

POLYAMIDE 6/GRAPHENE OXIDE NANOHYBRIDS

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Abstract - Graphene oxide (GO) was prepared by oxidation of graphite flakes by a mixture of H₂SO₄/H₃PO₄ and KMnO₄ based on Marcano's method. Two different masterbatches containing GO (33.3%) and polyamide-6 (PA6) (66.7%) were prepared both via solvent casting in formic acid and by melt mixing in a mini-extruder (Haake). The two masterbatches were then used to prepare PA6-based nanocomposites with a content of 2% in GO. For comparison, a nanocomposite by direct mixing of PA6 and GO (2%) and PA6/graphite nanocomposites were prepared, too. The oxidation of graphite into GO was assessed by X-ray diffraction (XRD), Micro-Raman spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) analyses. All these techniques demonstrated the effectiveness of the graphite modification, since the results put into evidence that, after the acid treatment, interlayer distance, oxygen content and defects increased. SEM micrographs carried out on the nanocomposites, showed GO layers totally surrounded by polyamide-6, this feature is likely due to the strong interaction between the hydrophilic moieties located both on GO and on PA6. On the contrary, no interactions were observed when graphite was used as filler. Mechanical characterization, carried out by tensile and dynamic-mechanical tests, marked an improvement of the mechanical properties observed. Photoluminescence and EPR measurements were carried out onto nanoparticles and nanocomposites to study the nature of the interactions and to assess the possibility to use this class of materials as semiconductors or optical sensors.

Keywords: graphene oxide, PA6, silica, functionalization, nanohybrid.

Introduction

Recently, graphene have received significant attention, due to its exceptional electronic, mechanical, thermal and optical properties, which make it indicated for its use in various fields, such as optoelectronics and biomedicine [1-3]. Its most common derivative, the graphene oxide (GO) could replace oxidized CNTs for many application fields, as the presence of a large amount of carboxyl and alcohol moieties could promote the GO functionalization with other compounds. In this sense, many efforts have been devoted to combine the unique properties of this 2D carbon lattice with some additional functionalities covered by other compounds. Among the compounds investigated, amorphous silica is a promising class of nanomaterials, since it is widely used for biomolecule/drug immobilization and delivery, host-guest chemistry or thin film technology applications [1-2]. Furthermore, in this work silica nanoparticles were used to exfoliate the lamellae of GO, thus improving their dispersion within the polyamide 6 matrix.

Experimental

The PA6 adopted in this work was a commercial sample of Radilon S35 F 100 NAT, supplied by Radicinova (Italy). The GO was prepared by oxidation of neat graphite (initial size=75 μm, purity=99.9%) in a strong acid mixture (H₂SO₄:H₃PO₄ 9:1) in presence of

potassium permanganate as oxidant [3]. Two different silica nanoparticles were used: AEOX50 (specific surface=50 m²/g, d=40 nm) and AE300 (300 m²/g, d=7 nm). The oxidation step of graphite into GO was confirmed by FTIR, XPS, Raman spectroscopy, XRD, dispersion tests in water, AFM and SEM. The GO-silica nanohybrid films were produced by solvent casting in water. In order to promote the exfoliation of GO lamellae, were prepared both masterbatches PA6/GO and silica/GO nanohybrids. The two masterbatches with the polymer (66.7% PA6, 33.3% GO) were produced via solvent casting in formic acid (GO 2) and by melt mixing (GO 3). The GO/silica nanohybrids (GO-AE300 and GO-AEOX50) were produced by hydrothermal solvent casting at 120 °C in water. The coupling reaction between GO and silica was confirmed by FTIR and XPS.

The PA6-based nanocomposites were loaded with 2% (wt/wt) of graphite and neat GO (GO 1), masterbatches and silica-containing nanohybrids were loaded in order to keep constant (at 2%) the content in GO. The materials were vacuum-dried at 120 °C overnight prior to use. PA 6 was fed to the mixer and processed (T=240 °C, v=100 rpm) for 1 minute, thereafter the fillers were added and mixed together with the PA6 for 3 minutes. Tensile tests were performed according to ASTM D882.

Results and Discussion

Fig. 1 reports the elastic modulus of all the nanocomposites prepared in the frame of this work. Graphite-containing composite shows the worst mechanical performance. This issue has expected, as the area to volume ratio for this filler is dramatically lower than nanosized fillers. Moreover, due to the oxygen moieties onto its surface, GO shows better affinity to PA6 with respect to neat graphite, as confirmed by breaking properties (here not reported). Among the various approaches to include GO within the polymer matrix, direct mixing (GO 1) of GO together with PA6 represents the less efficient method, whereas the masterbatch prepared via solvent casting (GO 2) allows to achieve the best increase in these properties. When silica is used to functionalize GO, the mechanical properties of nanocomposites filled with GO-AE300 and GO-AEOX50 drastically increase and the elastic moduli measured for both the silica-GO filled PA6 reach values of almost 2000 MPa. The capability of silica to exfoliate the GO lamellae is confirmed by SEM analysis (see fig. 2) and probably this feature leads to the achievement of a better morphology in terms of exfoliation/intercalation thus resulting in a better load transfer.

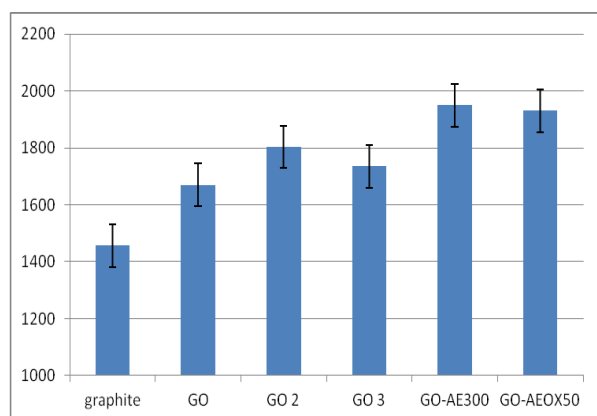


Figure 1 – TEM micrographs PA6/CNT 1 (a), PA6/f-CNT 1 (b), PA6/f-CNT 2 (c-d).

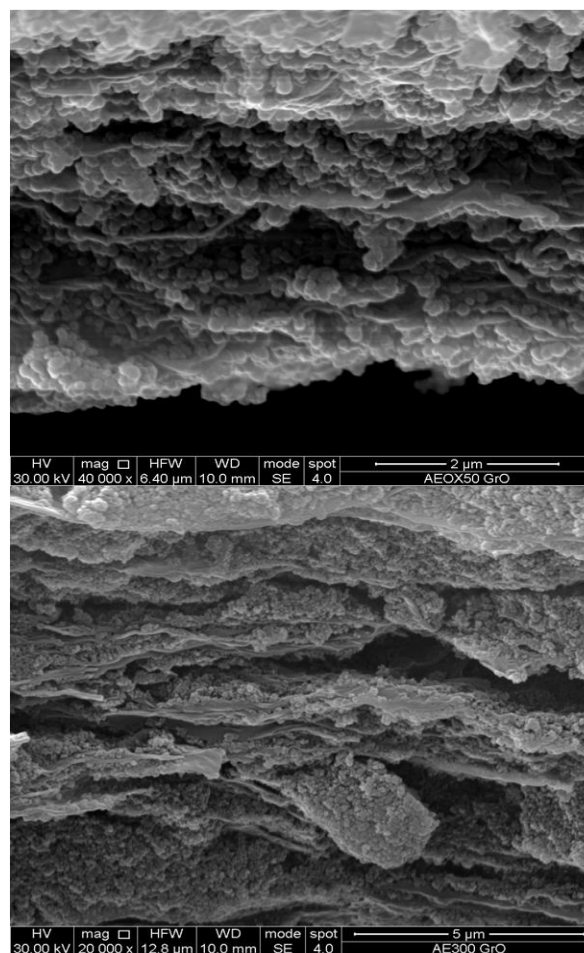


Figure 2 – Electrical conductivity as a function of the potential for PA6 based nanocomposite fibers.

Conclusions

The results of this work suggest that the mechanical performance of the PA6/GO system can be improved when a better dispersion/exfoliation of the GO is obtained. This can be achieved by a simple masterbatch with the PA6 or coupling GO with silica nanoparticles via esterification. Furthermore, this class of nanocomposites could be particularly suitable for the realization of electronic devices and/or sensors.

References

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