Covalent and non-covalent functionalization of carbon nanotubes: effect on thermal and mechanical properties of structural nanocomposites

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ABSTRACT

In this work, unfunctionalized carbon nanotubes (CNT), covalently functionalized CNT with diaminodiphenyl sulfone (DDS) ligand (CNT-DDS) and CNT modified with benzoxazine terminated PDMS (CNT-PDMS-Bz), obtained through a noncovalent approach, were dispersed within an aeronautical epoxy matrix. DDS may play an important role as additional hardening agent for epoxy curing systems and the strong intrinsic interactions of CNT with a benzoxazine precursor give rise to the formation of a reinforced network with outstanding thermo-mechanical properties [1]. Recently, carbon nanotubes have received a great attention as nanofillers for epoxy-based structural systems, due to their unique combination of mechanical, electrical, thermal properties and others [2-3]. Moreover, the CNT surface can be easily modified with several functional groups carrying specific functionalities through different strategies, such as covalent functionalization and a very promising strategy to modify the surface of the carbon nanotubes without compromise their structural integrity involving the noncovalent functionalization of CNT with molecules showing a strong affinity with graphitic surfaces of CNT [4-5]. The goal of this work was to enhance the interactions of CNT with epoxy matrix in order to enable a much better dispersion of CNT within the epoxy polymer through non-covalent and covalent functionalization of their graphitic sidewalls compared to pristine CNT and to improve the thermal and mechanical properties of the final epoxy nanocomposites. We have used functionalized carbon nanotubes that form covalent bonds with cross-linked epoxy matrix to clarify the role of the matrix-filler interphase in the enhancement of mechanical and thermal properties in the structural nanocomposites. Our results demonstrate that the functionalization of the CNT facilitates the transfer of both mechanical load and thermal energy across the matrix-filler interface. The functionalization of CNT was successfully proved by FTIR and Raman spectroscopies and the effectiveness of the dispersion attributable to functionalization is clearly visible from the SEM images shown in Figure 1. The adopted unfilled epoxy matrix TBD is characterized by a volume conductivity at room temperature of about 6.00×10^{-14} S/m, whereas TBD+1%CNT nanocomposite shows a DC

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conductivity value of 2.92×10^{-1} S/m. It is worth noting that also the introduction of CNT-PDMS-Bz and CNT-DDS functionalized nanofillers significantly affects the electrical behavior of the nanocomposites leading to an abrupt transition from an insulating to a conducting behavior. In fact, the DC conductivities of the TBD+0.5%CNT-PDMS-Bz and TBD+1%CNT-PDMS-Bz samples reach respectively the values of 1.65×10^{-2} S/m and 1.06×10^{-1} S/m, whilst TBD+1%CNT-DDS sample reaches the value of 8.81×10^{-3} S/m. The dynamic mechanical analysis shows that all the formulated carbon nanotubes reinforced resins are suitable for a very wide range of structural applications, giving high values of the storage modulus and glass transition temperature (Tg) (see Figure 1). All the nanocomposites were found to be more thermally stable compared to unfilled epoxy matrix TBD. Thermogravimetric analysis of the nanocomposites highlights a stabilizing effect of the carbon nanotubes in the first stage of the degradation (see Figure 1). In conclusion, a surface modification of CNT following two different approaches, i.e. covalent anchoring and physical absorption is beneficial to obtain a more homogeneous dispersion of functionalized CNT within the host polymer matrix improving the state of the polymer/nanoparticle interface and enhancing the thermo-oxidative stability of nanocomposites. In particular, the noncovalent approach maintaining the intrinsic properties of CNT with numerous supramolecular interactions allowed to obtain the highest healing efficiency value (see Figure 1). The healing efficiency has been evaluated from the evolution of the relative elastic modulus during time.

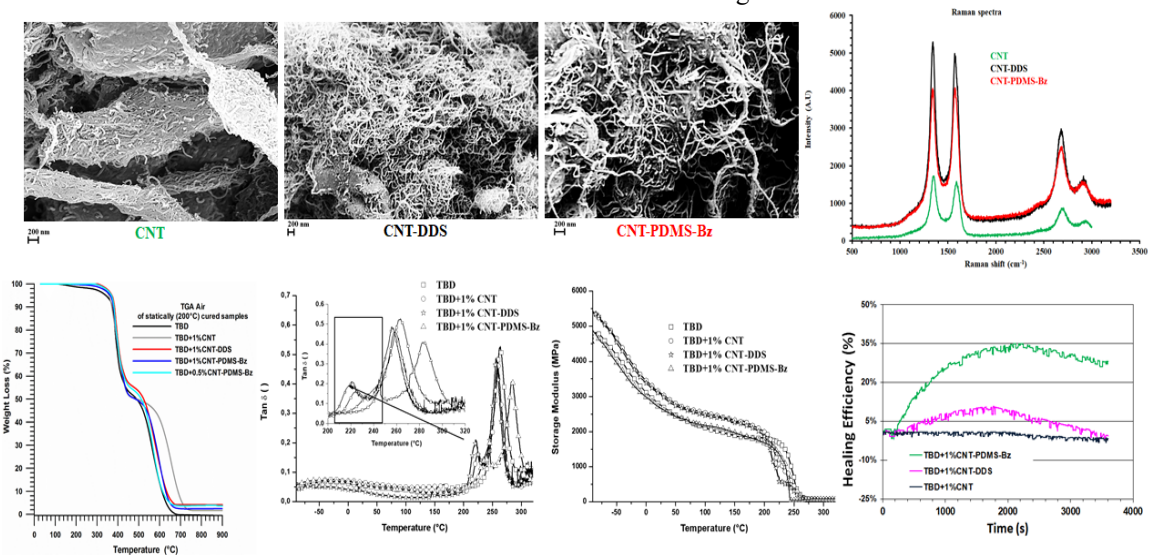

Figure 1: SEM micrographs and Raman spectra of unfunctionalized CNT and functionalized CNT-DDS and CNT-PDMS-Bz (see on the top); TGA curves, loss factor (tanδ), storage modulus and healing efficiency of carbon-based nanocomposites (see on the bottom).

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