Bio-based polyamide/carbon nanotube nanocomposites

Itziar Otaegi, Gonzalo Guerrica-Echevarría and José Ignacio Eguiazábal

Department of Polymer Science and Technology and POLYMAT
Faculty of Chemistry, University of the Basque Country UPV/EHU
Paseo Manuel de Lardizabal 3, 20018, Donostia (Spain)
itziar.otaegi@ehu.eus

Introduction

Polyamides (PA) are engineering polymers with very good thermo-mechanical properties, widely used, among others, in electric, electronic and automotive applications. Most commercial polyamides are produced by polycondensation of diamines and dicarboxylic acids. Diamines are mainly derived from fossil fuel, but dicarboxylic acids can be obtained from renewable resources such as castor oil (1), producing a bio-based polyamide. Currently available commercial bio-based polyamides include PA1010, PA410 and PA610.

Polyamide/carbon nanotube nanocomposites (PA/CNT) have been widely studied (2). One of the most important benefits of CNT addition to polymeric matrixes is the possibility to obtain electrically conductive materials (3). Conductivity is achieved when a three-dimensional network of interconnected nanotubes is formed within the matrix. This occurs upon reaching the named electrical percolation concentration (p_c). Moreover, it is well known that incorporation of CNTs improves mechanical properties of polymeric materials. PA/CNT nanocomposites show enhanced mechanical and conductive properties with respect to the pure matrix, with percolation concentrations varying between 0.4-4 wt. % CNT (4, 5).

Materials and methods

The bio-based polymeric matrix was a polyamide 410 provided by DSM. Its properties are comparable to those of conventional technical polyamides such as PA6 or PA66, but as it is based on dicarboxylic acids derived from castor oil (that constitutes some 70% of the polyamide), its carbon footprint is reduced in almost 100% with respect to its competitors. Multi-walled carbon nanotubes (MWCNT), with an outside diameter of 20-30 nm and purity higher than 95%, were provided by Cheaptubes. In an attempt to improve the dispersion of the nanotubes and, consequently, reduce the percolation concentration achieved when the pristine nanotubes were directly added to the PA410, a PA6/MWCNT masterbatch containing 15 wt. % of MWCNT (Plasticyl® PA 1503, provided by Nanocyl) was also used.

PA410/MWCNT nanocomposites containing from 1 to 6 wt. % of MWCNT were prepared by melt-mixing in a twin-screw extruder at 270ºC and a screw speed of 200 rpm. Alternatively, PA6/MWCNT masterbatch containing 15 wt. % of MWCNT was diluted with PA410 to obtain nanotube contents of 1-4 wt. %. Thus, PA410/PA6/MWCNT nanocomposites were also prepared by melt-mixing at the same processing conditions of PA410/MWCNT nanocomposites. Standard test specimens for tensile tests were obtained by injection molding, and compression molding was used to generate standard sheets for electrical conductivity measurements. The mechanical properties of the nanocomposites were measured by tensile tests. The nanostructure of the composites was analyzed by transmission electron microscopy (TEM), whilst a multimeter and a picoammeter were used to perform the electrical conductivity measurements.

Results and discussion

The Young's moduli of the PA410/MWCNT and PA410/PA6/MWCNT nanocomposites are shown in Figure 1. As can be observed, the addition of the nanofillers caused, in both cases, an increase in the Young's modulus. However, the increase raised up to 4.6% in the case of 5% nanofiller loading for PA410/MWCNT nanocomposites, and to 9.4% in the case of 4% nanofiller loading for PA410/PA6/MWCNT nanocomposites, with respect to the pure matrix.

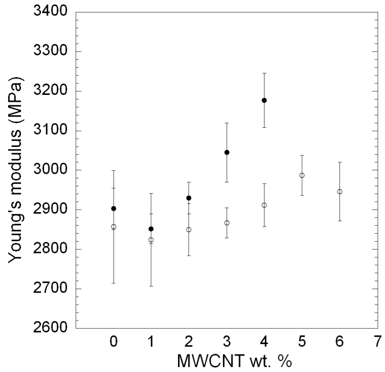

Figure 1: Young's modulus of PA410/MWCNT nanocomposites (○) and of PA410/PA6/MWCNT nanocomposites (●).

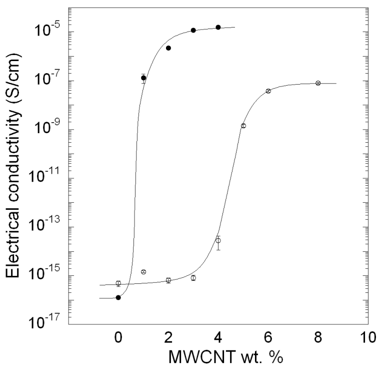

Figure 2: Electrical conductivity of PA410/MWCNT nanocomposites (○) and of PA410/PA6/MWCNT nanocomposites (●).

The electrical conductivity of PA410/MWCNT and PA410/PA6/MWCNT nanocomposites is shown in Figure 2. As can be seen, in PA410/MWCNT nanocomposites, conductivity increased with MWCNT content leading to an electrical percolation threshold between 3 and 5 wt. %. The percolation concentration decreases significantly in PA410/PA6/MWCNT nanocomposites, which falls between 0 and 1 wt. % due to the use of the masterbatch. Moreover, in this case, the conductivity values obtained are higher –3 orders of magnitude– than in the first approach. The calculated value for the electrical percolation threshold for PA410/MWCNT nanocomposites was 3.98 wt. %, whereas for PA410/PA6/MWCNT nanocomposites it was 0.65 wt. %. TEM micrographs of PA410/MWCNT and PA410/PA6/MWCNT containing 4 and 1 wt. % of MWCNTs, respectively, which correspond to the concentrations closest to the percolation concentration in each case, are shown in Figure 3. As can be observed, PA410/PA6/MWCNT nanocomposites show a much better dispersion level of MWCNTs, with carbon nanotubes appearing very finely dispersed within the matrix. This fact is directly related to the better mechanical properties, as well as the lower percolation concentration, observed in the case of the ternary nanocomposites.

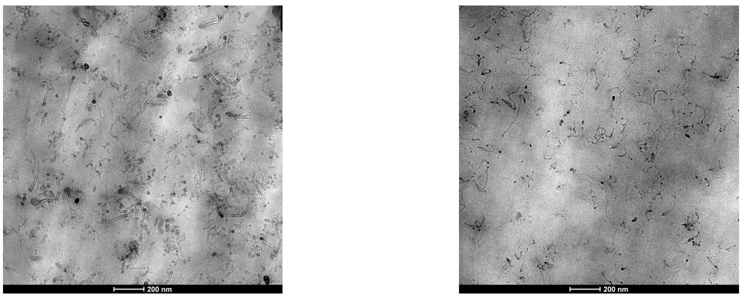

Figure 3: TEM micrographs of PA410/MWCNT nanocomposite containing 4 wt. % of MWCNTs (on the left) and of PA410/PA6/MWCNT nanocomposite containing 1 wt. % of MWCNTs (on the right) (x25000).

Conclusions

Bio-based polymeric nanocomposites have been obtained with enhanced electrical conductivity and rigidity by the addition of MWCNTs to a polyamide 410. A significant reduction in the percolation concentration, together with better mechanical properties, was achieved by using a PA6/MWCNT masterbatch. Further work is still needed to improve the deformation and impact properties by, for instance, adding an impact modifier.

References

1. M. Niaounakis. *Biopolymers: Reuse, Recycling, and Disposal,* Elsevier, 2013, 1-75.
2. H. Meng, G.X. Sui, P.F. Fang, R. Yang. *Polymer*, 2008, 49(2), 610-620.
3. I. Alig, P. Poetschke, D. Lellinger, T. Skipa, S. Pegel, G.R. Kasaliwal, T. Villmow. *Polymer*, 2012, 53(1), 4-28.
4. G. Gorrasi, S. Bredeau, C. Di Candia, G. Patimo, S. De Pasquale, P. Dubois. *Macromolecular Materials and Engineering*, 2011, 296(5), 408-413.
5. O. Meincke, D. Kaempfer, H. Weickmann, C. Friedrich, M. Vathauer, H. Warth. *Polymer*, 2004, 45(3), 739-748.
6. M. Weber, M. R. Kamal. *Polymer Composites*, 1997, 18(6), 711-725.