improvement in relation with the mass loss.

4.2 Differential Scanning Calorimetry



(a) (b)

FIGURE 4.2. Heat flow v/s Temperature

The introduction of CF2 into ABS led to a meaningful increase in its decomposition temperature, exhibiting a notable improvement of 5.49°C compared to ABS in isolation. Moreover, the integration of MWCNT2 into ABS+CF2 exhibited an additional enhancement in the decomposition temperature, showcasing a further increase of 11.55°C compared to the ABS+CF2 composite.

The addition of CF2 to PETG resulted in a notable enhancement in the decomposition temperature, showing an improvement of 30.32°C compared to PETG alone. Further, the incorporation of MWCNT2 into PETG+CF2 demonstrated an additional improvement in the decomposition temperature, with an increase of 18.34°C when compared to PETG+CF2. The remarkable thermal stability of carbon fiber, when incorporated into nanocomposites, results in a significantly lower heat release rate compared to traditional PETG & ABS blends. The key to this improvement lies in the exceptional insulating properties of uniformly dispersed MWCNTs within the composite. This acts as a challenging physical obstruction, effectively hindering the movement of unstable products during the decomposition process.

5. CONCLUSIONS

The conclusions derived from the investigations can be summarized as follows:

➢ 3D printing techniques have proven successful in seamlessly processing polymer composites comprising PETG and ABS, resulting in flawlessly manufactured products with no observable defects.

➢ Thermogravimetric test suggests that the PETG material mass loss was consistent even with the addition of reinforcements contrasted with ABS which presented immense mass loss reduction by supplementing reinforcements.

➢ Differential scanning calorimetry analysis revealed a notable enhancement in the decomposition temperature of PETG, with an increase of approximately 48.66°C attributed to the incorporation of reinforcements. Furthermore, ABS demonstrated a rise in temperature of 17.04°C, which was associated with the introduction of reinforcements.

➢ These findings underscore the promising implications of incorporating MWCNTs into nanocomposites, not only for enhancing thermal stability but also for improving overall safety and performance characteristics.

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