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Improved Carbon Nanotubes Dispersion Through Polar Dispersant Agents In Polyamide

Elisabetta Morici, Rossella Arrigo, Rosalia Teresi and Nadka Tzankova Dintcheva

Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy

Abstract. The potential enhancement of the nanocomposite properties, with respect to the neat matrix, is strictly related to uniform distribution and dispersion of the nanofillers in the host polymer. In this work, two dispersant agents, particularly a polar wax and a silanol polyhedral oligomeric silsesquioxanes POSS, have been used in order to improve the dispersion of bare and functionalized carbon nanotubes in polyamide matrix. To ensure a good compatibility between matrix and nanofillers, the dispersing agents having specific polarity have been chosen, in order to match that of the matrix. Significant alterations of the mechanical and rheological behaviour due to dispersion action of used additives have been noticed and discussed, also considering the obtained morphology.

Keywords: Dispersion; CNT; PA; Dispersant agent; POSS; Tegomer.

PACS: 82.35.Np; 82.35.Lr; 81.05.Qk

INTRODUCTION

The performance of polymer based nanocomposites depends on both the nanofiller and the polymer-nanofiller interaction at the interface; the latest explains because the dispersion of nanoparticles in polymeric matrices is directly related to the properties of the resulting materials [1]. Moreover it is well-known that a poor dispersion of nanofillers induce premature loss of the in-service manufactured properties. Among the wide variety of nanofillers, carbon nanotubes (CNT) are an ideal candidate for use as reinforcing nanofiller for high-performance nanocomposites because of their distinctive geometric features such as nanometric diameter and high-aspect ratio, characteristic physical properties and low density. In particular, uniformly distributed carbon nanotubes (CNT) throughout the polymer media allow to fully take advantage of the exceptional physical and mechanical properties of nanotubes themselves, among others, the robustness and the electrical conductivity and to produce nanocomposites with unique electrical, magnetic, self-healing, thermal and mechanical properties [2]. Unfortunately a homogeneous dispersion of CNT in nanocomposites is very difficult to obtain, because of a strong tendency to agglomerate and aggregate. The first challenge is to separate the nanotubes which, initially, are aggregated because of the Van der Waals forces. Physical approaches are based on transfer of local shear stress onto nanotubes in order to break bundles. Techniques such as shear mixing [3], sonication, ball milling have been employed for this purpose. Although using these methods well dispersed CNT in the host polymeric matrix are obtainable, suitable process conditions are necessary, as well as suitable medium viscosity or high nanofillers concentration; additionally, CNT may be physically damaged during processing. On the other hand, chemical approaches are designed to optimize the interaction energy between polymeric matrix and CNT since unfavorable interactions are accountable for the nanoparticles agglomeration. In this perspective, the dispersion of CNT could be assisted also by using solvents but the processing should provide a step for the evaporation of the solvent, that have to be shortened as much as possible to avoid CNT re-aggregation phenomena, as result of a continuous CNT concentration increasing in the system. So preparation methods such as the solution-blending are likely practicable on a small scale and, therefore, are not industrially appealing. The most used chemical techniques to improve CNT dispersion in polymeric nanocomposites regard the functionalization and/or modification of the nanoparticle surface, of the polymeric macromolecules, or the addition of a compatibilizer [4]. However, covalent modifications to attach a functional group to the nanotubes involve the use of chemical reactions that may result in variation of the carbon nanotube walls, increasing defects

concentration on the surface: the modification of surface can change properties, as electronic properties, and compromise nanocomposite performance. As compared to other methods, the use of dispersing agents preserves many important properties of nanotubes making this a proper strategy to improve the extent of their dispersion in the nanocomposites. However the choice of compatibilizers have to be carefully evaluated, as the dispersant itself can affect and compromise the overall properties of the resulting materials. Furthermore it is appropriate that the dispersing agent polarity match that of the matrix to ensure a good compatibility between matrix and dispersing agent.

In this work to enhance dispersion of bare and functionalized CNT in polyamide matrix, two dispersant agents have been tested: a polar wax and a silanol polyhedral oligomeric silsesquioxanes POSS. Polar waxes are a class of polar dispersing agents, highly temperature stable, able to improved processability. It was shown that amphiphilic Tegomer® E525, a polar wax, increase the dispersion degree of an organically modified nanoclay in a polyethylene matrix, at relatively low loading levels [5]. Silanol POSS, with probed dispersant ability, are incompletely condensed silsesquioxanes containing three Si-OH groups, able to create a stable system with the solid nanoparticles to disperse even at high temperatures [6]. The dispersion state of bare CNT and carboxylic functionalized CNT (COOH-CNT) has been assessed through morphological (scanning electron microscopy (SEM) observations), mechanical and rheological analysis. This work is devoted to improve the nanotubes dispersion and distribution within polyamide matrix since the achievement of a well-dispersed CNT morphology remains one of the main challenges in polymer nanocomposites manufacturing using the melt blending procedure.

EXPERIMENTAL PART

The materials used in this work were: -Polyamide-6 (PA) commercialized by Radici Group (Italy) under the name of "Radilon S", density 1.13 g/cm^3 and intrinsic viscosity of 1.5 dL/g measured at 30°C in 80 vol-% formic acid; -Multi-Walled Carbon Nanotubes (CNT) and carboxylic functionalized CNT (COOH-CNT) (COOH content =1%) commercialized by CHEAPTUBES (USA). Main characteristics are: O.D. $> 50 \text{ nm}$, $L=10\text{-}20\mu\text{m}$ and purity $> 95 \text{ wt}\%$. The CNT were added at 3 % wt./wt; - Polar wax Tegomer® E 525 (TEG) produced by Evonik Goldschmidt Italia s.r.l. (IT). TEG is a finely grained white powder with a melting point close to 100°C and a melt viscosity of $200 \text{ mPa}\cdot\text{s}$ at 140°C . It was added at 1 wt%; - Trisilanolphenyl POSS® (TSPH) produced by Hybrid Plastic (USA), having molecular weight $M_w=931,34 \text{ g/mol}$ and chemical formulae $\text{C}_{42}\text{H}_{38}\text{O}_{12}\text{Si}_7$. The TSPH was added at 1 wt%.

The preparation of PA and PA based systems was carried out using a Brabender mixer at $T=240^\circ\text{C}$ and mixing speed 50 rpm for 5 minutes. The additives were added in the melt polyamide after 2 min.

Scanning Electron Microscopy (SEM) investigation was performed on nitrogen-fractured radial surfaces of all the fibres by a Philips (Netherlands) ESEM XL30 equipment.

Mechanical tests were carried out using an universal Instron machine (mod. 3365). The values of elastic modulus, E, tensile strength, TS, and elongation at break, EB, were calculated as the average of ten tests.

The rheological characterization, was performed using an ARES G2, plate-plate rotational rheometer, operating at $T = 240^\circ\text{C}$.

RESULTS AND DISCUSSION

SEM analysis was used to observe the cross-section of PA and PA based systems. In Figure 1 the micrographs of investigated samples are reported. First of all, it is noteworthy that both TEG and TSPH have a beneficial effect on the morphology of the matrix, due to the enhancement of PA processability. The morphology of samples not containing dispersing additives, i.e PA/CNT and PA/COOH-CNT, is not uniform and randomly oriented CNT are present. Functionalized CNT containing nanocomposites show a better dispersion degree with respect to those containing bare CNT due to the interaction between carboxylic groups of CNT and the polar matrix. As noticeable in the micrographs of dispersing agent containing samples, the CNT bundles diameters are smaller than that of PA/CNT and PA/COOH-CNT samples. In particular, the dispersion degree seems to be improved because the interaction between CNT and TEG or TSPH are able to avoid nanotubes aggregates formation, so CNT become better dispersed in the matrix, especially in the PA/TSPH/COOH-CNT sample. Indeed, in the latest, sample individually dispersed CNT seem to be detected.

Results of mechanical analysis are reported in Table 1. Let us firstly consider the systems without dispersing agents. The adding of CNT and even more of COOH-CNT, leads to an enhancement of both elastic modulus (E) and tensile strength (TS) values and a decrease of elongation break (EB), because of their well known filler effect.

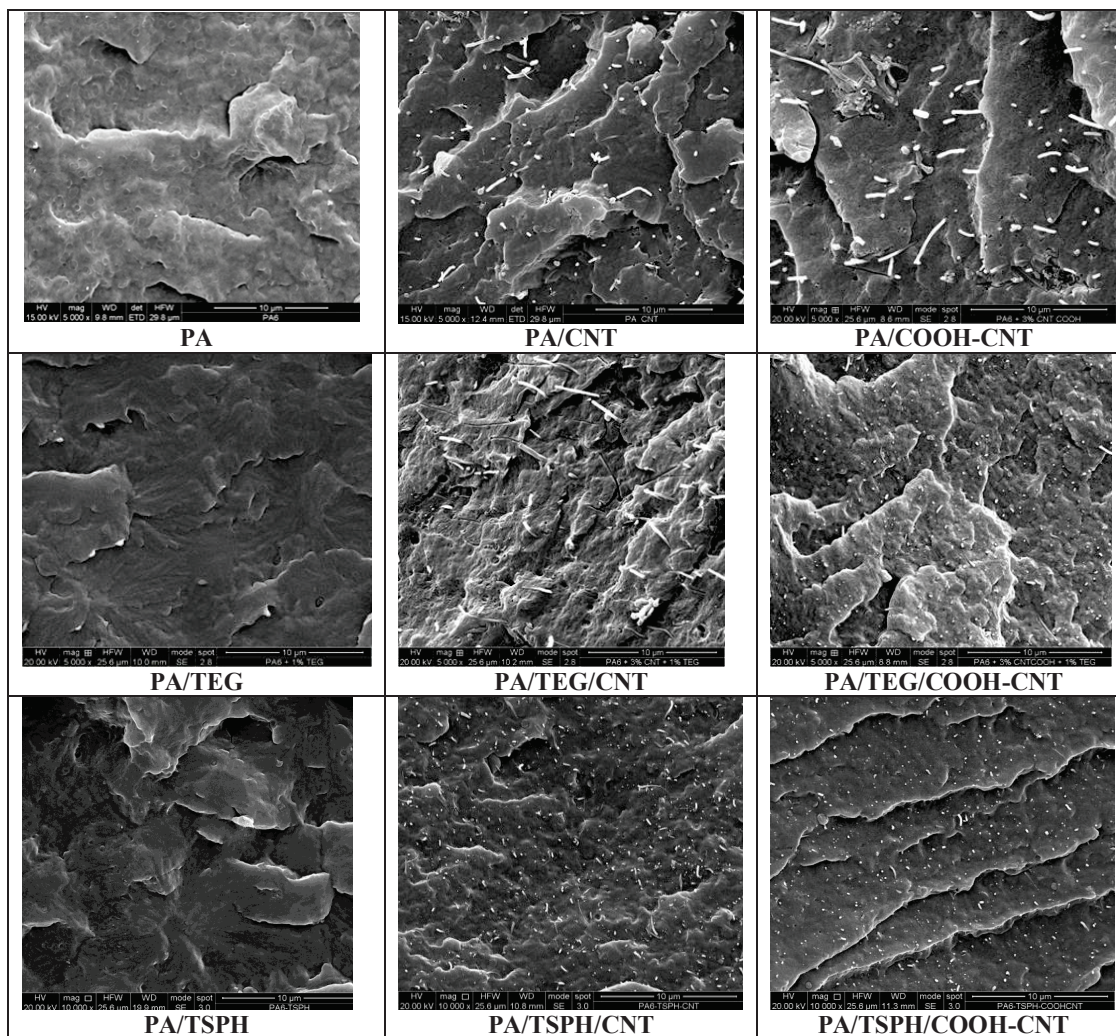


FIGURE 1. SEM micrographs of PA and PA based systems.

Additionally, in presence of functionalized CNT we have to take into account the interactions between COOH functionalities and polar groups in the matrix, responsible for a better interfacial adhesion between PA macromolecules and nanofillers. The increase of E and TS values of the PA/TEG and PA/TSPH samples can be ascribed to an improvement of crystallinity degree of the systems, and to the interactions established between the additives and PA chains, respectively. A dramatic increase of the E and TS is detected in the nanocomposites containing dispersant agents. Moreover, the recorded decrease of EB is commonly observed in well dispersed CNT filled nanocomposites [7]. The beneficial effect of TEG and TSPH on the tensile properties of bare and functionalized CNT based nanocomposites, can be related to the CNT distribution in the host matrix and to the interfacial adhesion between polymer and nanofillers. Indeed, the mechanical behaviour is significantly affected by the effectiveness of the stress transfer at polymer/particle interface.

Rheology can be used as an indirect evaluation method for the study of the dispersion state of the nanofiller in polymer-based nanocomposites. Indeed, this technique is able to detect the presence of interconnected structures that are related to well dispersed particles in the matrix. In Figure 2, the complex viscosity as a function of the frequency for neat PA and COOH-CNT containing nanocomposites is reported. The increase of the complex viscosity values of PA/TEG/COOH-CNT and PA/TSPH/COOH-CNT with respect to the PA/COOH-CNT is due to the presence of

the dispersing agents leading to a better dispersed nanofillers. Furthermore, these two nanocomposites show a well pronounced yield stress suggesting the formation of semi-3D interconnected structures in the systems.

TABLE 1. Main mechanical properties of all investigated samples.

Sample	E (MPa)	TS (MPa)	EB (%)
PA	1115	25	220
PA/CNT	1226	35	135
PA/COOH-CNT	1295	37	105
PA/TEG	1168	30	181
PA/TEG/CNT	1238	37	145
PA/TEG/ COOH-CNT	1313	72	41
PA/TSPH	1302	28	65
PA/TSPH/CNT	1333	58	48
PA/TSPH/ COOH-CNT	1538	69	30

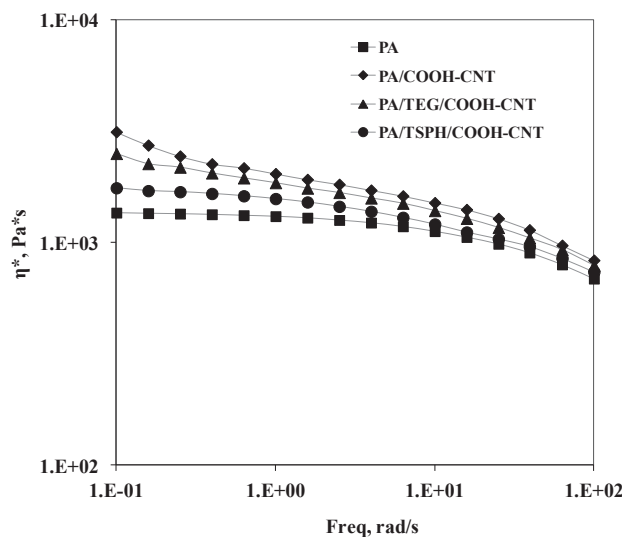


FIGURE 2. Viscosity curves of PA and COOH-CNT containing systems.

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