Dispersion and re-agglomeration of graphite nanoplates in polypropylene melts under controlled flow conditions

CrossMark

C. Vilaverde, R.M. Santos, M.C. Paiva, J.A. Covas *

Institute for Polymers and Composites/I3N, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

ABSTRACT

The kinetics of GnP dispersion in polypropylene melt was studied using a prototype small scale modular extensional mixer. Its modular nature enabled the sequential application of a mixing step, melt relaxation, and a second mixing step. The latter could reproduce the flow conditions on the first mixing step, or generate milder flow conditions. The effect of these sequences of flow constraints upon GnP dispersion along the mixer length was studied for composites with 2 and 10 wt.% GnP. The samples collected along the first mixing zone showed a gradual decrease of number and size of GnP agglomerates, at a rate that was independent of the flow conditions imposed to the melt, but dependent on composition. The relaxation zone induced GnP re-agglomeration, and the application of a second mixing step caused variable dispersion results that were largely dependent on the hydrodynamic stresses generated.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene, a single layer of carbon atoms packed into a honeycomb crystal plane, is receiving intensive worldwide attention owing to its unique characteristics, namely mechanical, thermal, electrical and barrier properties [1,2]. It is a promising material for applications in sensors [3], electronic and photonic devices [4], clean energy [5], drug delivery and tissue engineering [6], biomaterials [7] and in polymer nanocomposites [8]. Graphene and its derivatives – graphene oxide [9–12], reduced graphene oxide [13–15], graphene quantum dots [16,17], graphene nanoribbons [18] and graphene nanomeshes [19] – have been produced by different routes, such as chemical vapor deposition (CVD) [20], growth on crystalline silicon carbide (SiC) [21] and mechanical exfoliation of graphite [22]. However, the current low throughput of these techniques severely limits the application to large-scale processes. Graphite nanoplates (GnP) [23], a thin form of graphite with thickness ranging from that of graphene to approximately 100 nm, have recently attracted attention as an economically viable alternative for the development of functional and structural nanocomposites [24]. GnP-based polymer composites can be prepared by solution mixing and melt mixing. The former can achieve a suitable dispersion of GnP into polymeric matrices, but requires the use of hazardous organic solvents for the dissolution of most synthetic polymers [25]. On the other hand, melt blending is compatible with existing industrial procedures, providing the hydrodynamic

stresses and residence times necessary to exfoliate and disperse GNP.

The incorporation of graphite nanoplates in PP could yield composites adequate for a range of technological applications [25–31]. Kalaitzidou et al. [26] showed that addition of GnP will simultaneously improve the barrier, thermal and mechanical properties. It was also demonstrated that even at loadings as low as 0.01 vol.%, GnP is an effective nucleating agent of β-PP crystals, which exhibit higher impact strength and toughness in comparison with the α-form [27]. GnP thickness and diameter influence the reinforcing effect, greater improvements in flexural strength and tensile properties having been obtained with smaller nanoplates [28,29]. Similarly, Milani et al. [31] reported that incorporation of GnP significantly increased the tensile properties and shifted upwards the degradation temperature of PP by more than 20 °C (at a concentration of 12.3 wt.%), but only those composites with higher filler content exhibited an increase of the electrical conductivity ($\approx 10^{-8}$ S cm^{-1}). Song et al. [25] also observed an increase of the initial degradation temperature of PP of approximately 26 °C, but at much lower GnP content (0.42 vol.%).

No systematic studies have apparently been published about the extent, mechanism and kinetics of the dispersion of GnP in polymer melts (in general, and particularly on PP) and on how they are influenced by the processing conditions and filler content. The work presented here investigates this topic, using a prototype modular small-scale extensional mixer that allows good control of the flow conditions of the polymer melt. Material samples can be obtained along the length of the mixer. Thus, the evolution of

* Corresponding author.

nanoparticle dispersion can be assessed and correlated with processing/reprocessing conditions and GnP concentration. The electrical conductivity of the composites was monitored. Compared to previous studies of the dispersion of carbon nanotubes (CNT) in the same polymer, the evolution of GnP dispersion in PP seems to be more gradual. Moreover, as observed before for CNT composites, as soon as hydrodynamic stresses are relieved significant re-agglomeration takes place.

2. Experimental

2.1. Materials

Polypropylene copolymer Icorene CO14RM® (Ico Polymers, France), with a melt flow index of 13.0 g/10 min (190 °C, 2.16 kg) and a density of 0.9 g/cm³ was used as matrix.

Graphite nanoplates xGnP® Grade C-750 (XG Sciences, Inc., Lansing., U.S.A.) – denoted here as GnP – have, according to the manufacturer, a size distribution ranging from very small (100 nm) to relatively large flakes (1–2 μm), an average thickness of approximately 2 nm and a typical average surface area of 750 m²/g. The morphology of as-received graphite nanoplates (in powder form) was observed by transmission electron microscopy (TEM), using a JEOL JEM1010 equipped with a CCD Orius camera and a tungsten filament as electron source, at an acceleration voltage of 100 kV. Particles were dispersed in a butyl alcohol solution (1.2 g/l) under sonication (CREST 230T ultrasonic bath, 80 W) at room temperature for 2 h and then directly deposited onto a cooper grid for subsequent observation. Optical microscopy (OM) was also carried out on a BH2 Olympus microscope coupled to a Leica DFC 280 camera. In this case, 10.0 mg of GnP were gently dispersed in 4.25 ml of epoxy resin, then spread onto a glass slide and dried at room temperature for 24 h. A quantitative particle analysis (Fig. 1a)) performed on optical micrographs revealed GnP agglomerates with a projected average area of 6.7×10^5 μm². The figure also shows representative TEM and OM images.

2.2. Composites preparation

A prototype small-scale extensional mixer was attached to a Rosand RH8 capillary rheometer and used to manufacture the PP/GnP composites. The mixer contains a sequence of converging/diverging channels that create a strong extensional flow component near to the axis, the design following the concept developed by Nguyen et al. [32] and used to disperse layered mineral silicates in different polymer matrices [33]. The efficiency of this approach for dispersing carbon nanofibers and carbon nanotubes (CNT) in PP

melts has been demonstrated [34]. Using the same device, Jamali et al. [35] observed the re-agglomeration of CNT upon reprocessing (i.e., after re-feeding the rheometer with previously prepared nanocomposites). In the present work, the geometry of the mixer was modified in order to study nanoparticle re-agglomeration effects without the need to cool the composite, pelletize and re-melt. As illustrated in Fig. 1(b), the device used here comprises a reservoir, where the polymer and GnP are fed in powder form and heated to a melt, a first mixing zone (equivalent to the conventional compounding stage, i.e., where the nanocomposite is prepared by melt mixing), a relaxation chamber (where the melt is subjected to quasi-quiescent conditions) and a second mixing zone (where reprocessing takes place, this being equivalent to processing of a previously compounded material). The first mixing zone consists of a vertical stack of ten 2 mm thick circular rings with alternating internal diameters (1 and 8 mm), thus creating a series of five converging/diverging (8:1 and 1:8) channels. The relaxation chamber is 24 mm long and has a diameter of 18 mm. The second mixing zone creates a second series of five sequential converging/diverging flows. Two different set-ups were assembled, designated as "set-up 1" inducing a 8:1 and 1:8 convergence/divergence (repeating the geometry of the first mixing zone), and a "set-up 2", inducing a 4:1 and 1:4 convergence/divergence sequence (using ten rings with internal diameters of 2 mm and 8 mm). The assemblage of rings is mounted inside a sleeve that can be quickly removed from the body of the device, which is maintained at 200 °C.

PP and 2 or 10 wt.% of GnP were pre-mixed in powder form and fed into the reservoir of the rheometer. After pre-heating for 5 min, the ram moved downwards at constant speed, forcing the melt through the mixer and out of the device in the form of a continuous filament. Three ram speeds were tested, corresponding to the average shear rates indicated in Table 1. Once the experiment was concluded, the sleeve containing the rings was removed and the individual parts were detached from each other. The nanocomposites contained in the 8 mm rings and in the relaxation chamber were collected and immersed in liquid N₂, to freeze the GnP dispersion morphology. In this way, samples of composites along the axis of the mixer were made available. Table 1 includes an estimation of the maximum residence time of the melt in the mixer, obtained from the definition of $\bar{t} = V/Q$, where V is the volume of the flow channel and Q is the volumetric output.

2.3. Composites characterization

The dispersion of the GnP agglomerates in the PP matrix was assessed by transmission optical microscopy. Nanocomposite sec-
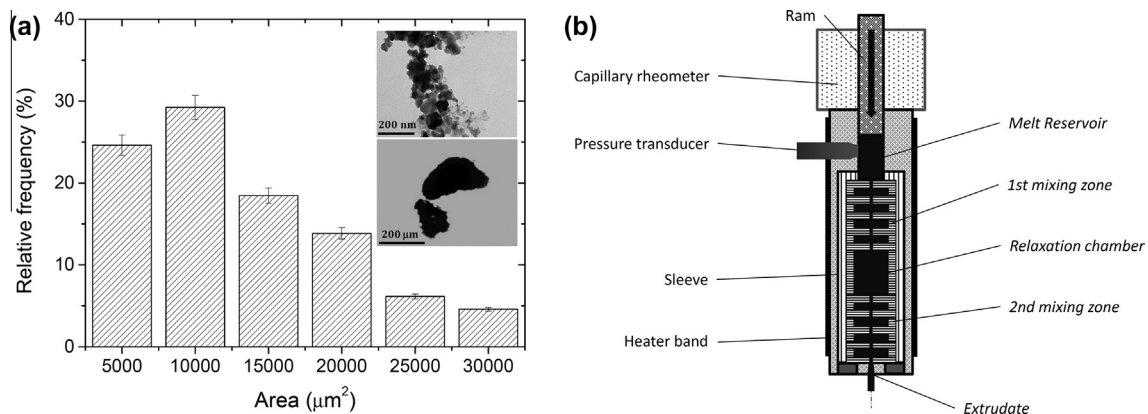

Fig. 1. Particle size distribution of as-received GnP (a) and schematic representation of the prototype mixer used for the composites preparation (b).