The influence of carbon nanotube functionalization on the dispersion in polypropylene by melt blending

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Abstract

Polymer composites containing carbon nanotubes (CNT) are expected to present exceptional electrical, mechanical and thermal properties, even at low incorporation content. Polypropylene (PP) has a wide spectrum of applications due to its processability, good balance of physical properties and price, thus PP/CNT composites have a high potential for applications requiring electrical conductivity and/or high mechanical strength. The practical application of PP composites is hindered by the ability to achieve good CNT dispersion using industrial-scale melt mixing processes. This problem is inherent to all CNT/polymer mixtures due to the physical form of the CNT, that grow in the form of highly entangled agglomerates of several microns or even millimeters. Also, the chemical inertia of the CNT surface leads to a poor polymer/CNT interface.

The present works focuses on the study of the joint effects of chemical functionalization and melt blending on CNT dispersion in PP, and on the electrical and tensile properties of the resulting composites. The CNT modification was performed using a non-aggressive method that preserves the aspect ratio of the tubes [1] and the functionalization reaction was tailored considering compatibility with the PP matrix. The as-received and functionalized CNTs were melt blended with PP by twin-screw extrusion and the processing conditions were varied. The dispersion was assessed by optical and scanning electron microscopy, showing a large dependence on the processing conditions, and also on the functionalization route.

The functionalization products were studied by XPS and TGA that confirmed the formation of cyclic amine groups bonded to the CNT surface (CNT250). The CNT thus functionalized were further reacted with maleic anhydride grafted PP, forming PP-functionalized CNT (CNT250/PP-g-MA). XPS spectra showed the extensive coverage of the CNT surface with PP and the formation of amide bonds between CNTs and grafted PP, as illustrated in Figure 1.

The melt mixing studies focused the analysis of the dispersion of large CNT loading of 4 wt. % [2]. It was observed that the CNT dispersion was generally improved for composites processed at higher screw speed and lower throughput. The composites formed with polymer modified CNT showed distinctive nanotube dispersion, presenting a large number of small CNT agglomerates, as opposed to a smaller number of large CNT agglomerates observed for the composites with non-functionalized, as depicted in Figure 2. The electrical properties of the composites correlated with dispersion level attained, as shown in Figure 3. The incorporation of polymer-functionalized CNT in PP led to an improvement in tensile modulus greater than 30% relative to the composites with similar composition of non-functionalized CNT. However, the electrical resistivity was higher for the CNT250/PP-g-MA composites.

References

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[2] R. M. Novais, F. Simon, M. C. Paiva, J. A. Covas, Composites: Part A, 43 (2012) 2189.

Acknowledgements

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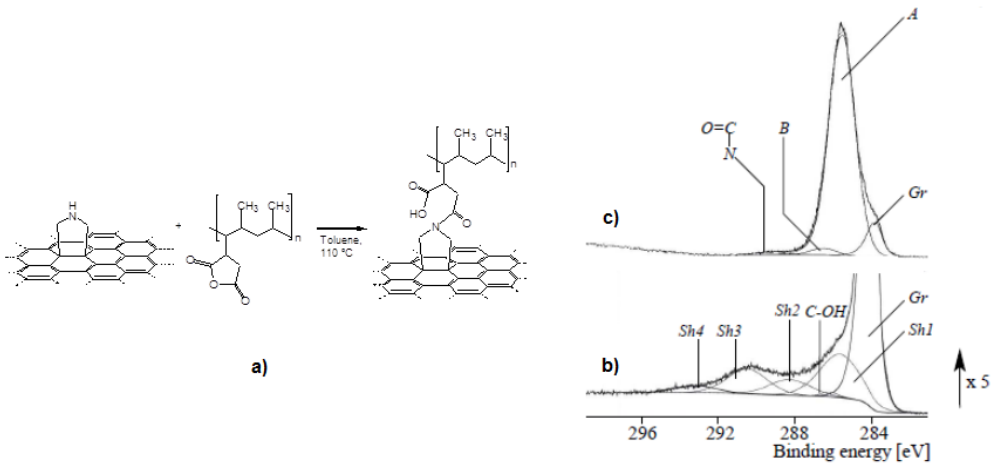

Figure 1. CNT functionalization products: a) reaction of the pyrrolidine groups with the maleic anhydride grafted on PP-g-MA; XPS high-resolution C 1s spectra acquired from: b) unmodified CNTs, and c) CNT250/PP-g-MA. The intensity of the spectrum presented for c) is fivefold that of spectrum b).

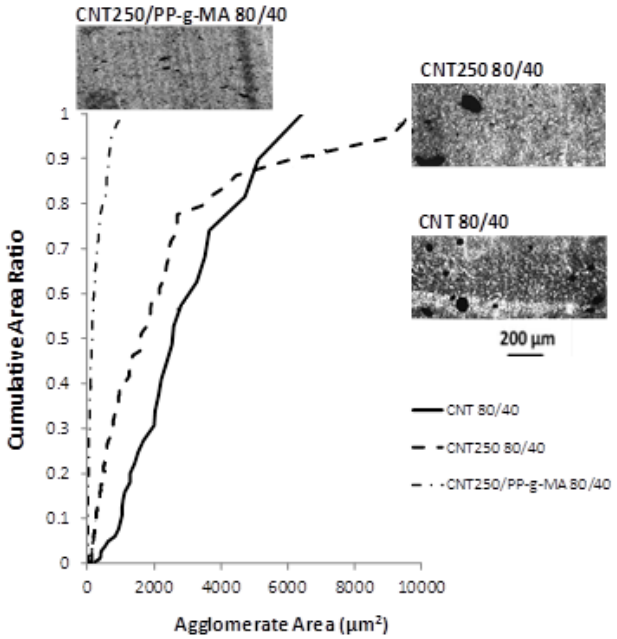

Figure 2. Comparison of the cumulative agglomerate area ratios measured for composites processed at 80 rpm and 40 g/h. The insert optical micrographs illustrate the agglomerate dispersion attained.

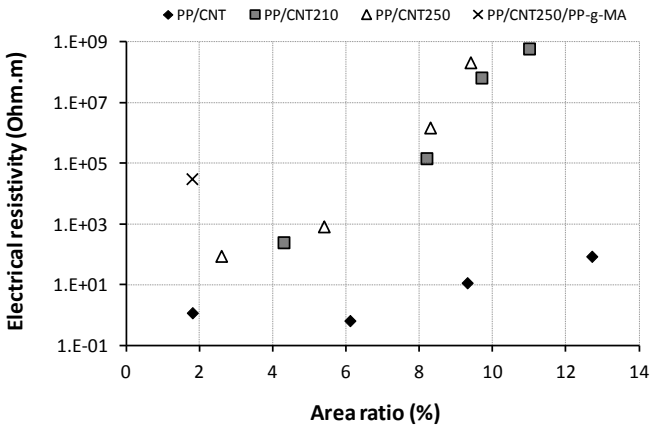

Figure 3. Correlation between agglomerate area ratio (ratio between the composite area covered by CNT agglomerates and the total composite area analyzed) and electrical resistivity for composites with 4 wt% of as-received and functionalized CNTs produced under various processing conditions.