SPE Plastics Research Online
10.2417/spepro.006332

Improving the electrical properties of polyamide nanocomposites

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Preferential localization of multiwall carbon nanotubes at the polyamide interface gives rise to a high aspect ratio that can be maintained after processing, even at low filler contents.

The dispersion of conductive fillers, such as carbon nanotubes (CNTs), in a polymer matrix or a polymer blend can give rise to electrically conductive polymer composites (CPCs).[1–3] To obtain such CPCs, melt mixing technologies (e.g., extrusion and injection molding) are often used to great advantage in industrial end-use applications. Polyamide 12 (PA12) and polyamide 6 (PA6) are both industry commodity polymers. There are, however, some drawbacks to the use of PA6 in CPCs. Such problems include a high sensitivity to notch propagation under impact test (especially at temperatures below 0°C), high moisture sorption, and poor dimensional stability.

It has been suggested that PA12/PA6 blends could be used to overcome some of the problems with PA6 composites.[4] To obtain a good level of electrical conductivity, however, it is usually necessary to add large amounts of CNTs to the composites. In addition, a morphology in which the CNTs migrate to the interfaces between polymers (instead of being randomly distributed in the immiscible blend) could theoretically occur. This would lead to the formation of a segregated structure with a lower percolation threshold and thus present an alternative way to improve the electrical conductivity of the composites.[5]

The principal aim of our work[6] was therefore to design new CNT nanocomposites—with an immiscible blend of polyamides as a matrix—that have good electrical conductivity and a low percolation threshold. We used rheological tests and alternating current (AC) measurements to determine the percolation threshold of our nanocomposites. We also conducted a detailed investigation of the electrical conductivity frequency dependence in the samples. Furthermore, we used transmission electron microscopy (TEM) to examine the morphology of the nanocomposites and the CNT localization in the polymer matrix.

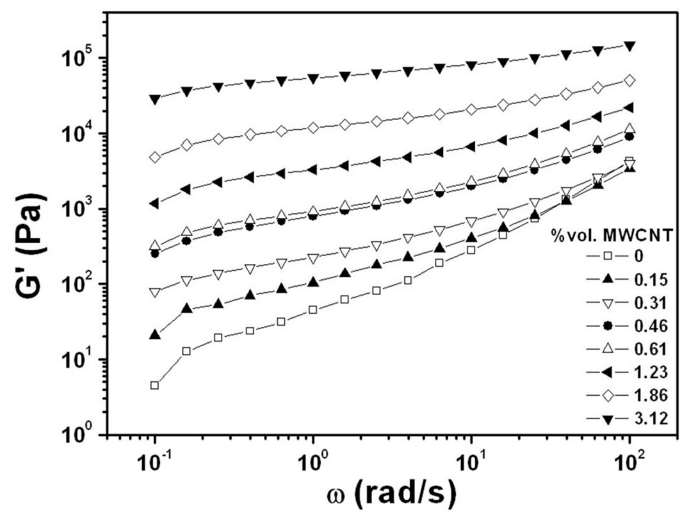

Figure 1. *Storage modulus (G′) measurements, as a function of angular frequency (ω), for polyamide 12/polyamide 6 (PA12/PA6) composites with varying multiwall carbon nanotube (MWCNT) contents, expressed as volume % (%vol). The measurements were obtained at 235°C, with a TA Instruments ARES rheometer (25mm parallel plate and 1mm gap).*

We conducted the rheological measurements to characterize the percolation state of the multiwall CNTs (MWCNTs) and their dispersion within the polyamide (i.e., PA12/PA6) blends. We observe a shift to a plateau in a plot of the storage modulus (see Figure 1), which indicates that the percolated network starts to form at an MWCNT content of about 0.31 volume % (%vol). Furthermore, our dielectrical analysis results (see Figure 2) clearly show that the conductivity plateau occurs at an MWCNT content of between 0.15 and 0.31%. This means that the percolation threshold, i.e., the transition to the conducting phase, is located in the same range.

We used TEM images (see Figure 3) to localize the CNT particles within the polyamide blends. Our micrographs indicate that the two

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polyamides (PA12 and PA6) are distributed in two different phases (a so-called island-sea morphology) and that the CNTs are mainly found at the interface between the polyamides, as seen in Figure 3(b). This preferential localization is the desired morphology for forming a segregated network and for achieving a low percolation threshold.[5] Obtaining this morphology, however, depends on two key factors: first, the viscosity ratio between the immiscible polymers and, second, the interfacial energy of the CNT/polymer composites. For our study, the viscosity ratio of the PA12/PA6 blends was 0.54 and the CNT particles were pre-dispersed within the lower viscosity polyamide (PA12). This allowed us to achieve a good dispersion of the nanotubes/agglomerates within the polymer matrix during the mixing process and, therefore, obtain a segregated network.

To assess whether the observed preferential localization of CNTs at the polyamide interface reduces the percolation threshold, we made calculations using our rheological and dielectrical data. We obtained percolation threshold values of 0.258±0.001%vol and 0.09±0.01%vol for the electrical and rheological power law adjustments, respectively. Both of these values are lower than data in the literature.[7,8] To obtain electrical conductivity, it is necessary to establish a conductive percolated network across the material. This requires a CNT content greater than that which produces the rheological percolation. For this reason, the value of the electrical threshold is higher than the rheological one. It is impossible, however, to obtain such low threshold values if the high aspect ratio of the MWCNTs is not maintained after melt mixing

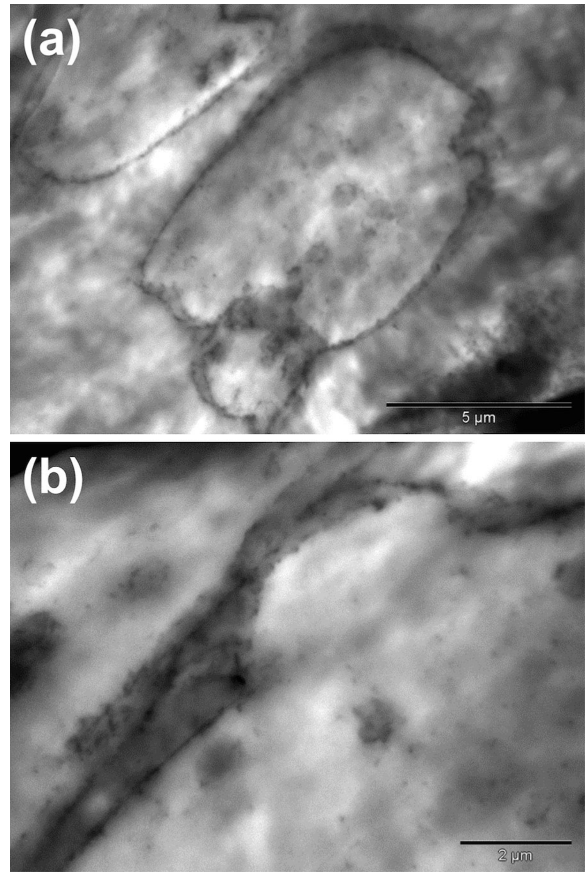

Figure 3. Transmission electron microscope images of (a) the PA12/PA6/MWCNT composite containing 0.46%vol CNT particles, and (b) a close-up image of the interface between the two polyamide phases. Images were obtained using a JEOL JEM-1010 instrument.

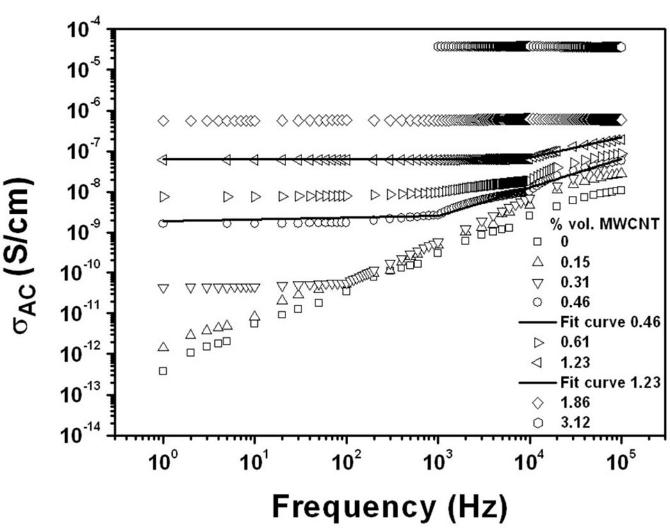

Figure 2. Experimental results illustrating the frequency dependence of conductivity (σ_{AC}) for the PA12/PA6 composites with different MW-CNT contents. Measurements were made on a TA Instruments dielectric analyzer (DEA 2970 iv). AC: Alternating current.

(high levels of shear tend to break the CNTs into shorter segments). To corroborate this finding, we calculated the aspect (length to diameter) ratio for our samples. We performed these calculations using our conductivity data and a previously proposed model.[6,9] With this model, we obtained an aspect ratio of 98.1. For comparison, the initial aspect ratio of our samples was 158. Our modeled value denotes the minimum decrease in the CNT aspect ratio that occurred during the melt blending (i.e., by extrusion and subsequent nanocomposite molding).

We have conducted rheological and dielectrical measurements on a set of CNT/polyamide (PA12/PA6) composites. The low percolation thresholds we obtain are consistent with the preferential localization of the CNT particles at the interface between the two polyamides. This morphology—which we observe in TEM images of the samples—may

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encourage the formation of a segregated conductive network in the polymer matrix. The percolation threshold of the conductive polymer composites can thus be reduced in this way. We also observe a small decrease in the aspect ratio of the CNT particles after material processing has occurred. This could be beneficial to achieving high conductivities at low CNT contents, and therefore for producing low-cost electrical applications with improved mechanical properties. As part of our future work we plan to test whether the observed localization of the nanotubes at the interface promotes, or allows, better mechanical properties.

The authors acknowledge financial support from the Xunta de Galicia-FEDER program of consolidation and structuring competitive research units (GRC2014/036).

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