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A Novel Strategy to Achieve Enhanced Reinforcement and Decreased Damping in CNT-Nanocomposites †

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Abstract

In recent decades, polymer-carbon nanotube (CNTs) composite materials have attracted much attention for their potential applications in unique lightweight materials with distinctly superior mechanical properties. For structural applications, high strength can be delivered and conveniently tuned in nanocomposites by guaranteeing a good load-transfer at the CNT/polymer interfaces which is conventionally achieved with the help of complex chemical functionalization approaches.

In this paper, the mechanical properties of Nickel-coated carbon nanotube (Ni-CNT) reinforced Polyamic acid- nanocomposite (Ni-CNTs /PAA) and (CNTs/PAA) arepresented in terms of material rigidity and damping capacity. The Ni nanoparticles on the CNTs outer walls, help to induce an interlocking mechanism at the CNTs/matrix interface. A significant Elastic modulus increase is thus observed for this type of samples. On the other hand, the Ni-CNTs/PAA nanocomposite, decreases its damping capacity when compared with bare CNTs/PAA nanocomposite. It is worth noting that the recorded rigidity increase and damping decrease is reached despite the significantly smaller amount of CNTs (40% lower weight fraction) contained in the Ni-coated samples. The investigated nanocomposite types were in fact conceived with the same total weight, thus with the same amount of filler without taking into consideration the higher weight of Ni nanoparticles. The results here reported proof the concept that when metal nanoparticles coat the CNTs outer walls, an important improvement of the CNTs-matrix load transfer can be reached without the need to undergo into complex CNTs functionalization procedures. This is an advantage since chemical functionalizations typically have the drawback of introducing defects on the CNT walls.

Keywords: Carbon nanotube; Polymer-matrix composites (PMCs); Nano composites; Coating; Magnetic nanocomposites

1. Introduction

The unique mechanical, electrical, and optical properties [1-4] of multiwall carbon nanotubes (MWNTs) make them very attractive for the fabrication of new advanced materials, particularly polymer composites with improved performance, or with new properties. Numerous studies on MWNTs showed that an effective utilization of carbon nanotubes (CNTs) in composite applications strongly depends on the ability to disperse the CNTs homogeneously throughout the matrix [5-7] Obviously, good interfacial bonding and interactions between nanotubes and polymers are the necessary conditions for improving the mechanical properties of the composites. A significant number of different surface treatment and functionalization techniques have been devised for improving the dispersion and interfacial adhesion between the CNTs and polymer matrices. As a result, the composites were proved to exhibit higher mechanical properties than those without treatment through the formation of stronger interfacial bonds and more homogeneous dispersion of CNTs [8].

Recently, many researchers have attempted to deposit metals or metal compounds onto the CNTs surface. In order to make magnetic nanocomposites. This kind of nanocomposites have potential applications in various areas such as magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging. Therefore, studies on magnetic nano composites, especially on magnetic CNTs composites, are rapidly expanding.

Despite several studies on the metal-coated CNTs within a metal matrix [9-13], the studies for Ni-coated CNTs with polymer matrix [14] are few. In this study, we investigate the mechanical response of polyamic acid (PAA) nanocomposites that are reinforced with Nickel coated MWNTs, . The CNT-Ni/PAA composites are prepared by solvent casting technique and subsequently the rigidity and damping capacity are measured and compared with values obtained for the films made of uncoated MWNTs in the PAA matrix.

2. Fabrication process

Materials: MWNTs (Purity>95%, OD: 50-80 nm) and Nickel-coated MWCNTs (Purity>98%, OD: 50-80 nm, 60wt% Nickel+38wt% MWCNTs) are purchsed from US Research Nanomaterials Inc., while NMP(N-Methyl-2-pyrrolidinone, Purity:99.5%) is purchased from Sigma Aldrich Co., and polyamic acid (PAA) from HD MicroSystems Co..

First 12wt % of MWCNTs or Ni-MWCNTs are added into NMP and the mixture is sonicated for 45 min. At the same time Polyamic acid and NMP are mixed with mechanical stirring. The PAA solution is then added to the MWCNTs/NMP suspension and sonicated for another 20 min at 0 °C. Nanotube aggregates were not observable by eye. The MWCNTs/PAA dispersions are cast onto glass slides, and are then dried on vacuum oven at 95C for 1.5 h to remove solvent.

3. Mechanical characterization

Thin nanocomposite rectangular specimens were obtained by cutting the nanocomposite films in stripes of 3.5 mm in width and 15 mm in length, while their thickness was measured to be between 35 μm. A dynamic mechanical analyzer DMAQ800 was employed to perform monotonic and cyclic tensile tests by using the tension film clamp. A preload of 0.1 N was first applied, then a force rate of 2 N/min was set for both the monotonic and cyclic tensile tests. In the monotonic tensile tests, useful to characterize the materials elastic regions, a maximum strain of 5% was reached. The loading/unloading tensile tests were performed in the elastic region and, two cycles at the maximum stress amplitudes of 15 MPa and 20 MPa, respectively, were obtained. The tests were repeated on 5 specimens for each nanocomposite material.

3. Results and discussion

The representative stress–strain curves are reported in Figure 1. As expected, the nanocomposite with nickel-coated CNTs shows a significantly enhanced mechanical response with respect to the pristine CNT/PAA nanocomposite. When the two nanocomposite materials are loaded they exhibit an elastic behavior up to a strain of 1%. A Young modulus of 1.497 GPa and 1.936 GPa for the pristine CNT/PAA and Ni-CNT/PAA nanocomposites, respectively. Such outcome proves the effectiveness of the nickel nanoparticles which increase the density of the van der Waals interaction forces at the CNT/matrix interfaces. A 29% improvement of the elastic modulus is delivered in the interface-engineered nanocomposite with respect to the nanocomposite with unmodified interfaces.

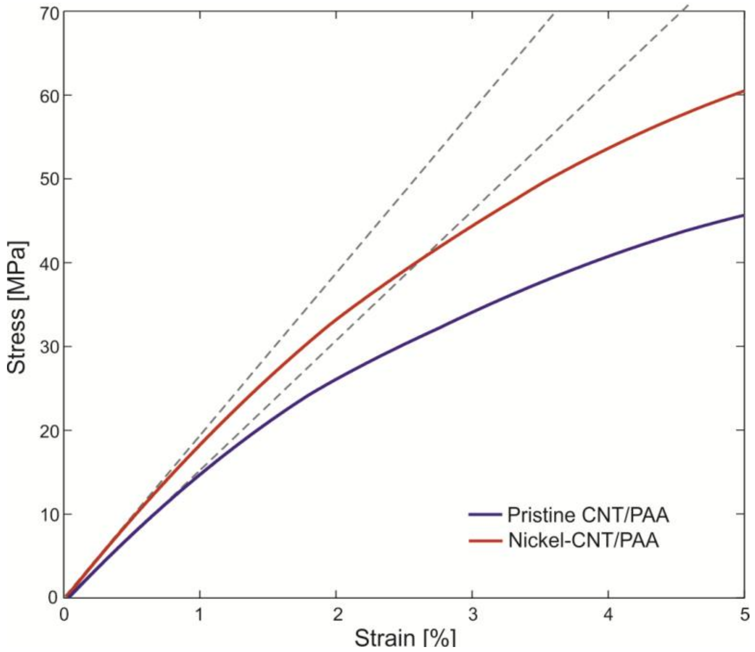

Figure 1. Monotonic tensile tests at a constant force rate of 2 N/min for the pristine CNT/PAA nanocomposite and nickel-coated CNT/PAA nanocomposite. The representative stress-strain curves are obtained by averaging and interpolating the test data of five specimens per each material.

The loading/unloading stress-strain curves are reported in Figure 2, performed in the materials elastic region (below 1.5% strain). Besides the reinforcing effect provided by the nickel coating of the CNTs, an additional effect on the nanocomposite damping capacity is also observed. The nickel-CNT/PAA nanocomposites show narrower hysteretic cycles with respect to the pristine CNT/PAA nanocomposites. The hysteresis arising in the nanocomposites with the nickel nanoparticles interface modification is mainly due to the viscoelastic behavior of the PAA matrix, characterized by free and short oligomer chains. Indeed, PAA chains show high mobility and are kept together by weak interaction forces. The PAA chains easily slide each other and adjust their configurations once loads are applied. On the other hand, the PAA chains near to the nickel-coated CNTs must interact with the nickel nanoparticle and transfer the load to the CNT nanofiller through them. Due to the stronger electrostatic interaction forces between the polar PAA oligomer chains and the metallic nanoparticles, the nickel-CNT/PAA nanocomposite is characterized by strong interfaces with good adhesion between the matrix and nanofiller.

The hysteresis in the pristine CNT/PAA nanocomposites is instead the result of two contributions, i.e., (i) the contribution of the PAA matrix inter-chains sliding, and (ii) the contribution of the interfacial frictional sliding between the CNTs and the PAA chains, a phenomenon well known as stick-slip [15]. This energy dissipation phenomenon observed in pristine CNT/PAA nanocomposites is easily activated due to the weak adhesion at the unmodified CNT/matrix interfaces. Low interfacial shear stress levels are required to overcome the weak interaction forces at the interface and trigger the slippage of the PAA chains with respect to the CNTs.

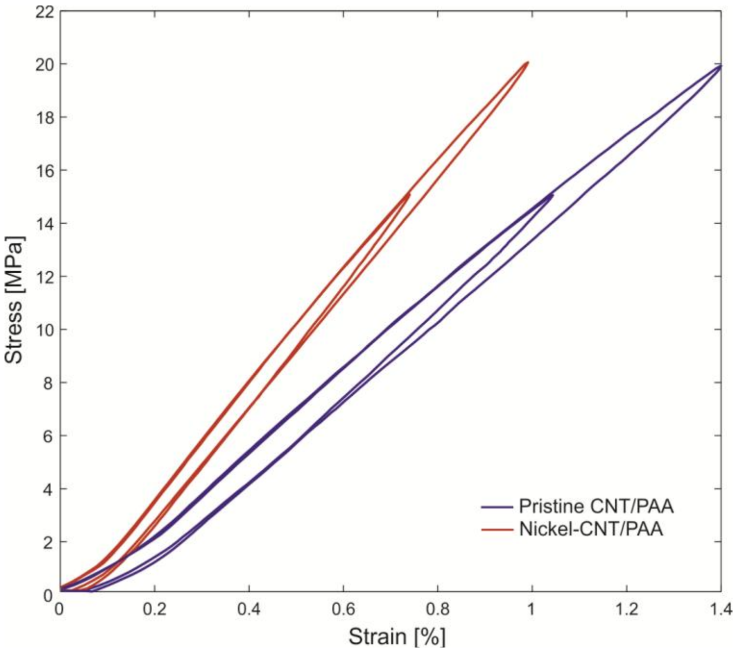

Figure 2. Cyclic tensile tests at a constant force rate of 2 N/min for the pristine CNT/PAA nanocomposite and nickel-coated CNT/PAA nanocomposite. Loading/unloading cycles at two stress amplitudes (15 MPa and 20 MPa, respectively) are obtained per each material.

In particular, the equivalent damping ratio of the two nanocomposite materials is computed by directly measuring the dissipated energy as the area enclosed by the loading/unloading cycle, and the elastic strain energy as the area under the loading branch. The equivalent damping ratios were found to be 1.418% and 1.064% for the pristine CNT/PAA and nickel-CNT/PAA nanocomposites, respectively. Therefore, the interface-engineered nanocomposites have a reduced damping capacity of 33% with respect to the pristine nanocomposites due to the strengthening effect of the nickel nanoparticles which increase the interfacial shear stresses needed to activate the stick-slip energy dissipation phenomenon.

The carried out mechanical tests proved the effectiveness of the selected interface engineering approach. By exploiting nickel nanoparticles, a significant enhancement in the nanocomposite elastic response is observed. The nickel nanoparticles CNTs coating has the advantage of not damaging the CNTs outer sidewalls structure, in contrast to other interface treatments, such as covalent functionalization, which requires the use of acids to create defects sites on the CNT surface and attach functional groups [16]. Furthermore, it is worth to point out that the CNT weight fraction in the nickel-CNT/PAA nanocomposites is only the 40% of the weight fraction of CNTs employed in the pristine CNT/PAA nanocomposites. Indeed, the interface modified nanocomposites were fabricated by replacing the weight of pristine filler with the same weight of modified filler. Therefore, the weight of the modified filler is in part given by the heavy nickel nanoparticles (i.e. 60% of the weight is due to nickel). This strategy was employed in order to compare two ultra-lightweight nanocomposite materials with the same total weight. Although Ni-CNT/PAA nanocomposite contain less carbon nanotubes, thus, there is less interfacial surface area available for the load transfer mechanism, excellent enhancements in the material mechanical properties are obtained.

Conclusions

In this paper it is shown that metal (Ni) nanoparticles can successfully be used as an alternative method to improve load transfer between CNTs and a hosting matrix. In this case study, in particular, the matrix is composed of short oligomer chains, that, together with the Ni nanoparticles, create an interlocking mechanism that represents the foundation of the mentioned load transfer improvement. The improvement in CNT-matrix interfacial properties is reflected into the elastic modulus increase and in the decrease of the material damping capacity. In particular Ni-CNTs nanocomposites show a 29% improvement in elastic modulus and a 33% decrease in damping. The advantage of this approach is that mechanical properties improvement is reached without structural damage of the CNTs outer walls, in contrast with standard chemical functionalizations.

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