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Abstract. In recent times the blending of different biodegradable materials to produce nanocomposites with improved properties has been a significant point of discourse by many researchers. This study reports a melt blend of poly (lactic acid) (PLA), polyamide (Nylon 66) and graphene nanoplatelets (GnP). The thermal stability and chemical functional characteristics of the nanocomposites produced were succinctly investigated using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR). The blending was carried out by using a twin-screw extruder at a revolution speed and time of 50 rpm and 20 minutes, respectively. The composition of GnP in the PLA/PA66 was varied from 0 – 5 wt.%. The results showed that the increased of the GnP concentrations improved the thermal stability of the nanocomposites. It was also observed that a strong interaction between the polymeric materials as demonstrated by the FTIR analysis. The use of a low concentration of graphene in PLA/PA66 blend has been demonstrated to improve the thermal stability of the nanocomposites.

1. Introduction

Poly (lactic acid) is classified as biopolymer thermoplastic utilized from renewable resources and often used as a substitute to a petroleum-based polymer. As for now, PLA has gained extensive research due to high-strength, high-modulus, eco-friendly, biocompatibility, processability and 25–55% less energy in PLA production [1]. Despite all the advantages, PLA is lacking in term of reactive side chain groups, less rate of degradation, mostly poor in toughness and hydrophobicity [2]. Therefore, blending with a tough polymer is capable to overcome all these drawbacks and improve the functionality of PLA [3].

Polyamides-66 (PA66) or known as nylon-66 is widely used in engineering thermoplastics, with various applications. PA66 is classified as a semi-crystalline thermoplastic polymer which possesses excellent properties such as low density, processability, good strength, solvent resistance, self-lubricating, and good abrasion resistance [4]. Thus, PA66 is a good candidate for blending with PLA which requires high strength properties. PA66 has been blended with polypropylene and other polyolefins [5]. Novello et al. [6] also investigated the blend of PA66 with polyethylene terephthalate (PET) and short glass fiber (SGF) and found that the blend showed a good impact, tensile and flexural

properties. Like any other polymer blends, the binary blending of PLA/PA66 normally showed incompatible as both of the polymers are brittle and resulted in poor mechanical properties. In order to overcome immiscibility issues between PLA with PA66, the addition of nanofiller is required to achieve the desired properties.

Currently, graphene is well-known high surface area nanofiller and it possess excellent mechanical properties such as stiffness and strength [7-8] due to its unique structure which consist of sp2 hybridized of one-carbon atoms packed in a honeycomb-like lattice [9]. Several studies have been conducted in the small capacity of graphene loaded in PLA blends. Bijarimi et al. [10] had studied the various capacity of GnP loaded in the PLA/PA6 blends with 0.5, 1.0, 3.0 and 5.0 wt%. They reported that the 5% GnP has resulted in increasing the thermal and mechanical properties of PLA/PA6 blend. On the other hand, Chieng et al. [11] had prepared plasticized PLA-based nanocomposites by adding various concentrations of graphene nanoplatelets (GnP) and analyzed the mechanical, thermal properties and crystallinity. The results shown that the addition of 3% of GnP in the reinforced plasticized PLA (p-PLA) increased the elongation at break and tensile strength of the nanocomposites by 60.6% and 26.5, respectively. The thermal analyses displayed that increasing the GnP content triggers a significant increment in thermal stability but not the crystallinity. In this study, the effect of various concentrations of GnP loaded in PLA/PA66 blends were investigated in terms of thermal stability and chemical characteristics by using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR).

2. Materials and methods

2.1. Materials
The polylactic acid (IngeoTM -Biopolymer 2002D-grade) was provided by Unit Technology Ltd, China. It has density, melt flow index and melting temperature of 1.24 g/cm^3, 4–8 $g/10$ min and 160-170ºC, respectively [12]. Polyamide66 (PA66) was supplied by DuPont Co. Ltd. It has a density and melting temperature of 1.14 g/cm^3 and 263ºC respectively. M-grade GnP was supplied from XG-Sciences (US Michigan) it has a surface area between 120 to 150 m^2/g, the average thickness between 6-8 nm and the density 2.2 g/cm^3 [13].

2.2. Sample composition and blending procedure
In this study, a thermally stable material was fabricated by blending different proportion of PLA, PA66, and GnP. The blend ratio was fixed at 60/40 PLA/PA66 for all samples by increasing the concentration of GnP in PLA/PA66 nanocomposites. The blends were mixed manually using a glass beaker and then prepared by using twin-screw extruder. The temperature profile at the feed section was 290°C, decreasing to 253°C at the head of the die zone. The rotation speed of the screw fixed at 50 rpm/min. The compound is blended twice for each blending compositions and blended slowly to ensure homogenous blend [12]. The dimension of the die used were of 1 mm thickness and 20 mm width. The total amount of weight of each blend is 100 grams. Table 1 depicts the sample composition and concentration.

Table 1. Sample composition and concentration.

| Composition	PLA (wt.%)	PA66 (wt.%)	GnP
PLA	100	0	0
PA66	0	100	0
PLA/PA66	60	40	0
PLA /PA66 /GnP 0.5	60	40	0.5
PLA /PA66 /GnP 3	60	40	3
PLA / PA66/GnP 5	60	40	5

2.3. Characterization

The thermal stability of the material under heat was determined as well as the chemical surface. The samples with an average weight of 1-2 mg were characterized by using differential scanning calorimetric (DSC) with a nitrogen atmosphere. The nanocomposites thermal properties were examined via utilization of DSC as well. The sample was prepared in the aluminum pan with pierced lids and heated up to 300ºC at 10ºC / min steady rate. The glass transition temperature, melting and crystallization temperatures were analyzed and recorded. DSC was used to identify the crystallinity of the polymer through the polymer related heated (fusion). The change in sample mass during heating was evaluated by using thermogravimetric analysis (TGA). Chemical reactions or physical transformations can cause mass decompositions while the sample heating. Mettler Toledo TGA/SDTA 851e apparatus was used to evaluate the thermal stability of PLA and blends. Samples with average weight of (6 ±7 mg) were added to the alumina crucibles. As a reference, an empty alumina crucible was employed. The temperature, weight and derivative of the sample and heat flow were identified after heating from ambient temperature at increasing rate of 20ºC per minute.

The Fourier transform infrared (FTIR) was used to analyze the chemical properties of nanocomposites blends. The infrared (IR) spectra were recorded using a Spectrum 400 FT-IR and spectrometer by with 4 cm^{-1} resolutions and 10 scans in the 4000–500 cm^{-1} spectra region with resolution over 33 scans [14].

3. Results and discussion

3.1. Thermal analysis

The DSC curves of PLA, PLA/PA66 and PLA/PA66/GnP nano-composites are shown in figure 1. The glass temperatures of PLA/PA66/GnP nano-composites for different weight per cent of 0.5, 3 and 5 wt.% were found not to change extensively with the addition of GnP. The result obtained for each of the polymeric material blends, therefore, revealed that there is no difference in the heat flow for PLA/PA66 and PLA/PA66GNPs. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) values derived could not be estimated.
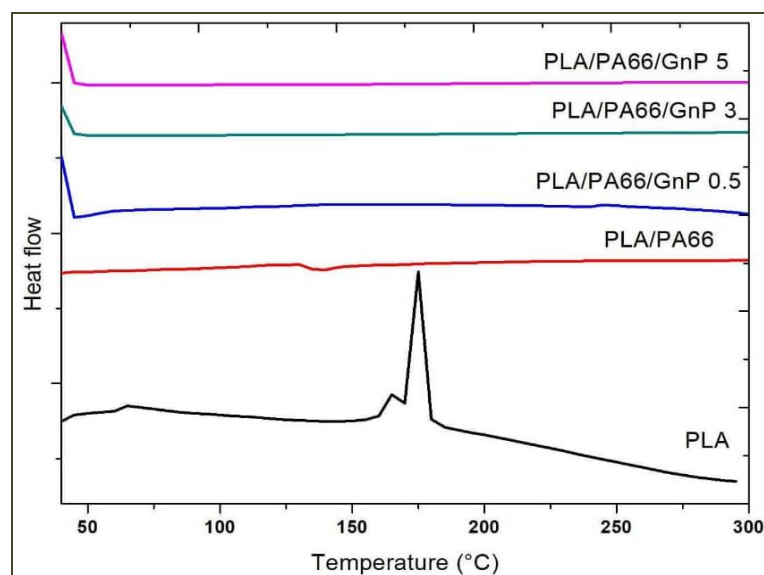
Figure 1. DSC graph of PLA, PA66 and PLA/PA66/GnP nanocomposites.

Figure 2(a) depicts the degradation temperature of PLA, PA66, PLA/PA66 and PLA/PA66/GnP nanocomposites. It was noticed that the incorporation of graphene in PLA/PA66 matrix significantly enhanced the thermal stability due to the good dispersion of GnP in the nanocomposites as shown in the TGA plot. However, the degradation and weight loses at $T_{5\%}$, $T_{10\%}$, $T_{25\%}$ and $T_{50\%}$ for PLA, PA66, PLA/PA66 and PLA/PA66/GnP nanocomposites are summarized in table 2. The pristine PLA blend shows an initial mass loss of 5% at temperature of 299.77ºC and loss of 50% at temperature of 346.85ºC. On the other hand, the PLA/PA66/GnP 3 blend shows an initial mass loss of 5% at temperature of 324.74ºC and loss of 50% at temperature of 407.03ºC. In the derivative thermogravimetric (DTG) curve, maximum degradation temperature for all blends can be seen in figure 2(b). It was observed that there were two peaks in the DTG curves which indicate the PLA and PA66 degraded individually due to the immiscible blend of the two polymers.
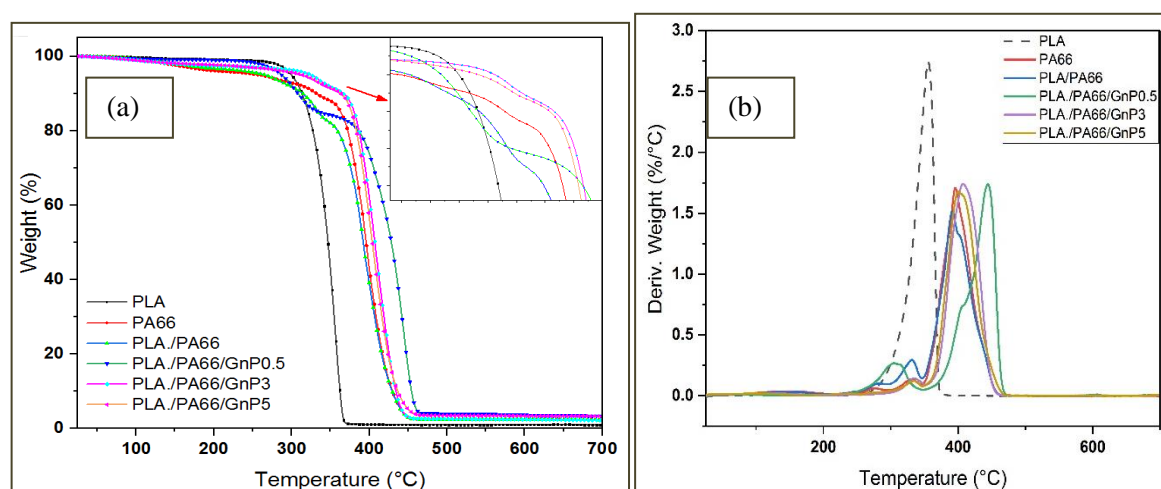

Figure 2. (a) TGA graph of PLA, PA66, PLA/PA66 and PLA/PA66/GnP and (b) DTG graph of PLA, PA66, PLA/PA66 and PLA/PA66/GnP.

Table 2. The degradation of weight loses at $T_{5\%}$, $T_{10\%}$, $T_{25\%}$ and $T_{50\%}$.

Sample	$T_{5\%}$	$T_{10\%}$	$T_{25\%}$	$T_{50\%}$
PLA	299.77	313.21	331.99	346.85
PA66	258.31	331.97	377.51	395.85
PLA/PA66	265.03	314.26	369.45	392.21
PLA/PA66/GnP0.5	287.54	308.2	398.09	428.42
PLA/PA66/GnP3	324.74	366.23	390.97	407.03
PLA/PA66/GnP5	313.39	363.02	387.72	403.86

3.2. Functional group chemical analysis
In this study, the functional group characterization of the sample was observed using the Fourier transform infrared spectra of PLA, PA66, PLA/PA66 and PLA/PA66/GnP as illustrated in figure 3. From the PLA spectrum, four central regions were identified and this includes the –CH stretching at 2900–3010 cm^{-1}, –C=O stretching at 1680–1817 cm^{-1}, C–H bending at 1340–1485 cm^{-1} and –C–O stretching at 1000 –1240 cm^{-1}. Despite the increment of GnP loadings in the blend systems, the characteristic peaks for the PLA were conspicuously dominant. The observation conducted on other polymeric materials shows the presence of peaks which indicated that chemical interaction was observed in the polymer configuration [15]. This indicated a strong interaction between the polymeric materials blended as supported by Chieng et al. [11].
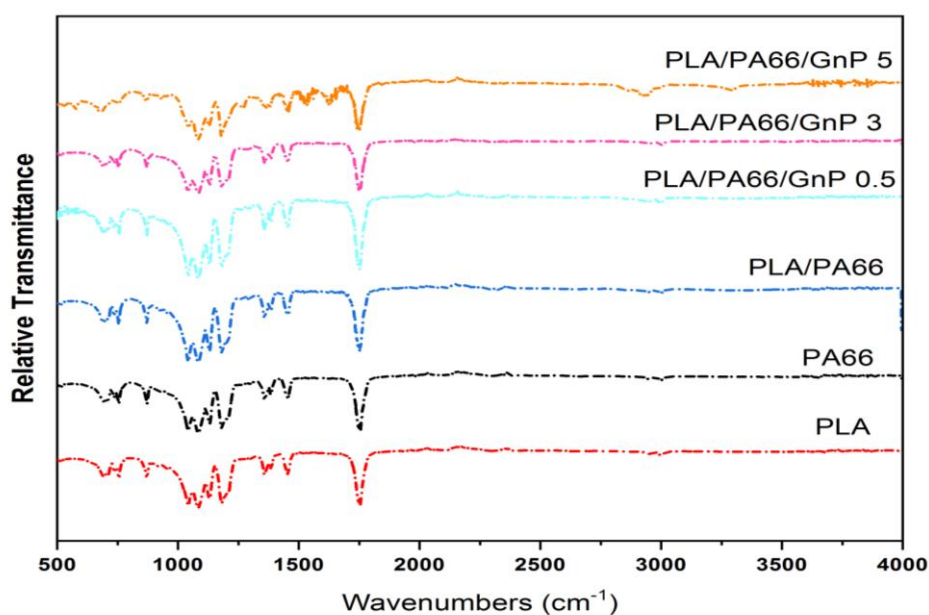
Figure 3. FTIR of PLA, PA66 and PLA/PA66/GnP nanocomposites.

4. Conclusions

PLA/PA-66 blends with different loadings of GnP were prepared by melt blending method and their thermal and chemical properties were investigated. The thermal analysis by thermogravimetric analysis (TGA) indicated that there was a significant improvement of thermal stability in the blends containing graphene as the loadings of GnP was increased. DSC thermogram of PLA/PA-66 also exhibited a reduction in cold crystallization temperature to zero after the addition of graphene nanoparticles. Based on both analyses it was shown that 3% of GnP loaded obtained the optimum thermal stability. Moreover, the results from FTIR also confirmed the interaction between graphene and PLA/PA66 phases. From this study, it can be concluded that the thermal stability of PLA/PA66 could be enhanced by incorporating GnP and suitable for industrial application.

Acknowledgements

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