Dispersion of graphite nanoplates during melt mixing

José Covas, Eunice Cunha, Maria C. Paiva, and Loic Hilliou

The behavior of pristine and functionalized particles within polypropylene was investigated with the use of a prototype small-scale mixer.

Graphite nanoplates (GnPs) are exfoliated graphite particles in the form of thin flakes—with large surface areas and nanosized thicknesses—that tend to agglomerate because of van der Waals interactions. GnPs are commonly used to reinforce composite materials. It is expected that maximum composite performance levels should occur when GnP agglomerates are dispersed within the polymer matrix as primary 2D particles and they have good interfacial adhesion. Interfacial bonding between the GnPs and the polymer can be improved by tailored chemical functionalization of the graphite surfaces.[1–3] Dispersion of GnP agglomerates in polymers, however, is complex.

Melt compounding is an economically attractive process that is used successfully in industrial applications to prepare polymer composites. Previous studies of melt compounding with carbon nanofibers[4] and carbon nanotubes[5, 6] used a variety of mixing equipment (e.g., extruders, internal mixers, and prototype mixers). These investigations demonstrated that the intensity and type of hydrodynamic stresses, residence time, and interfacial adhesion play a major part in nanoparticle dispersion. Although the dispersion mechanism of carbon nanotubes in polymers is well studied, the equivalent GnP literature is still mostly focused on composite properties and applications.[7] Few studies concerning the dispersion of GnPs through melt mixing methods have so far been reported.

We have monitored the progression of dispersion for 'as-received' (i.e., pristine) and functionalized GnPs within a polypropylene (PP) matrix to investigate this complex process.[8] Our prototype small-scale continuous mixer, which we used for our experiments, is shown in Figure 1. With our device we create repetitive converging/diverging flow sequences along its length. As such, a strong extensional stress component is generated. We are also able to precisely control flow rate and temperature.[4, 5] Once the experiments are completed, we can quickly dismantle the equipment so that the material samples at the various axial locations can be collected for subsequent characterization. We obtained the functionalized graphite nanoplates (F-GnPs) through
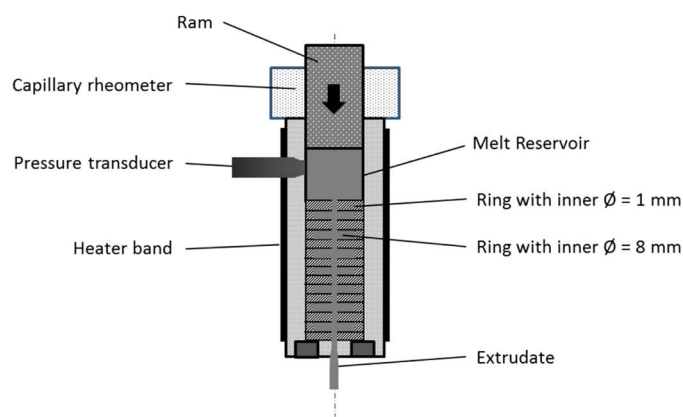

Figure 1. Schematic diagram of the prototype small-scale continuous mixer. ϕ: Diameter.

covalent functionalization of the GnPs[9] and through grafting with PP that was modified with maleic anhydride.

We monitored how the pressure drop varied with the number of ring pairs (see Figure 1) that we used in the mixer. We conducted these tests for PP, PP with 2wt% GnP, and PP with 2wt% F-GnP matrices. For all these materials, our results exhibit a linear pressure increase with the number of pairs of rings. This behavior demonstrates that appending pairs of rings has an additive effect, i.e., there is no stress build-up in the mixer, nor any significant structural orientation at the tested shear rate. Adding pairs of rings is therefore equivalent to increasing the mixing time. We constructed shear–flow curves from the pressure data and equations for capillary rheometry.[10] We find that the pressure drop should predominantly be caused by flow along smaller channels (i.e., those with a radius of 0.5mm) and the apparent length (which depends on the number of stacked pairs of rings). The flow curve we obtained for the PP matrix—as shown in Figure 2(a)—closely matches the curve that is calculated using conventional rheometry. Our approach for obtaining rheological information has thus been validated. We also find that the viscosity of the PP material is similar to that of the composites made with 2wt% GnP and F-GnP, which is relevant for extrusion and

compounding. We measured the extrudate swell (when polymeric material is forced through a die) of the filaments—computed as the ratio between their diameter and the diameter of the die orifice—for different shear rates. As expected, we observe—see Figure 2(b)—that the extrudate swell increases with increasing shear rate for all our materials. In addition, the surface of the extruded material remained smooth and rheological defects were absent over the range of applied shear rates. We also observe (as for other polymer composites that contain different filler types)[11–14] that the addition of GnPs causes a decrease in extrudate swell.

We have also monitored the progression of GnP and F-GnP dispersion along the mixer, using a setup that consisted of eight pairs of stacked rings. We forced the composites—with 2wt% of nanoparticles—through the mixer at 500 and $2000s^{-1}$, whereas the composites that contained 4wt% of nanoparticles were only tested at $500s^{-1}$. We defined an agglomerate area ratio (A_R) as the ratio of the total area of all the surviving agglomerates to the total area of the analyzed composite.[4,6] The highest dispersion levels thus correspond to the lowest computed A_R values. Our A_R results—shown in Figure 3(a) and (b)—reveal that the dispersion of GnPs develops gradually along the mixer. The dispersion of F-GnPs, however, appears to level off for samples that were collected between the fourth and sixth ring pairs. The A_R values of the latter are systematically higher than those for their pristine counterparts. We observe these trends consistently along the mixer for the 2 and 4wt% GnP and F-GnP compositions.

Dispersion of GnPs in solid suspensions—as with polymer blends—may occur when sufficient stress levels and residence times are attained.[15] In our experiments, higher shear rates promoted greater stress levels at the cost of residence time (i.e., 202s for a shear rate of $500s^{-1}$ and 54s for a shear rate of $2000s^{-1}$). We find that

Figure 3. Measures of the progression of GnP dispersion in the PP matrix along the mixer. The area ratio (A_R) variation for the composites with (a) 2wt% GnP and F-GnP and (b) 4wt% GnP and F-GnP is shown. Scanning electron images of cross sections through the nanocomposites are also shown, for the composites reinforced with (c) 2wt% GnP and (d) 2wt% F-GnP. These materials were collected from the eighth pair of rings in the mixer.

residence time is therefore the dominant factor under the conditions we tested. In addition, higher levels of graphite incorporation cause an increase in A_R. The evolution of the dispersion indices, however, is qualitatively (and in some cases quantitatively) similar to that of the less-filled composite. Scanning electron microscope images of example cryo-fractured samples, with 2wt% GnP and F-GnP, are shown in Figure 3(c) and (d), respectively. These images demonstrate that there is improved interfacial adhesion of F-GnPs within the PP matrix compared with the non-functionalized GnP composite.

We have conducted a set of experiments to test how pristine and functionalized graphene nanoplates disperse within a polypropylene matrix. Our work demonstrates the importance of selecting and applying effective stress levels and residence times to optimize GnP dispersion and achieve maximum composite performance levels. In our future work we will explore the dispersion of GnPs in polymer matrices under different flow conditions, as well as the effect of melt relaxation on nanoparticle dispersion and re-agglomeration. We will also compare the GnP dispersion that we achieve by twin-screw extrusion processing with that achieved using the prototype equipment described in this work.
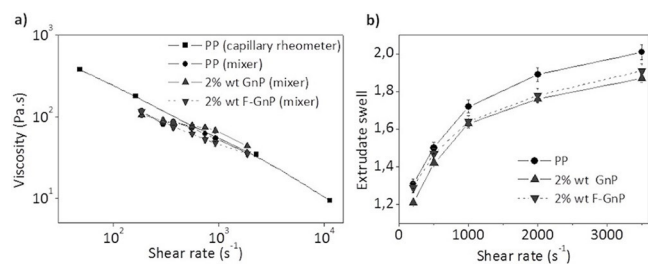

Figure 2. Shear flow behavior of polypropylene (PP) and PP composites, made with 2wt% functionalized graphene nanoplates (F-GnP) and non-functionalized graphene nanoplates (GnP). Shear flow curves are shown in (a). The variation of the extrudate swell with shear rate, for PP and the PP nanocomposites, is shown in (b). These measurements were conducted using the prototype mixer equipped with six pairs of rings.
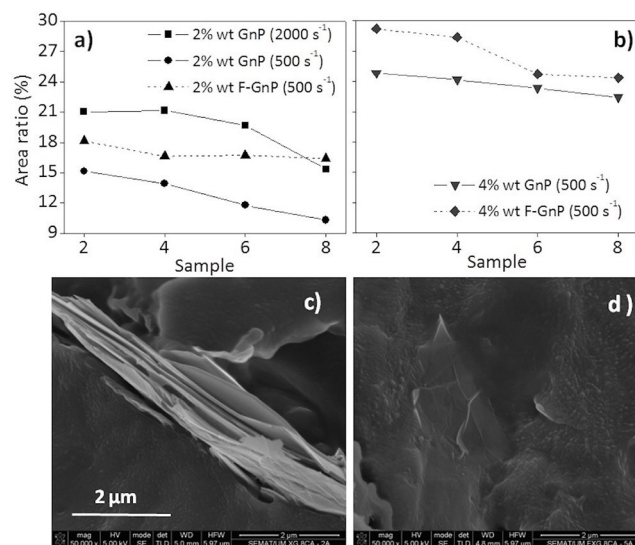
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