Thermal Characterization of Non-Functionalized Low Content Graphene Nanoplatelets (GNP) Added Nylon 66 Polymer

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ABSTRACT

Thermal behaviour of graphene nanoplatelets (GNP) reinforced nylon 66 nanocomposites were investigated using differential calorimetric scanning (DSC), thermogravimetric analyzer (TGA) and dynamic mechanical analysis (DMA). The influence of low content GNP on thermal properties of GNP/nylon 66 nanocomposites was studied for low GNP content (0.3, 0.5 and 1.0 wt%). DSC results indicate that addition of GNP increases crystallization temperature and degree of crystallinity of the nanocomposites. Thermal stability and mass loss were studied through TGA analysis. The results show that thermal stability and weight loss of GNP/nylon 66 nanocomposites slightly improve with the GNP addition with an increase in the onset of degradation temperature as much as 10 °C. DMA analysis shows that GNP in the nylon 66 matrix act similar to plasticizer; it decreases the storage modulus and glass transition temperatures of the nanocomposites. GNP addition also reduces tan δ indicating an improvement in the damping property of the nanocomposites. Overall, this study concludes that a minimal amount of 0.3 wt% of GNP is effective in improving the thermal properties of nylon 66 composites.

1. Introduction

Nylon 66 is a type of engineering polymers and has been commonly used as housing materials for portable electric and electronic devices. It has excellent thermo-mechanical properties and has great resistance from severe atmospheric instability [1]. Graphene, a two-dimensional sheet composed of SP2 carbon atoms arranged in a honeycomb structure, is fundamentally single layer of graphite, found in nature in the form of natural graphite flakes. Platelet carbon fillers such as graphite and graphene seem to be more important than other conventional adding materials for improving the conductivity network in composite materials [2]. The use of graphene as nanofiller in polymer nanocomposites has attracted significant research interest. The addition of very small amounts of graphene has been found to improve the mechanical, thermal and electrical properties of

nanocomposites [3]. For example, the volume percentage of GNP was shown to have a substantial impact on the thermal conductivity of NEPCM at various temperatures [4].

However, despite the potential properties of graphene nanoplatelets (GNP), preparation methods to integrate them in thermoplastics, such as in situ polymerization, solvent mixing, or melt mixing, they have low yield and high production costs due to the large number of solvents and energy required for the dispersion of nanofillers. Thus, there is a huge demand for a scalable and cost-effective fabrication technique of graphene-based nanocomposites. From an industrial point of view, melt compounding is the preferred technique as it is cost effective, environment friendly, and provides fast and continuous production [2].

Many researchers reported that nano composites based on graphene show greater strength, stiffness and lower cost as compared to nano composites based on clay or carbon filler [5,6]. The effect of GNP on the crystallization behavior of the composites has been analyzed via non-isothermal DSC experiments [7]. Thermogravimetric analysis (TGA) is widely used to investigate the thermal degradation of polymeric composites when the composite specimen is subjected to higher thermal loading [8]. The thermal stability of a substance suggests its ability to survive mechanical deformations at higher temperatures [9]. Dynamic mechanical analysis (DMA) is the most commonly used method for measuring viscoelastic properties such as storage modulus (E'), loss modulus (E") and damping factor (Tan δ) while applying continuous sinusoidal loads [10,11]. Storage modulus (E') measures the rigidity and stiffness of the polymeric structure. Due to the mobility of polymeric chain segments, E' decreases while increasing the temperature [12,13]. Loss modulus (E) reflects heat-released energy and is correlated with the viscous reaction of the polymer system. Tan δ or damping factor is the ratio between E' and E'' [14].

Several works in the literature have corroborated that hybridizing man-made synthetic fibers and plant fibers could improve the viscoelastic properties [15]. High content of carbonous materials has been reported to improve the thermal conductivity of polyamide composites [16-19]. Rashmi *et al.,* [16] found that the temperature of crystallisation and the degree of crystallinity of polyamide 11/GNP nanocomposites tend to increase with the increase in graphene loading. Rheological study highlighted improvement in storage modulus and complex viscosity with the increase in graphene weight percentage. Low-frequency plateau is observed at high graphene loading because of the pseudo-solid-like behavior of polymer melt [16]. Yang *et al.,* [17] discovered from the results of the DSC, that GOs had migrated from the PVDF masterbatch to the nylon 6 phase, and that extensive interactions between GOs and both components had resulted in GOs being partially stabilised at the immiscible blend interface. The melting peak area decreases with the increase in the amount of GOs, except for the 2 wt% GOs sample with multi-melting peaks. The occurrence of multi-melting peaks is due to crystallization hindrance, which is caused by a network of GO aggregations in PVDF domains, as observed using SEM. Thanh *et al.,* [18] noted that the glass transition temperature (T_g) of PA6 composites had slightly increased with an increase in xGnP content. In addition, the peaks in all blends have become wider than the neat PA6. Both effects indicate the xGNP containment of the PA6 chains. At the same time, the nature of this effect on the PA6 chains differs somewhat from that observed in nanocomposites based on MMT, where a slight shift from the original peak to a lower temperature was observed, accompanied by the appearance of a marked shoulder on the high-temperature side.

Kuila *et al.,* [19] discovered that dynamic mechanical analysis and differential calorimetric analysis showed that graphene in the PMMA matrix acted as a reinforcement filler; improved storage modules and glass transition temperatures for nanocomposites. Thermogravimetric analysis showed that the thermal stability of nanocomposites increased by about 35 °C. T_g of the nanocomposites as observed by DMA and DSC were shown to be 12 °C higher than that of neat PMMA. The

enhancements of E and T_g was due to the strong interactions between the polar groups of PMMA and remaining oxygen functionality of the graphene. Thermal and electrical properties of the nanocomposites also increased significantly compared with neat PMMA.

Although many studies have been conducted on high content graphene-filled polymer nanocomposites, existing literature suggests that relatively little work has been published to date on the influence of low graphene nanoplatelet content (≤1.0 wt%) on the thermal properties of PA66. Therefore, in this study, nylon 66 with addition of low GNP content will be prepared by melt blending and sonication process. The effect of GNP on the thermal properties (DSC, TGA and DMA) of nanocomposites will be investigated.

2. Methodology
2.1 Materials

Nylon 66 (Dupont, Zytel® 101F NC010) was used as the polymer matrix, without any purification. Graphene nanoplatelets (XG Sciences US) were purchased from Terra Techno Engineering. The graphene nanoplatelets (GNP) loading was varied in weight percentage at 0, 0.3, 0.5 and 1.0 wt%.

Sonication was performed to exfoliate the GNP prior to the mixing with nylon 66. The GNP was dispersed in ethanol at frequency of 40 Hz for 60 minutes using an ultrasonic instrument (Fisher Scientific Sonic Dismembrator) [15]. Nylon 66/GNP nanocomposites were prepared by mixing the GNP with nylon 66 by means of dry mixing method using a table top high speed mixture at room temperature for 5 minutes. All mixtures of nylon 66/GNP were extruded by co-rotating twin screw extruder (Sino PSM 30), in which the materials passed through heated barrels' zones and exited at the nozzle holes. The barrel temperature setting was kept constant (255-280 °C) for all sample formulations. Extruded samples were then cooled using water. Subsequently, the samples were cut into pelletized form by pelletizer machine. Figure 1 depicts a schematic diagram of the experiment work.
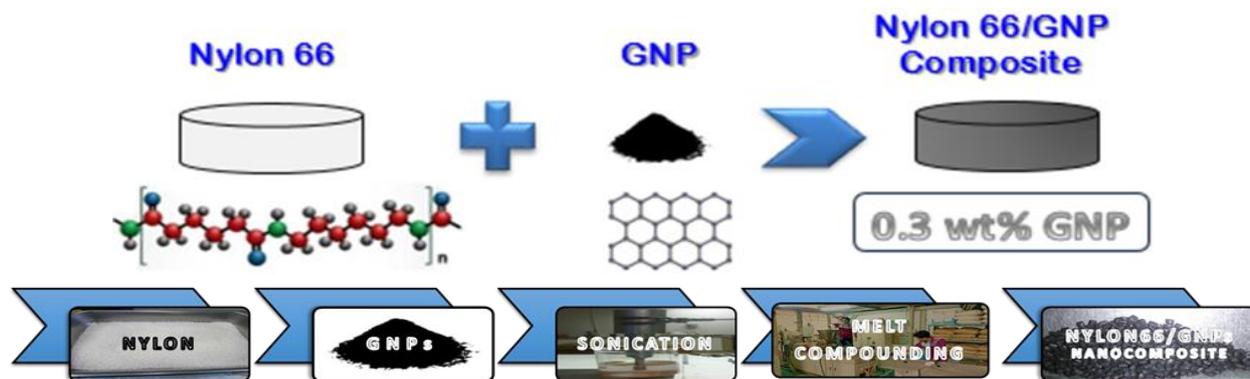
Fig. 1. Experiment work schematic diagram

2.2 Measurements

In order to investigate the thermal properties of the nylon 66 filled with various amounts of GNP, thermal analyses such as differential calorimetric scanning (DSC), thermogravimetric analyzer (TGA) and dynamic mechanical analysis (DMA) were performed. All samples were totally dried in vacuum oven at 100 °C and kept in a dehumidifying cabinet for 24 hours prior to testing.

For DSC analysis, the tests were performed under nitrogen condition using DSC7 device (Perkin Elmer) in the temperature range of 25 to 300 °C. The heat was calculated from the areas under the

curves as integrals between the onset points of the corresponding peaks. For the non-isothermal experiments, the enthalpy of fusion, ΔH_f was determined through Pyris software by analyzing the melting endothermic.

The percent crystallinity (X_c) of nylon 66 in the nanocomposites were calculated from the following equation:

$$X_c = (\Delta H_m \times 100) / \Delta H_{0m} \tag{1}$$

where ΔH_m and ΔH_{0m} are regarded as the enthalpy of fusion of the samples and the equilibrium melting enthalpy, respectively. The value of ΔH_{0m} for nylon 66 is 197 J/g.

All the important data for analysis and calculation i.e., melting temperature, glass transition temperature, heat of fusion was taken at second heating run. First heating run was carried for elimination of history of memory in the samples and its raw data was used to compare with the data of second heating run. All testing was carried three times, to confirm the reproducibility of the results.

Thermal stability is primarily a function of bond energy. When the temperature increases to the point where vibrational energy causes bond rupture, the polymer degrades. Therefore, in order to study on the thermal stability characteristic of nylon 66/GNP nanocomposites, TGA analysis was carried out using Perkin Elmer Pyrist 6 TGA analyzer. Samples (~5mg) were placed in a platinum pan and the experiments were conducted in nitrogen at a flow rate of 60 ml/min. Next, samples were scanned from 30 to 800 °C at a heating rate of 10 °C/min.

The dynamic mechanical analysis (DMA) is a powerful technique to determine the phase transitions and the relaxation process of different materials. In this study, the influence of GNP addition to the storage modulus (E') and loss modulus (E'') of nylon 66 nanocomposites were determined by using a DMA Q800 (TA Instrument) in a single cantilever configuration at a heating rate of 2 °C/min and a dynamic strain of 0.02% at 1 Hz. The test samples were prepared with a minimal length of 35 mm, width of 13 mm and thickness of 3 mm.

3. Results
3.1 DSC

The DSC thermograms of nylon 66 added with GNP at various loadings are given in Figure 2(a) and Figure 2(b). Meanwhile, the respective data of thermal properties are shown in Table 1. Incorporation of GNP into nylon 66 matrix results in increased percentage of crystallinity as compared to neat nylon 66. This suggests that there is a significant change in the microstructure of nylon 66 matrix. Meanwhile, DSC curve of nylon 66 shows a presence of two melting peaks as shown in Figure 2(a). It is well-known that nylon has two crystal forms, i.e., α-crystalline portion with hydrogen bonds between antiparallel chains and γ-crystalline with hydrogen bonds between parallel chains [20]. The melting temperature at 262.16 °C (peak 2) could be attributed to α-crystalline portion of matrix, while the melting temperature at 251.08 °C (peak 1) is attributed to the melting of the thermodynamically unstable γ-crystalline. Moreover, peak 1 was impaired with the introduction of GNP into the composites, suggesting the depressed c-form crystal of nylon 66 by well-dispersed GNP sheets [20].

As shown in Table 1, the presence of non-functionalized GNP does not alter the melting temperature, T_m of the nanocomposites. This indicates that the nylon 66 polymer has higher percentage of crystallinity compared to the nylon 66/GNP nanocomposites [21]. A significantly higher degree of crystallinity X_c, is found to be highest for nylon 66 containing 0.3 wt% GNP. Adding the 0.3 wt% GNP does not affect T_m, while X_c increases from 32.1 % to 42.2 %, compared to nylon 66. However, the T_m peak slightly shifts to lower temperatures with the increase of GNP loading from 0.5

to 1.0 wt%, but becomes weaker, indicating the depressed α-form crystallisation. The reason for this is associated to the strong restriction in mobility of the polyamide chains by the GNP, which was the leading dynamic factor in the formation of crystals through the free arrangement of polymer chains [22]. Melting temperature T_m is mainly related to the degree of hydrogen bonding in the chains which depends on the density of the amide groups. This also shows that the incorporation of GNP into matrix nylon 66 does affect significantly the degree of hydrogen bonding between the polymer chains.

The enthalpy of melting, ΔH_m was determined at a heating rate of 10 °C/min. This parameter is significant since its value is directly proportional to the overall level of X_c, possessed by polymer. The addition of 0.3 wt% GNP into matrix nylon 66 has increased the enthalpy of melting point from -63.17 to -83.14 J/g. However, it decreases with further addition of 0.5 wt% and 1.0 wt% GNP to -80.26 and -78.42 J/g, respectively.

Cooling thermograms of the nanocomposites in Figure 2(b) show only one crystallization peak. Table 1 depicts an increase in Tc value when 0.3 wt% of non-functionalized GNP is added into the matrix nylon 66, which suggests that GNP is acting as a nucleation agent for nylon 66 [7]. This indicates that activation energy for crystallization is increased, due to the addition of 0.3 wt% GNP into nylon 66 matrix [2]. GNP exhibit heterogeneous nucleation effect during composite crystallization because of its large specific surface area [23]. However, there is no further change in crystalline temperatures as GNP amount is further increased to 0.5 wt% and 1.0 wt%. On the other hand, enthalpy of crystalline, ΔH_c of nylon 66 decreases from 65.52 °C to 44.52 °C as 0.3 wt% GNP is added. The enthalpy of crystalline, ΔH_c of nanocomposites increases to 46.58 °C and 48.28 °C as the GNP content is further increased to 0.5 wt% and 1.0 wt%, respectively. Another observation is that the value of enthalpy of crystalline, ΔH_c is lower than enthalpy of melting, $-\Delta H_m$. This can be explained as some crystalline portions of polymer do not crystallize back. This is due to the presence of non-functionalized GNP that might have restricted the crystallization [24].
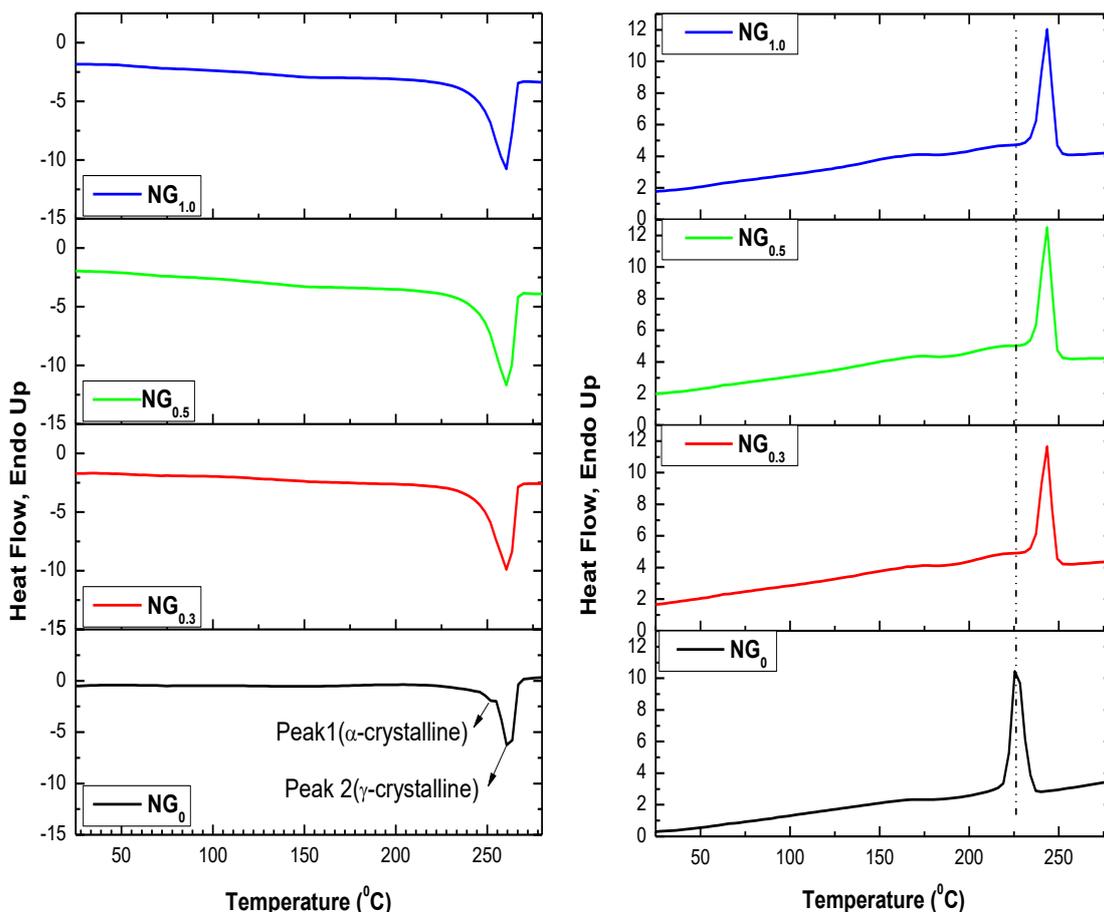
Fig. 2. (a) DSC thermograms of nylon 66/GNP during second heating and (b) DSC thermograms of nylon 66/GNP during cooling

Table 1
The DSC data for cooling and 2nd heating for nylon 66 added with different amounts of GNP

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	X_c (%)
NG0	Peak 1: 251.08	Peak 1: 1.20	226.69	65.52	56.47	32.06
	Peak 2: 262.16	Peak 2: 63.17				
NG0.3	261.67	83.14	243.24	44.52	52.66	42.20
NG0.5	261.24	80.26	243.45	46.58	52.17	40.74
NG1.0	260.63	78.42	243.42	48.28	51.66	39.80

3.2 TGA

Average results from 3 replications of test on various nylon 66/GNP composites are tabulated in Table 2. Meanwhile, the TGA and DTG curves of nylon 66 at various amount of GNP addition are depicted in Figure 3(a) and Figure 3(b), respectively. The TG curves of nylon 66 and its composites correspond to a single degradation stage with well-defined initial and final degradation temperatures. T_{max} and T_{final} as well as residue amount left of the nanocomposites are shown in Table 2. It is evident that at the 0.3 wt% GNP loading, both the T_{max} and T_{final} values have increased from 434.57 °C to 440.55 °C and 472.36 °C to 477.64 °C, respectively as compared to neat nylon 66. Meanwhile, the rate of degradation (dw/dt) decreases and the amount of residual char formation of nylon 66/GNP nanocomposites increases with increasing non-functionalized GNP. The residue left at 800 °C for NG0, NG0.3, NG0.5, and NG1.0 are 0.7097, 1.4150, 1.162 and 1.830 mg, respectively. It indicates clearly that the 0.3 wt% loading has better thermal stability as compared to 0.5 wt% and

1.0% loading of GNP. These results suggest that the incorporation of 0.3 wt% of GNP into the system has improved the structural destabilisation point of the composites. The increment is also attributed to the well dispersion of GNP in polymer matrix, which resulted in a strong barrier effect preventing the thermal degradation to a certain extent and resulted in the improvement in the thermal stability of the nanocomposites [24].

Table 2
T_{max}, T_{final} and residue left values for various GNP/nylon 66 nanocomposites

Sample	T_{max} (°C)	T_{final} (°C)	Residue (%)	Residue (mg)
NG0	434.57	472.36	14.141	0.7097
NG0.3	440.55	477.64	28.296	1.4150
NG0.5	436.97	473.52	23.258	1.162
NG1.0	427.32	472.99	36.603	1.8302
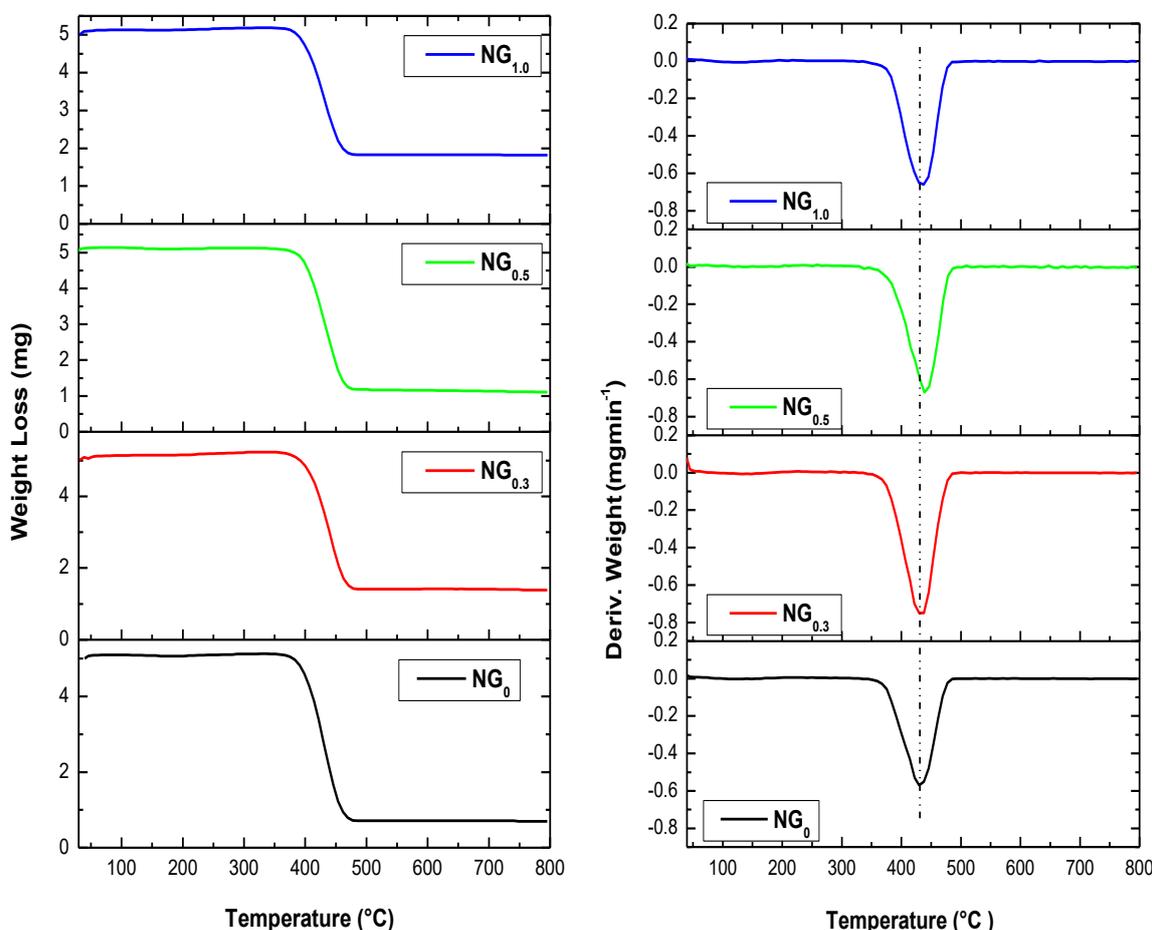
Fig. 3. (a) Thermogravimetric and (b) derivative thermogravimetric curves of nylon 66 and graphene nanoplatelet/nylon 66 nanocomposites

These results suggest that the integration of 0.3 wt% of GNP into the system has improved the structural destabilization of composites. The increase is also attributed to the well-dispersed GNP in the polymer matrix, which resulted in a strong barrier effect preventing the thermal degradation to some extent and improved the thermal stability of nanocomposites. This also indicates the positive effect of the GNP on the thermal stability of nanocomposites. In summary, the T_{max} and the residue value at 0.3 wt% are increased as a result of GNP addition, which illustrates the enhanced effect of GNP on nylon 66 thermal stability [25].

3.3 DMA

The temperature dependences of loss factor (tan δ), storage modulus and loss modulus for the nanocomposites with different loadings of GNP are illustrated in Figure 4, Figure 5 and Figure 6, respectively. Dynamic mechanical analysis (DMA) was used to study the viscoelastic properties of engineering materials by giving specific information on the storage modulus (E'), loss modulus (E'') and tan δ with regard to the temperature range. The storage modulus gives the modulus of elastic of produced nanocomposites at the same time as the loss modulus is a number of frictional losses incurred (energy dissipated) because of the movement of polymer chains. The complex modulus or E* of composites subjected to DMA test consists of storage modulus (E') and loss modulus (E'') as shown in Eq. (2).

$$E^* = E' + E'' \tag{2}$$

Storage modulus (E') represents the elastic energy received during deformation and stored into the material during a loading cycle, energy which is released at the end of the loading. Loss modulus (E'') represents the energy dissipated into the composite as heat during a loading cycle, and it is a means of measuring the vibration energy which changes itself into heat due to internal friction and it cannot be recovered.

3.3.1 Tan delta

The glass transition temperature (T_g), which represents one of the major viscoelastic transitions of a material, is often obtained from the maximum of the tan δ curve as shown in Figure 4. The results show that T_g shifts to lower temperature as GNP content increases from 0.3 wt% to 1.0 wt% of GNP. The decrease of T_g for higher GNP concentration is probably caused by the breaking of hydrogen bonding due to the presence of GNP in the polymer matrix.

It is also observed that neat nylon 66 (NG0) has the highest tan δ peak of 0.138. The value of tan δ at T_g is an indicator of restricted volume of polymer chains, whereby the mobility of the chains is constrained both by means of neighbouring crystallites or strong filler polymer interactions. It is also noteworthy that the peak height of nylon 66/GNP nanocomposites decreases greatly, indicating that the tan δ for the nylon 66 matrix were dramatically reduced by the incorporation of GNP. This indicates that the molecular mobility of the composites decreases with the introduction of GNP, and thus, the mechanical loss to overcome inter-friction among the molecular chains is reduced.

The main reason for the increase in T_g is that the vast interfacial area created by the graphene may affect the behaviour of the surrounding polymer matrix, while the change in free volumes between the polymer chains is due to a possible mechanism that can significantly contribute to the reduction in T_g following the modification of the nylon 66 polymer chain by graphene nanoplatelets. When nanoparticles increase free volumes, e.g., by cutting the chains apart the movability of the chains increases and the T_g drops.

Figure 4 also shows that the damping factor decreases in the nylon 66/GNP composites and the maximum values of the damping factor for each composite is obtained at smaller temperatures compared with the values of the damping factor of pure nylon 66. Stiffness of the nylon 66/GNP composites is higher than the stiffness of pure nylon 66. The smaller values of the maximum of the damping factor are due to the possible higher amplitude of the molecular movement of the nylon 66 chain [26].

Generally, the damping of the polymer is much greater than that of the fibers. The incorporation of inorganic fibers into polymer matrix will increase its elasticity and reduce its viscosity, and less energy will be consumed to overcome the friction forces between molecular chains. As a result, the tan d of the nylon 66 matrix decreases in the presence of GNP [26]. Idicula *et al.,* [27] reported that T_g-associated lower tan δ composites could withstand higher loads. This clearly indicates the improved load-bearing capacity of the composites after the addition of GNP. This is mainly due to the restriction of the intermolecular movement of the polymer chain [28,29].
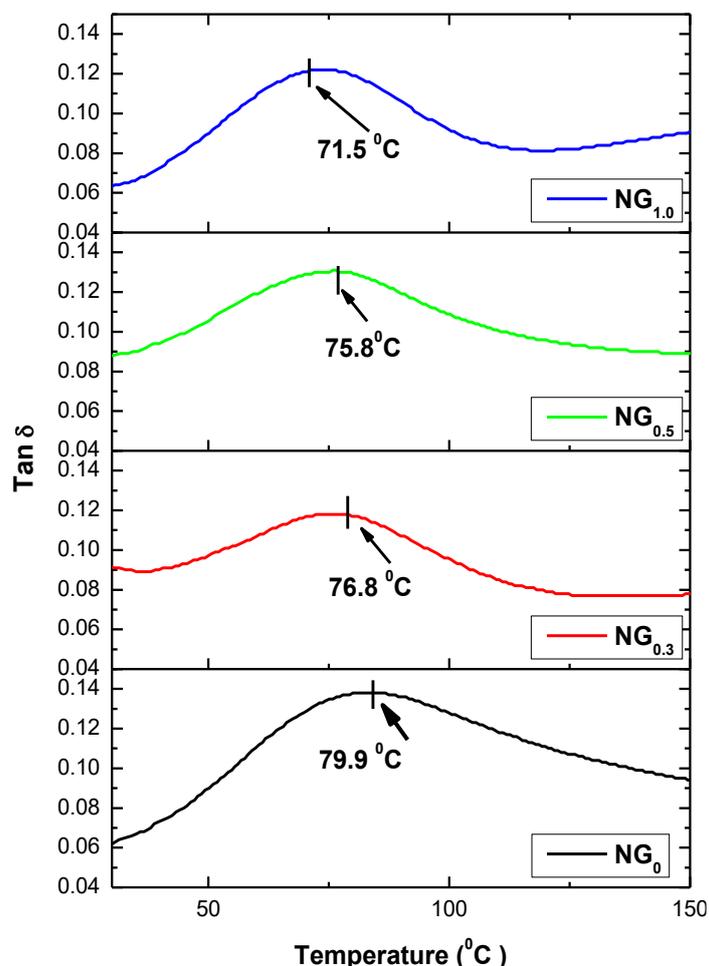
Fig. 4. Loading Effect on the tan δ of nylon 66 filled with various GNP amounts

3.3.2 Storage modulus

As shown in Figure 5, with the incorporation of GNP, the dynamic storage moduli of nylon 66 nanocomposites are found to decrease remarkably compared to that nylon 66, especially below the glass transition temperature (T_g) region. It is also observed that storage modulus decreases with temperature hence, the components became more mobile since it lost their close packing arrangement [30].

Meanwhile, the storage modulus value for 0.3 wt% GNP is higher than that 0.5 and 1.0 wt% GNP. This may be explained by the lower tendency for GNP agglomeration for the composites with lower GNP concentration [10]. Lower intermolecular interactions caused by agglomerations of GNP in nylon 66 matrix leads to a lower storage modulus as observed in NG0.5 and NG1.0 samples [30]. Similar observation have been reported by Rasana *et al.,* [29] in which higher nanofiller loading (CNT) has

reduced the storage modulus of glass fibre reinforced epoxy composites.
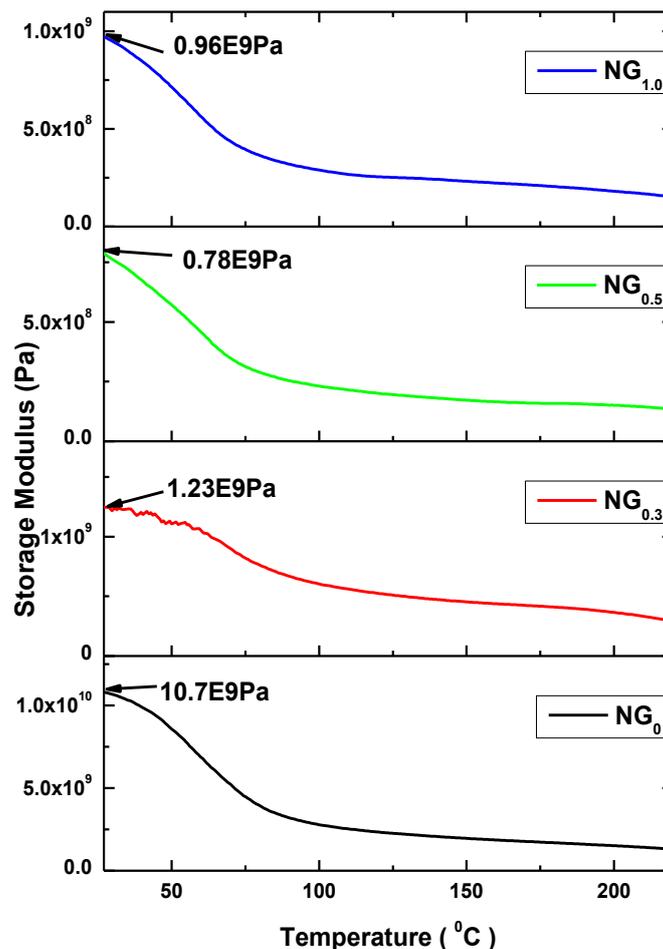
Fig. 5. Effect of GNP addition on the storage modulus of nylon 66/GNPnanocomposites

3.3.2 Loss modulus

Figure 6 demonstrates the loss modulus curves of nylon 66 and nylon 66/GNP nanocomposites. The loss modulus represents the energy dissipated as heat and reflects the internal motions of viscous segment per cycle under deformation.

Higher amount of dissipated energy was converted into heat energy under load for nylon 66 polymer as shown by an increase in its loss modulus as compared to nylon 66/GNP nanocomposites. The loss modulus peak of GNP nanocomposite is broader due to poorer interaction between nylon 66 and filler, hence reducing energy dissipation.

At 0.3 wt% of GNP, the loss modulus increases by two magnitude order at 10^9 Pa, compared to 10^7 Pa for 0.5 and 1.0 wt% of GNP. It shows that a minimal GNP addition is effective to enhance the loss modulus. At low GNP content, better dispersion is achieved, thus improved fibre/matix adhesion, which allows better energy dissipation. However, at a higher GNP concentration, the loss modulus decreases due to the agglomeration of GNP which loosens the polymeric structure. Similar findings have been reported by Rasana *et al.,* [29], in which the addition of higher nanofiller (CNT) has reduced the viscous dissipation of glass fiber-reinforced epoxy composites. Hossain *et al.,* [28] also reported that higher GNP loading decreased the E" of polymeric composites.
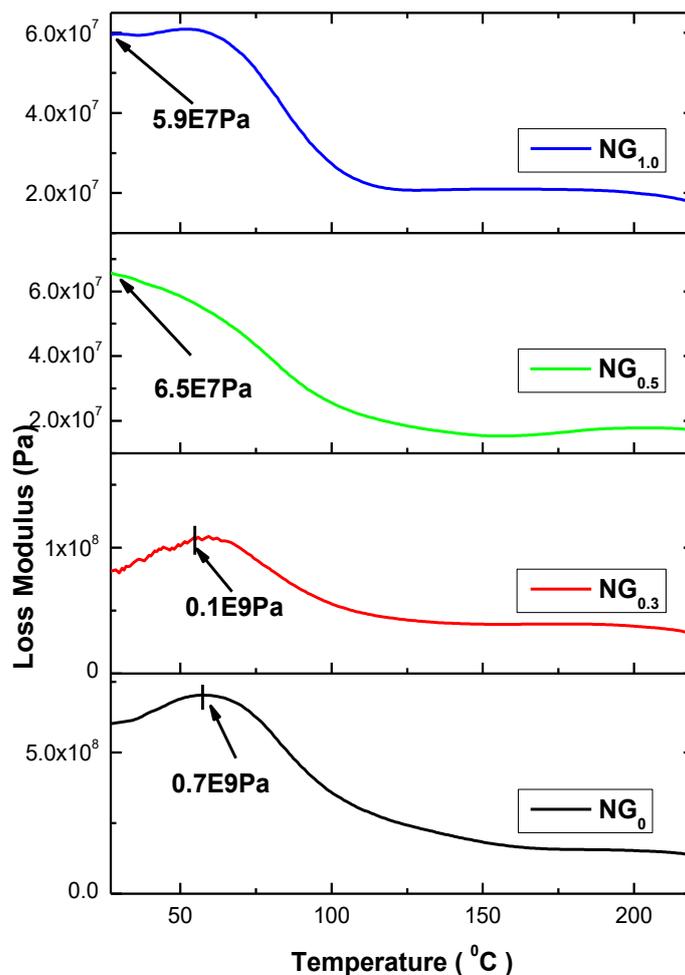
Fig. 6. Effect of GNP addition on the loss modulus of nylon 66/GNP nanocomposites

4. Conclusions

The potential of using graphene nanoplatelets (GNP) as reinforcement in nylon 66 for producing a nanocomposite with improved thermal performance was explored. The incorporation a minimal amount of GNP (3 wt%) in nylon 66 matrix is found to improve the thermal properties of nylon 66 as demonstrated by the increase (+6 °C) of the initial and final degradation temperatures. Addition of 0.3 wt% GNP showed the highest improvement in thermal stability, compared to the 0.5 and 1.0 wt% GNP addition due to improved structural destabilisation point of the composites. Addition of GNP is found to be effective in reducing T_g in nylon 66/GNP nanocomposites, in which they show a steady decrease of T_g with the increase of GNP content. While damping factor decreases with GNP addition in the viscous region, it shows an increase in the lower temperature region. This clearly indicates the improved energy absorption capacity of nylon 66 at room temperature with the addition of GNP.

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