



Formation of a complex constrained region at the graphite nanoplatelets–polyamide 12 interface



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ARTICLE INFO

Article history:

Received 6 March 2013

Received in revised form

19 April 2013

Accepted 6 May 2013

Available online 16 May 2013

Keywords:

Graphite

Interfacial interactions

Crystallization

ABSTRACT

The study focuses on understanding the interfacial interactions between graphite nanoplatelets (GNP) and polyamide 12 (PA12) in GNP/PA12 nanocomposites and the influence of GNP on the glass transition and crystallization of PA12. A complex constrained phase, consisting of immobilized amorphous and transcrystalline region, of PA12 at the GNP surface was determined. Strong correlation between the tensile modulus and the glass transition temperature and the amount of constrained phase, assessed through the thermo-mechanical and crystallization behavior of the composites, was found. The presence of the transcrystalline region was confirmed by the nucleating ability of the GNP. The complex constrained phase provides a secondary reinforcing mechanism. GNP reinforces PA12 not only because it is stronger but because it significantly alters locally the physical properties of the polymer. In conclusion, a strong link between the nano-scale interfacial interactions, the physical properties of the polymer and the bulk properties of the composites is highlighted and explained.

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1. Introduction

Understanding how nano-scale interfacial interactions influence macro-scale properties is key in manufacturing polymer nanocomposites (PNCs) with engineered properties for tailored applications. The high surface to volume ratio, small size and unique intrinsic properties of nanomaterials are expected to significantly enhance bulk performance of PNCs [1–4]. However, the expected property improvement has not yet been achieved experimentally due mainly to poor nanomaterial–polymer interactions [5–7]. Although the interface effects can be ignored in case of micro-sized reinforced polymer composites, they need to be accounted for in case of PNC because the interfacial interactions dictate the dispersion and agglomeration of the nanomaterials within the polymer, the stress transfer mechanism and significantly alter the physical properties of the polymer matrix dominating thus the bulk properties of PNCs in multiple ways [5,8–12].

Presence of interphase consisting of immobilized polymer segments with a size from few to hundreds of nanometers has been

reported [13,14]. The properties and size of interphase are dictated by the material system and processing methods used and depend also on the characterization methods and the certainty level of the measurements [15–17]. There are limited studies on the correlation between the amount of interphase, the microstructure and the bulk properties of semi-crystalline PNCs and the reported results often appear contradictory [18–20]. The effects of interfacial interactions on the nature and formation of the interphase have been assessed using methods such as atomic force microscopy (AFM), nano-indentation, or transmission electron microscopy (TEM). One of the limitations is that these characterization techniques normally produce qualitative information or in-plane data about local variations in the polymer properties at and near the interface [15,21–23]. Numerous studies have been conducted attempting to elucidate the modified chains dynamics originating from the nano-reinforcement polymer interactions. In particular, thermo-mechanical and calorimetric methods have been utilized to study the configurational rearrangement and relaxation processes of polymer segments near the surface of nano-reinforcements [14,20,24,25]. Presence of attractive interfacial interactions has been shown to result in significant shifts in the glass transition temperature (T_g) and tensile modulus of expanded graphite nanoplatelets/PMMA PNCs [26]. Changes in T_g , however, might not be solely conclusive for studying the interfacial polymer relaxation due to error range and lack of necessary resolution of the dynamic mechanical analysis (DMA) measurements [27,28]. Calorimetric

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information such as heat capacity has also been employed to determine properties of the interfacial zone containing polymer chains with altered immobilization [14,27].

In conclusion, the links between the interfacial interactions, the physical properties of the polymer and the macro-scale properties of the PNCs are not clearly understood. This study serves to provide better understanding of how the presence of GNP alters the physical properties of PA12 including glass transition and crystallization behavior; and how a polymer constrained region at the GNP surface, that influences the bulk properties of the GNP/PA12 PNCs, can be assessed. The results indicate that the constrained phase consists of immobilized amorphous and transcrystalline regions enabling a secondary reinforcing mechanism.

2. Materials and methods

PA12 powder (VESTOSINT® X 1553 white, Evonik Industries, Essen, Germany) a semi-crystalline thermoplastic with average diameter of 50–100 μm and T_m in the range of 176–184 $^\circ\text{C}$ is used as matrix. Exfoliated graphite nanoplatelets (xGnP™) from XG Sciences, with an average diameter of $\sim 1 \mu\text{m}$ and thickness of 10–20 nm is used as the nanomaterial. The neat PA12 powder was coated with GNP dispersed in isopropyl alcohol using sonication as reported in our previous work [29]. The GNP coated PA12 powder was then thoroughly dried in a vacuum oven at 100 $^\circ\text{C}$ for 10 h to minimize the hydrolytic degradation effect and was fed into a DSM Micro 15 cc Compounder (vertical, co-rotating twin-screw micro extruder) and 10 cc injection molding machine to fabricate GNP/PA12 PNCs with GNP content up to 15 wt%. The conditions used are barrel temperature of 190 $^\circ\text{C}$, screw speed of 60 and 100 rpm for 1 and 2 min respectively, mold temperature of 80 $^\circ\text{C}$ and a pressure of ~ 750 KPa.

The tensile properties were determined 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 were utilized. Each data point reported is an average of five repetitions. The thermo-mechanical behavior of the specimens was studied utilizing 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 to 150 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$. The X-ray diffraction (XRD) patterns of the neat PA12 and the PNCs were obtained using a X'Pert Pro Alpha 1 (PANalytical, Almelo, Netherlands) diffractometer in the Bragg–Brentano geometry using a monochromatic, filtered Cu $K\alpha_1$ radiation. The diffraction patterns were collected from the start angle of 8 $^\circ$ to 50 $^\circ$ (2θ) at a scanning rate of $\sim 3^\circ/\text{min}$ with divergence and scatter slit of 1/4 $^\circ$ and 1/2 $^\circ$ respectively. The X-ray equipment was operated at 45 kV and 40 mA. The morphology of the composites fractured surface was studied with a Zeiss DSM 940A scanning electron microscope (SEM) operating at 5 kV accelerating voltage. Prior to the SEM study a thin gold layer was applied to the surface to minimize charging effects.

Standard differential scanning calorimetry (DSC) and modulated DSC (MDSC) work was 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 equilibrate temperature of -30 $^\circ\text{C}$ to 200 $^\circ\text{C}$ at a heating rate of 3 $^\circ\text{C}/\text{min}$ and a heating-cooling rate of 5 $^\circ\text{C}/\text{min}$ on the MDSC and standard DSC modes, respectively. The MDSC makes it possible to decompose the total heat flow signal into reversing and non-reversing information. The reversing signal demonstrates heat capacity events including the glass transition and melting whereas the non-reversing signal most often contains kinetic events such as crystallization and crystal perfection. The reversing heat flow

curves upon the heating scan were used to study the melting behavior of the specimens. No annealing or additional scans or thermal history removal was used in order to compare the effects of manufacturing process on properties of the interest.

3. Results and discussion

3.1. Tensile modulus and glass transition temperature of the nanocomposites

The Young's modulus and the glass transition temperature, determined as the temperature value of $\tan \delta$ peak, of GNP/PA12 composites as a function of the GNP content are presented in Fig. 1. Both properties follow exactly the same trend, increase with GNP content up to 5 wt% reach a plateau value at intermediate GNP loadings in the range of 5–10 wt% and finally continue to increase with GNP content. It is noted that changes in T_g are related to the primary relaxation of polymer chains and the extent of the immobilized chains [14,20,30,31].

The non-monotonical increase of the modulus and T_g with GNP content indicates the presence of two competing effects: i) reinforcing effect of the high modulus graphite ($E = 500\text{--}600$ GPa) [32] and ii) formation of GNP agglomerates due to poor GNP dispersion within the polymer [20,33]. Other effects such as the effect of polymer's crystallinity and polymer chain mobility, which are altered upon addition of GNP, on the modulus of the composites, are also considered below. The results in Fig. 1 indicate the presence of a secondary reinforcement mechanism which contributes to the enhancement of both the tensile modulus and T_g and is notably influenced by the GNP content and the microstructure of the composites. The observations motivated detailed investigations into the altered dynamics of polymer chains as a result of the extensive GNP-PA12 interfacial interactions.

3.2. Assessment of the interfacial interactions

3.2.1. Immobilized amorphous phase

Increase of T_g with GNP content indicates increase of the immobilized polymer chains at GNP surface. The question is what this immobilized phase consists of, amorphous or crystalline

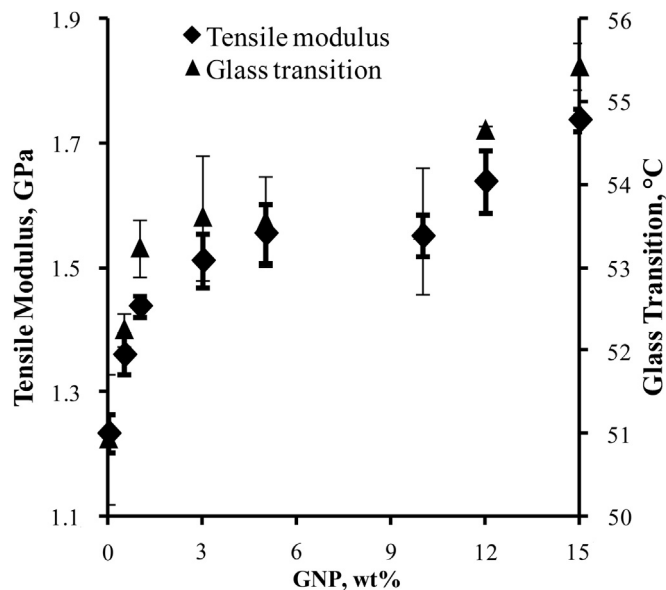


Fig. 1. Tensile modulus and T_g of GNP/PA12 PNCs as a function of the GNP content.

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