Incorporation of Multiwalled Carbon Nanotubes and Graphene Nanoplatelets on the Morphology and Properties of Polyethylene Terephthalate Nanocomposites

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In this work, the interaction effect between polyethylene terephthalate (PET) and multiwalled carbon nanotubes (MWCNTs) and graphene nanoplatelets (GNPs) on the morphology and thermal properties of the nanocomposites have been investigated. PET nanocomposites with the incorporation of 0.1 wt% and 0.5 wt% of MWCNTs and GNPs were prepared by the melt compounding and injection moulding method. The presence of MWCNTs and GNPs in the PET matrix was confirmed by the X-ray diffraction (XRD) technique. MWCNTs and GNPs acted as a nucleating agent which enhanced the crystallization of PET/MWCNT/GNP nanocomposites at both weight percentages. The result obtained from thermogravimetric analysis (TGA) showed that the incorporation of MWCNTs and GNPs into pure PET improved the thermal stability of the nanocomposites. The nanofillers served as efficient heat sinks which prevent thermal degradation of PET. From the fractured cross-section morphology in field emission scanning electron microscope (FESEM), the nanofillers displayed good dispersion in the PET matrix. Better dispersion distribution found in 0.1 wt% PET/MWCNTs/GNPs nanocomposites compared to 0.5 wt% PET/MWCNTs/GNPs nanocomposites which favor less mechanical and physical failures like crack, delamination, and agglomeration.

1. Introduction

Polyethylene terephthalate (PET) is a semicrystalline thermoplastic polyester derived from polyethylene terephthalate and purely unreinforced. PET polymer is one of the engineering plastics that have excellent processing characteristics with high strength and rigidity for a wide range of applications. It has good antiosmosis, low water absorbability, and good toughness characteristics which makes PET polymer good materials for food and beverage packaging application [1] The glass transition temperature depends on the level of crystallinity of PET polymer [2]. High crystallinity PET polymer tends to have much higher glass transition temperature. Furthermore, PET polymer is a low-cost material used for packaging material of electronics devices, which can be further modified to enhance electrical conductivity. This can be achieved by further addition of nanofiller such as exfoliated graphite, carbon nanotube, and graphene [3].

Recently, polymer nanocomposites have generated a significant amount of interest among material scientist. Polymer nanocomposites present a new alternative to conventionally filled polymers due to the enhanced properties of filled dispersion nanocomposites when compared to pure polymers. This is due to the nanometre sizes of fillers present in polymer nanocomposites. The introduction of nanofiller to the polymer matrix leads to improved mechanical properties, electrical conductivity, and flame retardant [4–6]. One of the vital features of nanocomposite research is using CNTs as carbon nanofillers in producing a high performance and lightweight composite [7]. TGA analysis also revealed that the PET-CNT nanocomposites also have enhanced thermal stability compared to unfilled PET [8]. This is due to the
barrier effects induced by the CNT filler which is dispersed in the PET. Furthermore, the combination of both nanofillers especially multiwalled carbon nanotube MWCNTs and graphene platelet GNPs lead to enhanced mechanical and thermal properties along with electrical and thermal conductivity of the nanocomposites [9] due to their synergistic effects [10]. The hybrid system between MWCNTs and GNPs leads to promote their dispersion in the matrix as the MWCNTs may bridge GNPs, thus offer more interface area between the matrix and the fillers which subsequently bring improvement at low filler fractions for applications in high-performance structural composites [11].

Consequently, the combination of the different composition ratios of carbon nanofillers in different shapes and sizes will build a piece of knowledge in understanding the compatibility of MWCNTs and GNPs that incorporates with PET matrix to have simultaneously excellent mechanical properties and high-performance polymer nanocomposites, extending their potential field of applications. Nonetheless, the van der Waals (vdW) interaction between nanofillers is known to lead to the formation of bundles and clustering in the polymer matrix. It remains the main challenge in polymer nanocomposite filled carbon nanofillers to improve the dispersion, distribution, and alignment of MWCNTs in a polymer matrix. It is known that the MWCNTs tend to form bundle and agglomeration due to the vdW forces between the nanofillers while GNPs tend to fold and stack due to high aspect ratio that restricts the motion of molecular chain of PET.

This paper studied the effects of MWCNTs and graphene nanoflakes as the nanofiller for PET nanocomposites. The PET nanocomposites are fabricated via the melt-compounding method using the internal mixer. Melt blending utilized both high temperature and high shear forces to disperse GNPs and MWCNT nano-filler in the PET matrix. However, the high weight percentage of CNTs resulting in decreasing the mechanical strength decreases from weak interfacial bonds form between the matrix and the fiber [10]. On the other hand, no study is reported on the effects of combination GNP and MWCNT hybrid fillers on the properties PET prepared via melt blending [12], especially on the low loadings of MWCNTs and GNPs. Therefore, the low content of MWCNTs and GNPs with the weight percent of 0.1 wt% and 0.5 wt% were used to produce a PET nanocomposite with well-dispersed nanocomposites. We expect to enhance the thermal properties and crystallization of PET nanocomposites. With this aim, the present work intends to correlate the morphology, crystallization, and thermal properties of pure PET and PET nanocomposites with different weight percentages of nanofillers prepared by melt-compounding. The dispersion of GNPs and MWCNTs in the polymer matrix was characterized using FESEM and XRD while the thermal properties of the prepared polymer nanocomposites were analyzed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2. Methods and Materials

2.1. Material. Thermoplastic PET pallet is used as matrix material in PNC fabrication. It was supplied by Recron (Malaysia) Sdn Bhd with 100% purity of PET, melting temperature of 244 ± 2°C, and an intrinsic viscosity of 0.8400 ± 0.02 dl/g. GNPs and MWCNTs with purity ≥98% are purchased from Sigma-Aldrich, having a density of 2.0-2.5 g/cm³ and ~2.1 g/mL, respectively. All chemicals involved in this study were used as received without any further purification.

2.2. Preparation of PET/MWCNT/GNP Nanocomposites. The fabrication begins with the drying process of PET, MWCNTs, and GNPs at the temperature of 120°C for 24 hours in the oven to expel excessive moisture trapped within the material. Different weights (0.1 wt% and 0.5 wt%) of nanofillers and PET were prepared through melt-compounding using Haake rheometer equipped with an internal mixer. The temperature of the chamber was set to 250°C, and screw speed was fixed at 50 rpm for 10 minutes throughout the process. The mixing process was assisted by the high shearing rotation of the roller rotor blade that placed inside the melting chamber. Subsequently, these composites were then moulded with injection moulding (Rayran) with temperature control 280°C, mould temperature 30°C, and using 7 bars of pressure for 6 seconds of injection time.

2.3. Morphological Investigation. The morphology of PET and PET nanocomposites was observed and evaluated using a field emission scanning electron microscope (FESEM), model JEOL JSM-5900LV. The dispersion of the nanofillers was examined from the cross-sectional surface area of fractured specimens, after coating the surface with a thin layer of gold to avoid electrostatic charging during observation. The comparison between micrographs at a different weight percentage of nanofillers was made at the same level of magnification.

2.4. Thermal Properties. The melting and crystallization behavior of MWCNTs and GNPs in the polymer matrix was studied by differential scanning calorimeter (DSC) measurements using Mettler Toledo under the nitrogen atmosphere. Several dynamic scans were done, which include heating from 20°C to 300°C to remove thermal history, cooling from 300°C to 20°C, and finally reheating to 300°C at a scanning rate 10°C/min for all scans. To understand the thermal properties of the samples, we determined the glass transition temperature ($T_g$), melting temperature ($T_m$) from the second heating cycle, and crystallization temperature ($T_c$) which are taken from the first cooling cycle. The percent crystallinity of the samples was calculated to capture thermal history using the following equation [13].

$$X_c = \left( \frac{\Delta H_m}{(1 - W_f)H_m} \right) \times 100$$  

where $X_c$ is the percent crystallinity, $\Delta H_m$ is the melting enthalpy of the sample, $H_m$ is the melting enthalpy of 100% crystalline PET (140 J/g) [14], and $W_f$ is the weight percent of MWCNTs and GNPs in the composites.
Figure 1: FESEM images of fracture surface of (a) pure PET, (b) PET/MWCNTs 0.1 wt%, (c) PET/GNPs 0.1 wt%, and (d) PET/MWCNTs/GNPs 0.1 wt%.

Figure 2: FESEM images of fracture surface of (a) PET, (b) PET/MWCNTs 0.5 wt%, (c) PET/GNPs 0.5 wt%, and (d) PET/MWCNT/GNP 0.5 wt% nanocomposites.
2.5. Thermal Stability. The thermal stability of the pure PET and PET nanocomposites was measured via thermogravimetric analysis (TGA). Mettler Toledo, TGA/SDTA 851 equipment, is used with continuous nitrogen flow over the temperature range 20°C to 600°C with a constant heating rate of 10°C/min for the TGA analysis. The temperature at onset ($T_{\text{onset}}$), the temperature of maximum weight loss ($T_{\text{max}}$), and the yield percentage of the samples were observed and analyzed.

2.6. X-Ray Diffraction Analysis. X-ray diffraction measurement (XRD) was performed with a PanAnalytical XRD model XPert X-ray diffractometer with Ni-filtered CuKα radiation ($\lambda = 1.542$ Å). Data were recorded in 2θ range of 20° to 80°.

3. Result and Discussions

3.1. Morphological Characterization. The uniform dispersion of nanoparticles in polymer matrices is significant in the fabrication of nanocomposites. Representative FESEM images of the fractured surface for the pure PET and PET nanocomposites of the 0.1 wt% and 0.5 wt% nanofillers at magnification 25000x are presented in Figures 1 and 2, respectively. As shown in Figures 1(b)–1(d), the nanofillers (MWCNTs and GNP) were dispersed homogeneously inside the polymer matrix via the melt-compounding method. The FESEM micrographs of pure PET figure shown in Figures 1(a) and 2(a) observed some spherical PET particles that previously reported observed more bristle and the interface between the chains with more space [15].

The morphology of cross-section of pure PET and PET nanocomposites with 0.5 wt% of nanofillers are shown in Figure 2 where some zones show the agglomeration of MWCNTs. This is due to the strong interaction between nanotubes and PET polymer matrix. The lower content of MWCNTs shows uniform dispersion where most of the MWCNTs dispersed individually in comparison with PET nanocomposites with higher MWCNTs contents. This can lead to composites failure with unsuitable impregnation of the filler into the matrix because of agglomeration of the higher filler content [16]. Figure 2(b) displays some aggregation formation which are circled in red. Nonetheless, a significant number of fully dispersed MWCNTs could be observed. The failure of nanofillers to disperse well within the polymer matrix could lead to a decrease in the surface area of the interphase reaction between MWCNTs and PET matrix, thus minimize the uniform size distribution. As depicted in Figures 1 and 2, an increase in the percentage of GNP does not affect the distribution of GNP in the PET matrix. GNP showed good dispersion in all samples nanocomposites, showing no agglomeration. This is due to the low melt

![Figure 3: DSC thermograms of pure PET and PET nanocomposites at (a) $T_g$, (b) $T_c$, and (c) $T_m$ in 0.1 wt% of nanofiller.](image-url)
viscosity of GNP-filled polymer nanocomposites in a certain range of filler loading. This indicates that GNPs have a better processibility compared with carbon nanotube. The two-dimensional planer geometry of GNP that resembles the layered clay-like structure also promoted the good dispersion in the PET matrix [12, 17, 18]. Good dispersion of the graphene sheet into the PET matrix is also contributed from the better interaction between the oxygen and hydroxyl functional groups of graphene with the polar groups of PET [19]. Similar morphologies for GNPs nanocomposites were observed in previous studies [20, 21].

3.2. Crystallinity Measurement. Studying the thermal behavior of the samples is needed to evaluate the thermal stability and the capability of the MWCNTs and GNPs to nucleate and crystallize the PET polymer. Figures 3 and 4 display the thermograms of DSC traces of PET samples and PET nanocomposites at a different weight percentage of nano-fillers (0.1 wt% and 0.5 wt%). From Table 1, we summarized the data of DSC analysis of PET and PET nanocomposites for both nanofillers.

Based on Table 1, the glass transition temperature \(T_g\) is 68.49°C which is lower than the value of all PET
nanocomposite. The \( T_g \) value of PET/MWCNTs 0.1 wt%, PET/GNPs 0.1 wt%, and PET/MWCNTs/GNPs 0.1 wt% is 69.92\(^\circ\)C, 70.00\(^\circ\)C, and 70.23\(^\circ\)C, respectively. By increasing the weight percentage of nano fillers loading in PET nanocomposites from 0.1 wt% to 0.5 wt%, the \( T_g \) value in 0.5 wt% of nano fillers is higher compared with 0.1 wt% of nano fillers. This is due to the restrain on the mobility of polymer chains that is affected by the presence of nanofillers. Theoretically, the glassy state is more stable as more energy required to break the chains from the attractive polymer matrix interface that limits the chain mobility, which in return increase the glass transition temperature (\( T_g \)). Increase \( T_g \) distresses the elasticity of the PET chain. According to a previous study, the interaction between polymer chains and reduction of chain mobility increases \( T_g \) together with the addition of nanoparticles [22].

From the results in Table 1, the crystallization temperature (\( T_c \)) for PET nanocomposites is higher than pure PET which shows that crystallization occurs at higher temperatures. The crystallization temperature (\( T_c \)) of PET nanocomposites with the presence of 0.5 wt% of nanofillers is higher than 0.1 wt% of nanofillers. Thus, a higher content of MWCNTs will increase the temperature value of \( T_c \), suggesting that MWCNTs could effectively act as nucleating agents in PET/MWCNT nanocomposites. This is due to the development of crystallization nuclei which shows the nucleating effects of the fillers [23]. Hence, small quantity of MWCNTs could successfully improve the crystallization of the PET matrix through heterogeneous nucleation [24]. The value of \( T_c \) in PET/GNPs 0.5 wt% is slightly higher than PET/GNPs 0.1 wt% resulting in the crystallization peak shifts towards higher temperatures. This is due to lower energy that is required for cold crystallization as the GNP content increases which indicates GNPs acting as a nucleating agent [25]. From Figures 3(c) and 4(c), DSC thermograms indicate that as the heat added, the melting temperature of pure PET is lower in comparison with the sample with addition nanofillers. The addition of nanofillers decreased the melting temperature (\( T_m \)) which indicates that the PET nanocomposites melts at lower temperatures by the existence of MWCNTs and GNPs as the nucleation sites of PET crystal.

The value of the degree of crystallinity was calculated from equation (1). From the equation, the degree of crystallinity (\( X_m \)) of pure PET is calculated to be 28.20% compared with PET/MWCNTs 0.5 wt% that is 45.48%. Meanwhile, the slight increase in crystallinity with the incorporation of nanofillers contents in 0.1 wt% and 0.5 wt% indicates that GNPs and MWCNTs act as a nucleating agent that promotes crystallization. This can be supported with the shifts of crystallization temperature (\( T_c \)) to lower temperature as the content of GNPs is decrease, which indicates that the additives lowered the activation energy for crystallization [25]. Furthermore, nanofiller content changes the crystal structure of PET with an increase in the percentage of the degree of crystallinity with a higher content of MWCNTs and GNPs as they provide the nucleation site for the growth of crystalline domains. This is due to more nucleating site presented by the nanofillers that promotes nucleation [26] [27].
3.3. Thermal Analysis. Thermal stability is an important property in the science and technology industry for polymer nanocomposites to observe the thermal degradation and thermal behavior with the change of temperature. This is important to further determine the reliability of the products to meet the industrial’s standard. The TG curves for 0.1 wt% and 0.5 wt% of nanofillers are depicted in Figures 5(a) and 5(b), respectively. The characteristics temperature of pure PET and PET nanocomposites are summarized in Table 2.

Pure PET displays a lower thermal decomposition compared with PET nanocomposites with the presence of nanofillers at both weight percentages. From Table 2, it is shown that the decomposition starts at 334.14 °C for pure PET with maximum degradation temperature, $T_{\text{max}} = 434.55$ °C. An increase in TGA onset temperature indicates higher thermal stability for the nanocomposites. The TGA onset temperature in nanocomposites containing 0.1 wt% and 0.5 wt% of MWCNTs is shifted to a higher value, which is $T_{\text{onset}} = 342.23$ °C and $T_{\text{onset}} = 330.75$ °C, respectively. Compared with the pure PET, this indicates that the MWCNTs could slightly improve the thermal stability. This is due to the existence of carboxylate CNTs (c-CNT) which lead to stabilization of PET matrix due to the higher crosslinking between MWCNTs and PET matrix and MWCNTs acted as a physical barrier that prevents the diffusion of volatile products out of the polymer nanocomposites [15] [24] [28]. The thermal decomposition can also be influenced by the depolymerization, commonly known as chain unzipping and random decomposition [29]. As shown in Table 2, the weight residue of PET/GNPs at 0.1 wt% and 0.5 wt% was enhanced in comparison to neat PET, which further enhanced the thermal stability. Based on previous study, this is attributed to 2-dimensional planar structure of the graphene sheet in the PET matrix that served as a protective layer which prevents the thermal degradation of PET [30]. Furthermore, the thermal stability of PET/GNPs in 0.1 wt% is higher compared to 0.5 wt% of GNPs, which is due to the well dispersed of the nanofillers within the PET matrix as shown in Figures 1 and 2.

3.4. XRD Analysis. Figure 6 illustrates the X-ray diffraction results of pure PET and PET nanocomposites. In pure PET, the diffraction of the PET polymer matrix causes wide diffraction intervals between 12° to 30° and between 30° and 40° that resolved into crystalline peak and amorphous background [31]. Peaks that attributed to the formation of graphite appeared approximately at $2\theta = 26.6^\circ$ and $2\theta = 26.54^\circ$ in each nanocomposite with GNP additives and correspond with graphene (002) plane. This shows the presence of graphene platelets that is also mentioned in previous study [32, 33]. The PET/GNPs 0.5 wt% display sharper crystalline peak indicating higher crystallinity compared with PET/GNPs 0.1 wt%, which is in agreement with Table 1. There was no significant peak of MWCNTs especially in the 0.1 wt% nanofillers content due to the small amount of MWCNTs present in the nanocomposites. However, the diffraction peak (002) for MWCNTs is observed approximately at $2\theta = 26^\circ$ that associated with the long-range order of the concentric arrangement of MWCNTs [34].

4. Conclusion

In this study, we concluded that PET nanocomposites were successfully fabricated with MWCNT and GNPs nanofillers dispersed at 0.1 wt% and 0.5 wt% via the melt-compounding method with internal mixer. We fabricated nanocomposites with good dispersion of MWCNTs and GNPs in PET matrix without any modification of the filler type. Distribution analysis by FESEM showed that PET nanocomposites with 0.1 wt% of nanofillers displayed a more uniform distribution of GNPs and MWCNTs compared with 0.5 wt% of nanofillers which shown some clustering of nanofillers especially in a sample containing 0.5 wt% of MWCNTs. The incorporation of MWCNTs and GNPs resulted in the improvement of crystallization of PET nanocomposites indicating that the nanofillers used acts as nucleating agents. Furthermore, the small quantity of MWCNTs and GNPs can slightly increase the thermal stability compared with pure PET due to the fillers acts as the barrier against thermal decomposition. Further development of PET/MWCNT/GNP nanocomposites will be performed.
for targeted application with an important role in future industrial applications.

Data Availability

The results data used to support the findings of this study are included within the article.

Conflicts of Interest

The author(s) declare(s) that they have no conflicts of interest.

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