STUDY OF INTERPHASE IN EXFOLIATED GRAPHITE NANOPlatelets/POLYAMIDE12 NANOcomposites

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1 Introduction

The high aspect ratio and small size of nanomaterials result in significant nanomaterial/polymer interfacial interactions [1]. One main result of these interactions is the reduced degree of mobilization of polymer chains at the interface leading to creation of an interfacial zone or what is identified in the literature an “interphase”. [2-4]. An ongoing challenge that obstacles the expected rapid growth in technology and commercial advancement of polymer nanocomposites (PNCs) is lack of sufficient understanding about the links between the interfacial interactions and macro-scale properties of PNCs [5-7]. Systematic results that explain the interplay among process, structure and mechanical performance of PNCs are being increasingly reported. However, the published results demonstrating how interfacial interactions at the nano-scale affect physical structure and property of polymer chains at the vicinity of nanomaterial surface are not sufficient or often appear contradictory [8-10].

It has been shown that the configurational rearrangement and relaxation processes of long polymer segments are significantly sensitive to the restrictions imposed on the chains by their local environment [11-13]. The correlation between the amount of the immobilized chains at the interface and thermomechanical/thermal properties such as the glass transition (Tg) has been widely reported [14-16]. However, the changes in Tg originating from the restriction of polymer chains were not always sufficient in order to evaluate the altered dynamics of polymer chains due to the error range and lack of necessary resolution of thermomechanical measurements.

This study is aimed at evaluating how interfacial interactions between the nanomaterials and polymer alter the structure and the physical properties of polymer chains at and near the interface in order to reveal mechanisms responsible for the mechanical property enhancement in PNCs. An experimental methodology is introduced to determine the links between the interfacial interactions and macro-scale properties including tensile and viscoelastic properties of a semi-crystalline PNC system. Effect of nanomaterials and polymer crystallization characteristics on structure and the amount of the polymer chains with retarded kinetics at or near the GNP surface is investigated with respect to changes in the viscoelastic properties of the PNCs. The relationship between the tensile modulus, the glass transition temperature and the amount of the immobilized polymer phase is assessed and correlated to a secondary reinforcing mechanism that favors both viscoelastic and elastic response of the PNCs.

2 Materials

PA12 powder (VESTOSINT® X 1553 white, Evonik Industries, Essen, Germany) with average diameter of 50-100 μm and Tm in the range of 176-184°C was used as the base polymer. Exfoliated graphite nanoplatelets (GNP) from XG Sciences, with an average diameter of ~1 μm and thickness of 10-20 nm were used as the nanomaterial.

3 Fabrication of Nanocomposites

In this study, the composites were made in a two-step process: i) compounding and ii) forming/shaping using injection molding (IM). The compounding method used is the coating method reported in [17] for compounding GNP with PP powder. The PA12 powder was coated with GNP up to 15 (wt%). As-received GNP was mixed in isopropyl alcohol (IPA) using ultrasonic energy (UIP500hd, Hielcher USA) for 45 min with amplitude of 80% and manual mixing of the neat PA12 powder in the solution [17]. The IPA of the nanocomposite powder was filtered and the residual coated powder was then thoroughly dried in a vacuum oven at 100 °C for 10 hrs to minimize the hydrolytic degradation. The GNP/PA12 compound
4 Characterization of Nanocomposites

The tensile properties of the specimens were determined according to ASTM D638 using an Instron 33R 4466 apparatus with a 500 N load cell and an extensometer (Instron 2630-101) with a gage length of 10 mm. A displacement control with a velocity of 2.54 mm/s was applied. The flexural properties were measured based on three-point bending test according to ASTM D790 on an MTS 810 Material Test System (MTS Systems Corp., Eden Prairie, MN) at a crosshead speed of 1.27 mm/min and a span of 50.80 mm. The impact resistance of the specimens was determined according to ASTM D256 using an Izod pendulum test. Each data point reported is an average of five repetitions.

The thermomechanical behavior was studied by dynamic mechanical analysis (DMA, Q800, TA Instruments) using the single cantilever mode at oscillation amplitude of 0.015 mm and a fixed frequency of 1 Hz. The composites were heated from ambient temperature to 150 °C at a heating rate of 5°C/min. Standard differential scanning calorimetry (DSC) and modulated DSC (MDSC) work were performed on a DSC Q2000 (TA Instruments, New Castle, Delaware, USA) using specimens of about 7-10 mg. Nitrogen was used for purging. Measurements were performed from the equilibrium temperature of -30 °C to 200 °C at a heating rate of 3 °C/min and a heating-cooling rate of 5°C/min on the MDSC and standard DSC modes, respectively. To estimate the interphase characteristics such as thickness and stiffness AFM experiments were performed. A Veeco AFM with Nanoscope V controller, operated in tapping mode using an aluminum coated cantilever (length of 225 μm, spring constant of 45 N/m, resonance frequency of 190 KHz), with silicon tip of 2 nm nominal radius provided by Nanoscience Instruments Inc. Phoenix, AZ is used. To avoid detrimental effects of the soft polymer substrate under the tip and occurrence of artifacts due to contaminations, tapping mode (v.s. contact mode) was used. Composites with 0.1 wt% filler content were studied in order to avoid interactions among fillers. The morphology of the composites was studied with a Zeiss DSM 940A scanning electron microscope (SEM) operating at 5 kV accelerating voltage. Prior to the SEM study the fracture surface was gold-coated to minimize the charging effects during the SEM observations.

5 Results and Discussion

5.1 Mechanical Properties

- Tensile Behavior

The Young’s modulus of GNP/PA12 composites as a function of the GNP content is presented in Figure 1. It is clearly shown that the modulus increases with GNP content up to 5wt% reaches a plateau value at intermediate GNP loadings in the range of 5-10 wt% and finally continues increasing with GNP content. To understand the observed trend in modulus of the PNCs, the viscoelastic properties of the fabricated parts as a function of GNP were investigated and compared. To better explain the observed trend in the Young’s modulus of PNCs, dependence of the thermomechanical properties on GNP content was examined.

- Glass Transition Temperature

Figure 1 shows dependence of the glass transition temperature ($T_g$) of GNP/PA12 composites, determined as the temperature value at the tanδ peak, on the GNP content. It is clearly shown that both the Young’s modulus and $T_g$ follow the same trend. It is noted that changes in $T_g$ are related to the primary relaxation of polymer chains and the extent of the polymer chains that are constrained at the interphase [18-21]. It has been shown that in addition to the intrinsic properties of the constituents, properties of PNCs are highly influenced by other main variables such as nanomaterial-polymer interfacial interactions as well as dispersion of nanomaterials [22, 23]. Therefore, the non-monotonical changes in the modulus and $T_g$ with increasing GNP content indicate the presence
of competing factors such as the reinforcing effect of the high modulus graphite [24] and the formation of GNP agglomerates due to poor GNP dispersion within the polymer [25, 21]. The hypothesis is that the degree of crystallinity of PA12 matrix as well as the extent of the polymer chain immobilization due to the pinning at the hard GNP and crystal surface are responsible for the observed shifts in both the Young’s modulus and T\textsubscript{g}. The comparison provided in Figure 1 then indicates the presence of a secondary reinforcement mechanism which contributes to the enhancement of both the tensile modulus and T\textsubscript{g} and is notably influenced by the GNP content, micro-structure and morphology of PNCs. Since changes in T\textsubscript{g} are related to the primary relaxation of polymer chains and the extent of the immobilized chains [18-21], the results motivated detailed investigations into the altered dynamics of polymer chains due to GNP-PA12 interfacial interactions.

- **Damping Behavior (tan δ)**

The presence of the immobilized amorphous phase is also confirmed by the damping behavior of the GNP/PA12 composites which was determined as a function of the GNP content. Table 1 gives the tan δ values within the linear viscoelastic behavior of PNCs as a function of GNP content. As clearly shown the tan δ peak (determined as value at T\textsubscript{g}) is altered and reduced by addition of GNP. The observations indicate that GNP restricts the segmental motions of the main polymer chains, which require more energy input that is higher temperatures during the relaxation transition around T\textsubscript{g}. The decrease of the tan δ with addition of GNP is related to decrease of the viscous and enhancement of the elastic response of polymer phase induced by pinning the polymer chains. The latter confirms formation of immobilized constrained region between GNP and PA12 matrix [26-28]. It is noted that immobilization of the polymer chains is more pronounced at low and intermediate GNP content. At higher loadings of GNP, unavoidable agglomeration compromises the GNP surface responsible for the pinning of the polymer chains [20, 24].

5.3 **Assessment of the Interfacial Immobilized Region**

- **Volume Fraction**

The fraction of polymer chains with enhanced degree of immobilization at the GNP surface was assessed by determining the variations in the viscoelastic behavior of the GNP/PA12 composites as a function of GNP content and temperature. A theoretical thermomechanical model reported in [29] is employed. The model allows for estimation of the fraction of the polymer chains that are constrained and thus do not contribute to the viscous response. The fraction of the constrained region, C, which may consist of an amorphous immobilized phase and/or the crystalline region, can be determined based on the shifts in energy dissipation and degree of crystallinity of the PNCs

\[
C = 1 - \frac{W_c}{W_0} (1 - C_0) \quad (1)
\]

where

\[
W = \frac{\pi \tan \delta}{(\pi \tan \delta + 1)} \quad (2)
\]

where \(W_c\) and \(W_0\) the energy loss ratio of the composite and neat polymer at T\textsubscript{g}, and \(C_0\) the degree of crystallinity for the pure PA12. The fraction of the amorphous immobilized phase can be found by subtracting the degree of crystallinity from the overall constrained region, C. The degree of crystallinity was calculated using the heat of fusion determined during melt of the specimens on MDSC heat flow spectra and according to the following equation

\[
\chi% = \frac{\Delta H}{\Delta H_m (1 - \frac{\text{wt}\%}{100})} \times 100 \quad (3)
\]

where \(\Delta H_m\) is the melting enthalpy of 100% crystalline PA12 equal to 209.3 J/g [30, 31]. Table 1 gives the degree of crystallinity of GNP/PA12 composites and the volume fraction of the constrained region determined using equation 1 as function of GNP content. Figure 2 shows that the fraction of the immobilized amorphous phase, defined as the difference of the entire constrained region and the degree of crystallinity, increases with addition of GNP and is more pronounced at low GNP content. It is shown that the fraction of the immobilized amorphous phase increases with addition of GNP and more pronounced at low GNP loading. The observed trend is in good agreement with the observed increase in T\textsubscript{g} and tensile modulus. As seen in Table 1, the degree of crystallinity decreases upon increasing the GNP content. It should be noted that when GNP is present, the polymer chains are either immobilized at the GNP surface which results in increase of T\textsubscript{g} or
are slowed down due to the reduced interparticle distance resulting in the decrease of degree of crystallinity. Although the degree of crystallinity decreases with GNP content, the composites become more elastic because the increased amorphous phase is immobilized at the GNP surface so it cannot contribute to viscous effects as discussed earlier. To better investigate the effect of GNP on physical structure of PA12, the crystallization behavior of the composites was studied using DSC. As shown in Table 1, the crystallization temperature onset \((T_{\text{onset}})\) increases with GNP content indicating that GNP is acting as a nucleating agent. Moreover, the results indicate a saturation nucleation effect at high GNP as reported also elsewhere \([25, 32]\). The saturation effect can be related to factors such as insufficient polymer chains to wet the surface of GNP and the presence of agglomerates at higher GNP content both of which negatively affect the nucleating efficiency of the GNP surface \([33-35]\). The results suggested presence of a fraction of interfacial constrained region with increased order of polymer chains leading to occurrence of a transcrystalline interphase.

- Evaluation of the GNP/PA12 Interphase

Information about topography and properties of the surface of composites and the interfacial GNP-PA12 region was obtained by employing AFM (tapping mode) height and phase imaging. Phase imaging measures the phase lag information in the oscillation frequency when the AFM tip interacts with areas/materials of different mechanical properties under the tip \([36]\). Figure 3a is a representative phase image of the top surface of 0.1 wt\% GNP/PA12 composite. Individual GNP s with an average diameter of 800 nm, which is within the diameter range provided by the supplier, as well as GNP aggregates are shown in Figure 3a. Figure 3b is a zoomed in phase image scanned over an arbitrary GNP-PA12 boundary shown in Figure 3a. It is clearly observed that there is a transition area, the interfacial region, between the PA12 matrix and the GNP. The thickness of this zone is determined using the AFM software by measuring the phase lag across lines (profiles) that are drawn over the interfacial boundary. Five such lines that are initiated from the polymer pass through the transition zone and terminate at the GNP are shown in Figure 2b. The phase lag variations across each line (profile) are shown in Figure 3c. Two distinct plateau values at \(-4\) degrees and \(-2\) degrees that correspond to GNP (left) and PA12 (right) respectively are shown. Note that the phase lag data is linked with the stiffness of the materials under the tip \([37]\). Therefore, it can be implied that the segment of the transition zone with a phase lag values lower than that of pure PA12 indicates existence of voids and weak GNP/PA12 interactions. It is noted that mechanical properties of the interphase reflect the type of nanomaterial-polymer interactions (attractive v.s. repulsive) and thus effectiveness of the load transfer. As shown earlier, \(T_g\) and crystallization temperature increase with the GNP content indicating the confinement effect of GNP on PA12 chains. This polymer immobilization supports the high average stiffness of the GNP-PA12 interphase presented in Figure 3c.

Topography information about the scanned area corresponding to the phase image is useful to ensure the property gradient detected over the interphase region is induced by neither multiple superposed GNP layers nor by stepped-height structure of an individual GNP. The latter may result in a difference in the overall stiffness of the composition under the tip. Figure 4a elucidates the AFM height image of the composites surface corresponding to the phase image represented in Figure 3a. To obtain detailed information about the variation in topography of the composite surface over the interphase zone and beyond, data analysis was performed by drawing lines over the boundary as is shown in Figure 4b that is a zoom-in image of Figure 4a. As shown in Figure 4c, the curves represent somewhat a flat topography along the profile lines. It is clearly observed that the change in height is less than 10 nm over the length of each segment (~650 nm). In particular, it is shown that the slight slop of the blue curve (corresponding to one profile line used in phase analysis) gained on the GNP surface occurs over a distance of ~ 250 nm while the property gradient was displayed within 40 nm. It can be implied that the slight slope change is induced by the local topography change around the GNP-PA12 boarder.

Changes in calorimetric heat capacity of reinforced polymers near \(T_g\) have been shown to provide information about the immobilized polymer chains at the interface. As reported, the interfacial interactions limit mobilization of amorphous polymer chains, which is needed for liquid like behavior of polymer above \(T_g\), and thus the entire cooperatively rearranging regions (CRR) near the interface \([38, 28]\). The result of this polymer chain immobilization is a reduction in liquid like motions of chains and thus the reduction in the increment of the heat capacity or the relaxation strength, \(\Delta C_p\), at
In this study, the calorimetric relaxation of immobilized polymer chains was linked to the CRR length to evaluate dependence of the interphase thickness on the GNP content. A model first introduced by Donth et al. was utilized to determine the CRRs length using the variations in the heat capacity from solid to liquid behavior of PNCs around \( T_g \) of the PNCs [38]:

\[
V_a = \frac{\Delta(C_v)}{\rho(6T)^2} K_B T^2
\]

(4)

\[
\delta = \frac{3}{\sqrt{V_a}}
\]

(5)

where \( V_a \) is the volume of the cooperative region, \( C_v \) is the specific heat capacity, \( \rho \) is density of the specimen, \( K_B \) is the Boltzman constant, \( \delta_T \) is temperature fluctuation, and \( \delta \) is the characteristic length of the glass transition. In this study, the heat capacity of the PNCs was determined using the MDSC heat capacity signals. Table 1 gives the values of \( \Delta C_v \) and the CRR characteristic length determined by the model for each composite system. It can be clearly understood that the theoretical characteristic length, which is a measure of the immobilized polymer chains, somewhat is interdependent of the GNP content and that the average of this length is about 5 nm. In addition, it is shown that the theoretical length is one order of magnitude less than that of the experimentally detected interphase in this study. Considering the poor interactions between the hydrophobic GNP and the hydrophilic PA12 an interaction zone (intephase) of 5 nm is logical. On the other hand, the low wetability of GNP by PA12 is overcome by the shear and elongation forces present during processing which are forcing the two materials to interact and result in the 40 nm thick interphase as observed by AFM.

The fracture surface of GNP/PA12 composites filled with 5 and 15wt% GNP is shown in Figure 5. GNP is better dispersed and distributed at 5wt% (Figures 5a) than higher content (Figures 5b) in PA12. It is indicated that the PNCs with high GNP wt% contain GNP aggregates, circled in the image. The difference in the observed morphology confirms the reduction in the available interface between GNP and polymer and thus compromise of the pinning effect of nanomaterials as the GNP content increases. The results are in good agreement with the observed variations in the amount of the constrained region as well as changes the Young’s modulus and \( T_g \) over the range of the GNP content used in the study.

6 Conclusions

The study examined correlation among the interfacial interactions, changes in physical properties of polymer and macro-scale properties of PNCs such as the Young’s modulus and \( T_g \) through an experimental approach. PNCs of 0-15wt% GNP/PA12 were fabricated using the coating method followed by injection molding. The results illustrated strong interplay among the Young’s modulus and \( T_g \) of the GNP/PA12 composites as well as the vol% of a complex constrained phase, which follow the same exact trend upon addition of GNP. The results suggested that the complex constrained phase, consisting of an amorphous immobilized and crystalline region, enables a secondary reinforcing mechanism that dramatically contributes to the macro-scale properties of semi-crystalline PNCs. An interphase with an average thickness of several tens of nanometers and a gradual stiffness gradient was experimentally visualized which confirmed presence of the observed immobilized region at the interface. The study provided a deeper insight into the role of interfacial interactions in enhancing elastic and viscoelastic performance of PNCs that can lead to design and fabrication of semi-crystalline PNCs with engineered properties.

References


Fig. 1. Tensile modulus and $T_g$ of GNP/PA12 PNCs as a function of the GNP content.

Fig. 2. Volume fraction of the amorphous immobilized phase as a function of GNP content.

Fig. 3. Representative AFM phase image of 0.1 wt% GNP/PA12 composites: a) individual and overlapping GNP on the surface of PA12 matrix, b) a magnification of (a) showing the profile lines along the interfacial interaction zone, and c) phase lag v.s. distance for the profile lines shown in (b) indicating thickness of the interfacial region.
Fig. 4. Representative AFM height image corresponding to the phase image illustrated in Figure 3a: a) topography of a 10×10 μm² scan size, b) a magnification of (a) showing the profile lines along the interfacial interaction zone between GNP and PA12, and c) height v.s. distance for the profile lines shown in (b)

Fig. 5. Representative SEM image of a) 5wt% and b) 15wt% GNP/PA12 fracture surface indicating presence of aggregates at high GNP content
Table 1. Dependence of tanδ, degree of crystallinity, crystallization temperature onset, ΔC_p and CRR length values of the GNP/PA12 nanocomposites on GNP wt%

<table>
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<tr>
<th>GNP wt%</th>
<th>tan δ @ T_g</th>
<th>χ%</th>
<th>C, %</th>
<th>T_{C onset} (°C)</th>
<th>ΔC_p (J/gr °C)</th>
<th>CRR length scale (nm)</th>
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<td>0.5</td>
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<td>165.3±0.1</td>
<td>0.32±0.01</td>
<td>4.8±0.2</td>
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<tr>
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