

UNDERSTANDING THE PROPERTY ENHANCEMENT MECHANISM IN EXFOLIATED GRAPHITE NANOPATELETS REINFORCED POLYMER NANOCOMPOSITES

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Keywords: polymer nanocomposite, interfacial interactions, exfoliated graphite nanoplatelets

Abstract

The focus of this study is to understand how exfoliated graphite nanoplatelets (xGnP) alter the elastic response of the polymers and reveal the mechanisms responsible for the property enhancement observed in xGnP reinforced polymer nanocomposites. The nanocomposites were made by coating and melt compounding followed by injection molding. Polyamide12 (PA12) was used as the matrix. The mechanical properties, including tensile strength and modulus, flexural strength, and thermo-mechanical properties such as the glass transition temperature (T_g) were determined as a function of the xGnP content. The results indicated that a fraction of the polymer chains can be extensively immobilized due to the confinement effect of the xGnP at its large surface area. This suggested presence of a secondary mechanism that is responsible for the PNCs' enhancement of the mechanical and thermomechanical properties. As shown, based on the rheological and morphological studies, the contribution of such a mechanism is highly affected by the level of xGnP agglomeration.

1 Introduction

The large specific surface area and small size of the nanofillers are responsible for the dominant physical/chemical interfacial interactions observed in polymer nanocomposites (PNCs). Such interactions result in i) nanofiller agglomeration due strong van der Waal forces and ii) a region with an extensive degree of immobilized chains along the nanofiller–polymer interface. The aforementioned interfacial phenomena contribute to the interfacial load transfer and hence the reinforcing efficiency of the nanofiller [1-4].

Fabrication of PNCs with predetermined properties is of great importance and is currently done in a non-systematic approach based on trail-and-error testing [5-7]. Therefore, studies have been conducted to modify and employ analytical or computational approaches to design PNCs with engineered properties for targeted applications. However, the majority of the models does not

account for presence of interfacial interactions at the nano-scale. Therefore, there is a need for better understanding of the reinforcing mechanisms induced by the interfacial interactions [8-11].

The presence and strength of the interfacial interactions depend on the material system used and the fabrication method employed to manufacture the PNCs. To investigate the effect of the interfacial interactions on the bulk properties of PNCs one needs to correlate the interactions with the thermomechanical and rheological performance of PNCs, which reveal information locally, and understand how this performance is related to the bulk properties such as the modulus of elasticity. As reported, the configurational rearrangement and relaxation processes of long polymer chain segments are significantly sensitive to local constraints [12-14]. The studies show that presence of the immobilized fraction of polymer chains results in a significant shift in T_g that coincides with the enhancement in the mechanical properties of PNCs. It has been reported that good dispersion of the nanofiller remarkably restricts the mobility of polymer chains and enhances the interfacial interactions due to the larger and accessible surface area of the nanofiller/matrix interface [15-17].

The goal of this study is to understand the property enhancement mechanisms which are dictated by the interfacial interactions in PNCs. xGnP/PA12 nanocomposites are fabricated using two different compounding methods: i) coating followed by melt-mixing and ii) direct melt mixing to study the effects of the dispersion state on the reinforcing mechanism. The mechanical properties, including tensile strength and modulus; and flexural strength were characterized. The low-frequency rheological behavior of the PNCs melt such as the dynamic viscosity and the thermomechanical properties including loss modulus and T_g were determined in order to provide an understanding of the correlation between the interfacial interactions at the nano-scale and the bulk PNC properties.

2 Material and methods

- Materials

Polyamide-12 (PA12) powder (trade name of VESTOSINT® X 1553 white, Evonik Industries, Essen, Germany) with average diameter between 50 μm and 100 μm and a melting temperature in the range of 176-184°C was used as the polymer matrix. Exfoliated graphite nanoplatelets (xGnP) was used as the nanofiller with an average diameter of ~1 micron and thickness in the range of 10-20 nm and was purchased from XG Sciences.

- Fabrication of Nanocomposites

The xGnP-PA12 PNCs were fabricated using a DSM Micro 15cc Compounder (vertical, co-rotating twin-screw micro extruder) and 10 cc injection molding machine. The materials were mixed at $T_{\text{barrel}} = 220$ °C and screw speed of 60 and 100 rpm for 1 and 2 min, respectively, and the melt was injection molded at $T_{\text{mold}}=80$ °C and a pressure of ~7.5 bar. Two different compounding methods were employed. The coating followed by melt mixing, and the direct melt mixing.

Coating followed by melt mixing: The PA12 powder was coated with xGnP up to 15 wt % using mechanical sonication of as-received xGnP in isopropyl alcohol (IPA) for 45 min. [18]. followed by manual mixing of the PA12 powder in the solution. The solution was then filtered and the composite powder was thoroughly dried in a vacuum oven at 100 °C for 10 hrs to minimize hydrolytic degradation. The xGnP-coated PA12 powder was then melt blended using the twin screw extruder connected to the injection molding unit. Direct melt mixing: The xGnP and PA12 powder were manually mixed and fed to the twin screw extruder connected to the injection molding unit.

- Characterization of PNCs

Flexural tests were carried out to measure the flexural modulus and strength according to ASTM D 790 on an MTS 810 Material Test System (MTS Systems Corp., Eden Prairie, MN). The three-point loading test with displacement control system was employed with a crosshead speed of 1.27mm/min and a span of 2in. The stress-strain relation including tensile modulus of xGnP/PA12 composites are determined as a function of filler wt% according to ASTM D638 using an Instron 33R 4466 apparatus. A 500 N load cell and an extensometer (Instron 2630-101) with a gage length of 10 mm are used. A displacement control with a velocity of 2.54 mm/s is applied. Each data point reported is an average of five repetitions.

The linear viscoelastic properties of the melt state were determined with a TA ARES® system (TA Instruments, New Castle, Delaware, USA) equipped with a 25 mm parallel plate geometry with the strain controlled system. The rheological measurements were carried out at 190 °C over a frequency sweep between 0.1 and 100 rad.s⁻¹ under N₂ atmosphere. The strain sweep tests initially were performed within the range of 0.1 to 100 percent to specify the linear viscoelastic limit of the melt. Then, the frequency sweep tests were conducted using the determined strain values within the linear behavior for each nanocomposite system. The storage and loss modulus of the specimens were determined using a dynamic mechanical analyser, DMA Q800 (TA Instruments). PNCs specimens with dimensions of 50 × 12.75 × 3.30 mm were tested at 3-point bending mode. A heating rate of 5 °C/min was used. The temperature range was from ambient to 150 °C. The tests were conducted at oscillation amplitude of 15 µm and a fixed frequency of 1Hz. Before each measurement, the instrument was calibrated to have the correct clamp position and clamp compliance.

The morphology of the fractured surface of the specimens was observed utilizing a Zeiss DSM 940A scanning electron microscope (SEM) operating at 5 kV accelerating voltage. The fractured surface of the PNCs was gold-coated prior to the SEM observations to minimize the charging effect.

3 Results and Discussion

3.1 Mechanical behavior

The effect of the compounding method on the flexural behavior of the PNCs is shown in Figure 1. As presented the coating method provides greater enhancement in the flexural strength of the

PNCs than the melt-mixing method. It is noted that the flexural strength is dictated by the load transfer ability at the xGnP/PA12 interface so it is more sensitive compared to the modulus to the presence of agglomerates. According to Figure 1 the coating method enhances significantly the flexural strength of xGnP/PA12 composites especially at higher xGnP contents indicating more homogeneous dispersion and distribution of xGnP within the polymer as confirmed also by SEM. Therefore, the coating method is utilized in the rest of the study.

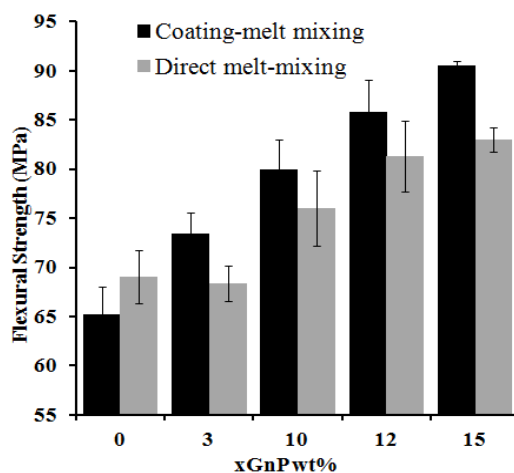


Figure 1. Comparison of the flexural strength of the xGnP/PA12 nanocomposites as a function of xGnP content: coating-melt mixing v.s. direct melt mixing

The tensile properties of the coated-melt mixed xGnP/PA12 are shown in Figure 2. As presented in Figure 2a there is an initial sharp increase in the tensile strength at low xGnP content with the strength decreasing as the xGnP content increases. This suggests that the tensile strength is compromised by the effects of xGnP agglomeration at xGnP content higher than 3wt%. Figure 2b demonstrates a sharp increase in the tensile modulus of the PNCs at low xGnP loadings that reaches a plateau value and is followed by a gradual increase with addition of the xGnP wt%. Two important observations can be made: i) better dispersion state of the xGnP up to 3wt% that leads to larger xGnP/PA12 interface, and ii) presence of severe agglomeration at concentrations above 3wt% that suppresses the stiffening effect of the xGnP.

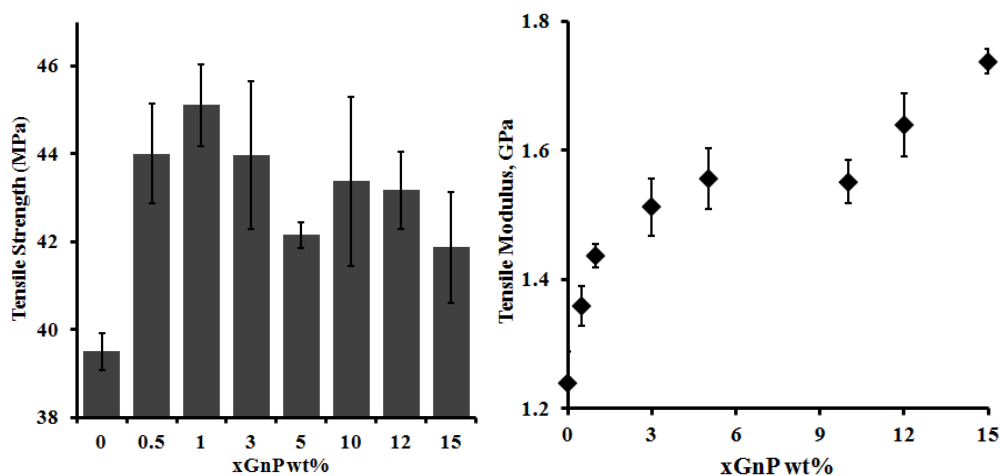


Figure 2. a) Tensile strength and b) tensile modulus of the coating-melt mixing processed xGnP/PA12 nanocomposites as a function of xGnP content

3.2 Melt rheology

To probe any correlation between the xGnP dispersion state and the xGnP/PA12 interfacial interactions, the rheological behavior of the melt PNCs was studied. A detailed comparison was made between the low frequency dynamic viscosity of the PNCs as a function of the compounding method employed for their fabrication. As presented in Figure 3 the low-frequency dynamic viscosity is sensitive to presence of nano-fillers and the strength of the interfacial interactions [16, 19, 20]. The results indicate stronger interfacial interactions are present in case of the coating method due to more available xGnP surface which is in good agreement with the findings from the flexural testing (Figure 1).

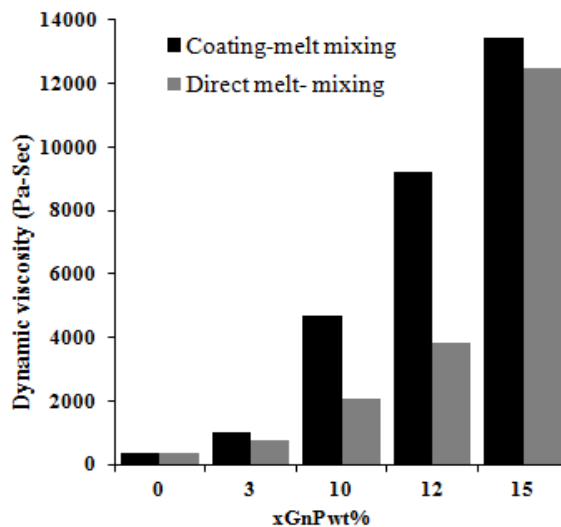


Figure 3. a) Low dynamic viscosity of coated-melt mixed v.s. melt mixed xGnP/PA12 nanocomposites measured at $\omega=0.1 \text{ rad.s}^{-1}$ as a function of xGnP content

3.3 Thermomechanical behavior

The effect of the interfacial interactions on the bulk properties of PNCs was further investigated by studying the thermomechanical properties of the composites including the loss modulus and glass transition temperature (T_g) as a function of xGnP content shown in Figure 4a and 4b respectively. It has been reported [21] that the shape and intensity of the normalized loss modulus is correlated with the interfacial interactions and the degree of immobilized chains. In this study, the loss modulus curves were normalized by dividing the modulus of a PNC by its loss modulus at T_g . The reduced temperatures were obtained by subtracting T_g from the temperature range used in experiments. As shown in Figure 4a, at temperatures above T_g the relaxation modes of the xGnP/PA12 composites are activated at higher temperatures with addition of xGnP (broadening of the loss modulus toward higher temperatures). The modes indicate presence of polymer chains with reduced mobility that is more pronounced at very low or high xGnP content. The evidence of presence of the immobilized region was further investigated by study of the shifts in T_g .

T_g is mainly associated with the large segmental motion of polymer chains in amorphous or semi-crystalline polymers. Factors including presence of hard regions such as nanofillers or crystallites can limit mobilization of the polymer chains due to mechanical interlocking or chemical interactions. The latter is expected to increase the T_g values in semi-crystalline PNCs.

Figure 4b elucidates shifts in the T_g with addition of xGnP wt%. It can be clearly seen that there exists a sharp increase in T_g up to 3wt% loading followed by a plateau level at higher xGnP content. The sharp increase in T_g is related to the better accessibility of the polymer chains to the surface of the xGnP even at very low nanofiller content. The available specific surface area is then reduced at xGnP content above 3wt% when agglomerates start forming which compromises the T_g . It can be clearly observed that the trend in T_g is in excellent agreement with that in the tensile modulus (Figure 1a). The comparison suggests existence of strong correlation between the tensile properties and the immobilized fraction of the polymer chains in the amorphous region.

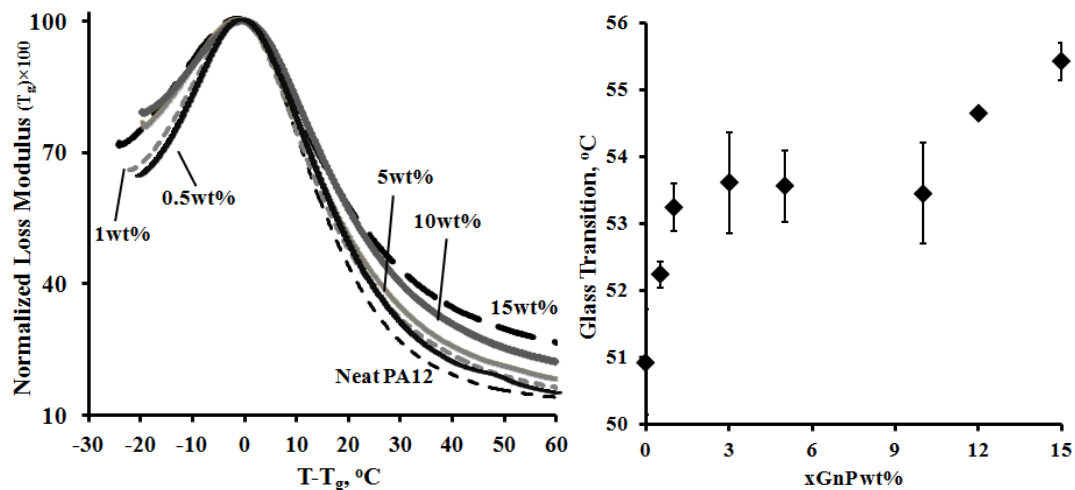
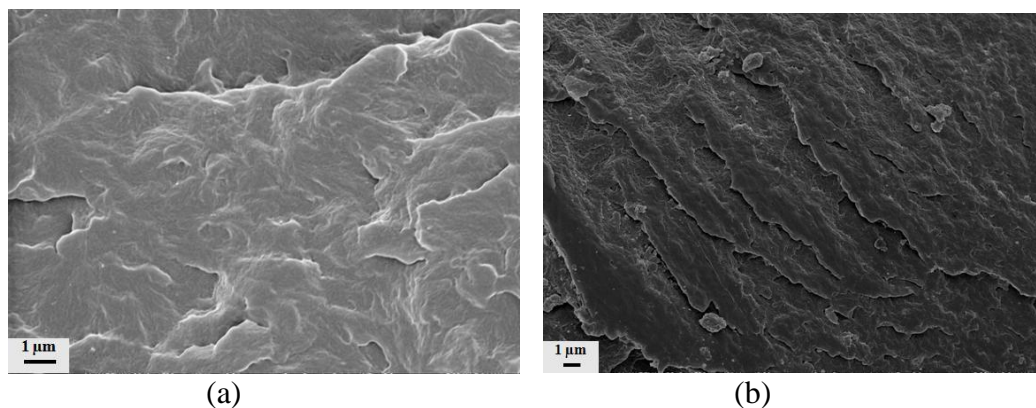
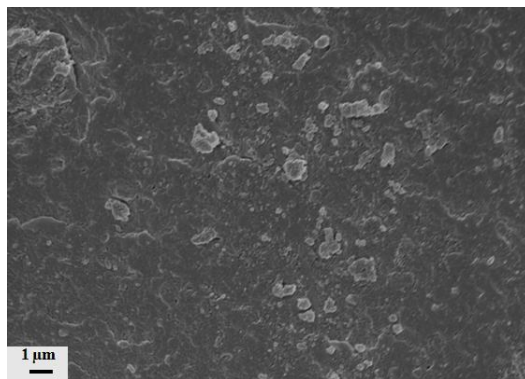


Figure 4. a) Normalized loss modulus of xGnP/PA12 nanocomposites v.s. the reduced temperature about T_g and b) glass transition temperature of the coated-melt mixed parts as function of the xGnP content

3.4 Morphology of xGnP/PA12 Nanocomposites

Figure 5a demonstrates the SEM images of the fracture surface of neat PA12 (Figure 5a) and coated-melt mixed specimens reinforced with 0.5 and 15 wt% xGnP (Figure 5b and c). Figure 5b shows uniform distribution of homogeneously dispersed xGnP that is maintained after the melt mixing process of the coated PA12 reinforced with low nanofiller content. However, non-uniform distribution of the xGnP is clearly seen in the case of the PNCs with high xGnP content. The results are in very good agreement with the observations in the study of the mechanical and thermomechanical performance of the PNCs (Figures 2 and 4).





(c)

Figure 5. a) SEM images of fractured surface: a) neat PA12, b) coated-melt mixed 0.5wt% xGnP/PA12 and c) coated-melt mixed 15wt% xGnP/PA12

4 Conclusions

It has been shown that the nano-filler content and method of preparation of PNCs through conventional extrusion injection molding influence the state of nano-filler agglomeration and the nano-filler – polymer interfacial interactions and hence mechanical behavior of the PNCs. In this study, nano-composites of xGnP-PA12 were fabricated using two compounding methods: coating-melt mixing and direct melt mixing. It was demonstrated that the coating- melt mixing method provided a more effective dispersion of nano-filler and hence greater enhancement in flexural strength and dynamic viscosity of the melt. It was shown that relatively more efficient interactions and, as a result, more effective dispersion of xGnP exists at low xGnP loading. A good agreement between the trend of T_g and tensile modulus was observed that indicates presence of a secondary reinforcing mechanism at the surface of the xGnP. This observation is linked to presence of immobilized polymer chains that contribute to the elastic response of the PNCs.

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