SYNTHESIS OF NANOCOMPOSITES BASED ON FLUORINE CONTAINING EPOXY RESIN REINFORCED WITH SURFACTANT FUNCTIONALIZED MWCNTs

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Abstract
This research proposes the synthesis of nanocomposite based on fluorinated epoxy resin reinforced with surfactant modified Multiwalled Carbon Nanotubes (MWCNT) in order to obtain new materials with significantly improved thermal stability. Surfactant functionalization was helpful to obtain advanced dispersion of the carbon nanotubes and compatibilization with the epoxy matrix.

1 Introduction
Fluorinated epoxy resins are known as hydrophobic materials with high resistance to the moisture environment. Carbon nanotubes (CNTs) are excellent candidates for improvement of thermo-mechanical properties of epoxy resins. Raw CNTs have a tendency to aggregate because of their large surface area and strong resultant van der Waals forces. The dispersion of CNTs is very important in order to achieve enhanced properties for epoxy based CNT composites, this parameter being improved considerably by functionalization.

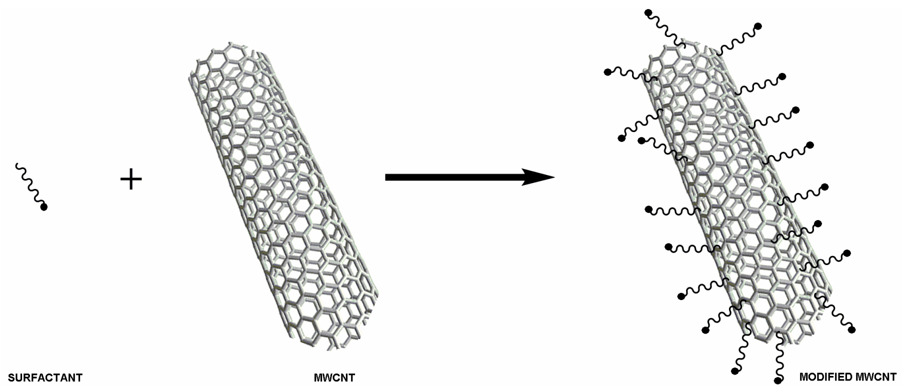

Figure 1. Functionalization of MWCNTs

1.1 Characterization of functionalized MWCNTs
Structural characterization of functionalized MWCNTs by FT-IR showed the presence of physically attached polyether surfactant molecules on MWCNT-X100 and MWCNT-SP135

through van der Waals forces exerted by the nanotubes evidenced by the appearance of the bands at about 1090 cm^{-1} and 1270 cm^{-1} corresponding to asymmetric stretching of the ether groups [2] from the surfactants molecules as one can see from Figure 2. These results confirmed that surfactants had been successfully absorbed on the MWCNT surface.

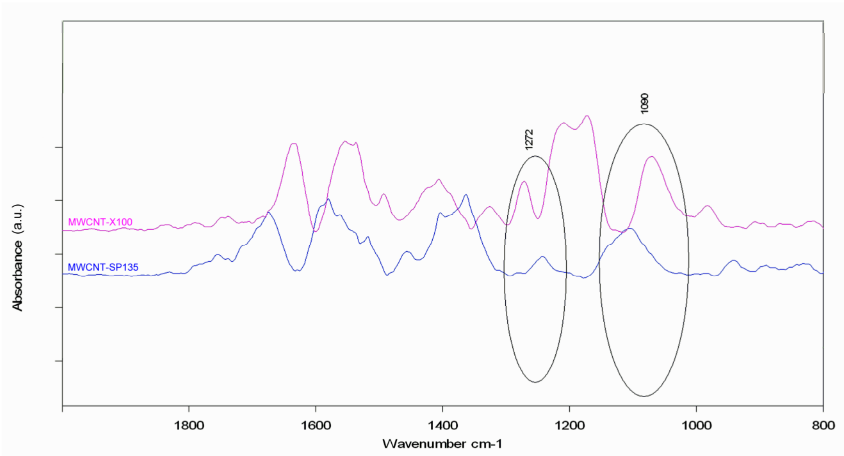

Figure 2. FT-IR spectra for the two types of functionalized MWCNTs

Raman Spectroscopy was used to show the presence of noncovalently attached surfactant molecules on the functionalized MWCNTs after the purification process. Thus, the spectra from Figure 3 show two significant peaks, one at 1593 cm^{-1} (the G band) assigned to tangential vibrations of MWCNTs and the second characteristin peak at 1331 cm^{-1} (the D band) corresponding to the disorder mode introduced in the C sp^2 electronic structure by other types of atoms [3]. The I_D/I_G ratio between the intensities of the two bands may give significant information about the noncovalent functionalization of the MWCNTs. It can be observed that the I_D/I_G ratio increases from 1.01 for the pristine MWCNTs to about 1.61 after noncovalent treatment, which is a proof that the attachment of surfactants molecules was achieved.

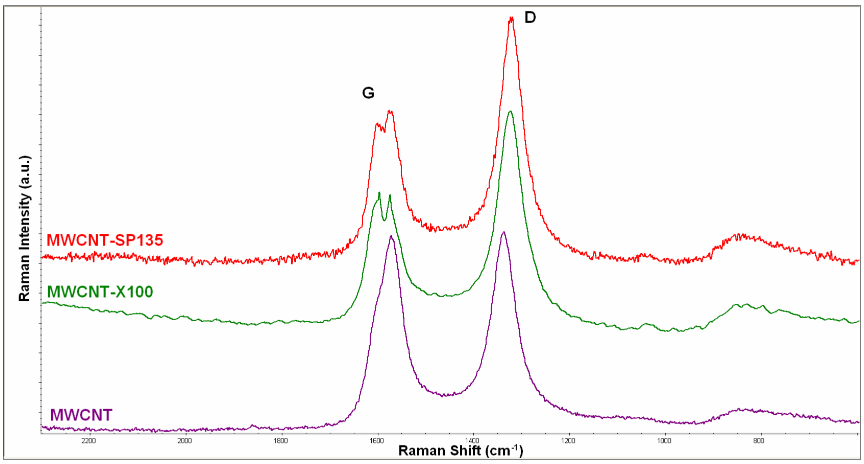

Figure 3. Raman spectra for the pristine and functionalized MWCNTs

XPS surface characterization of functionalized MWCNTs showed an increase of the oxygen content for the functionalized MWCNTs as shown in table 1 due to the presence of the surfactant molecules, being a powerful proof of the noncovalent attachment.

Nanotubes Type	At. C1s %	At. O1s %
MWCNT	99.12	0.88
MWCNT-X100	96.63	3.37
MWCNT-SP135	89.98	10.02

Table 1. XPS surface composition data for the pristine and functionalized MWNTs

1.2. Composites characterization

Thermal stability of the DGEFBA composites systems, defined as the temperature of 3% weight loss ($T_{d3\%}$), was obtained using TGA technique. Compared with the neat DGEFBA, the composites reinforced with only 0.3% of functionalized MWCNTs showed a ~20°C improvement of $T_{d3\%}$ as shown in Figure 4. Thus by combining the excellent thermal, mechanical, electrical and optical properties of MWCNTs with the low dielectric constant, low moisture absorption and thermal resistance of fluoroepoxy polymers it could be reunited all the condition for a high performance nanocomposite material to be obtained.

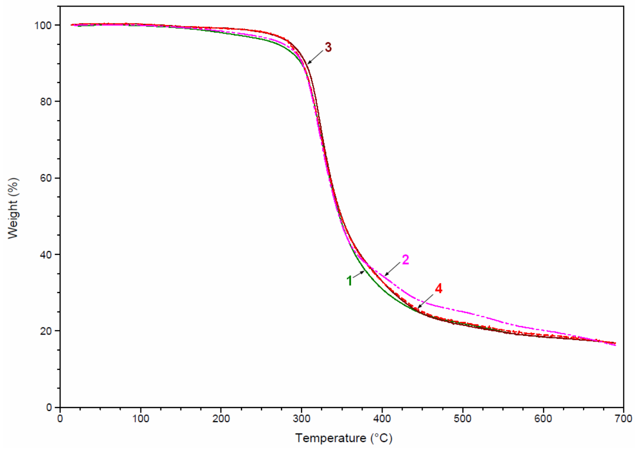

Figure 4. TGA curves for: DGEFBA_PXDED (1) and the composites reinforced with MWCNTs (2), MWCNT-X100 (3) and MWCNT-SP135 (4)

Fluorinated epoxy resins are known as hydrophobic materials with high resistance to the moisture environment. In the systems reinforced with pristine MWCNTs it was noticed a low compatibility with the nanotubes surface resulting in agglomerates. The SEM images for X100 surfactant functionalized MWCNTs (Figure 5 b) showed well dispersed nanotubes in the DGEFBA resin leading to the enhancement of the new composites thermal stability.

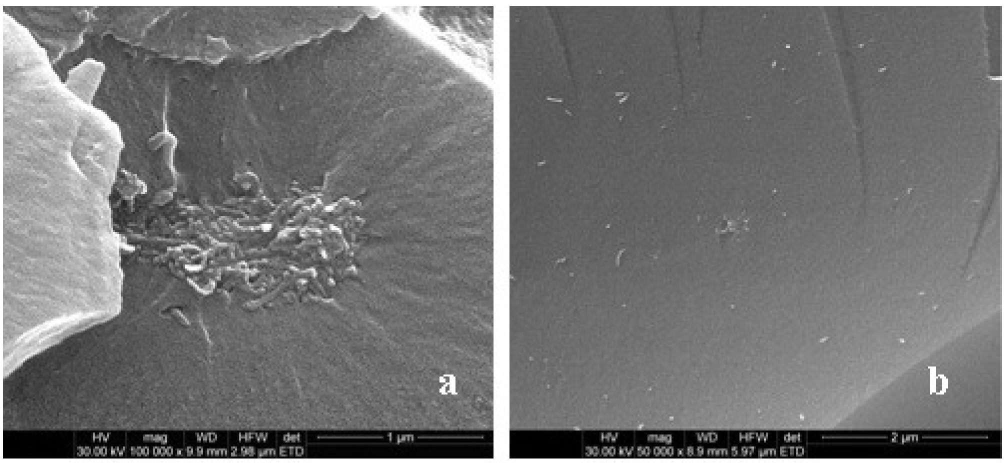

Figure 5. SEM images for DGEFBA composites reinforced with pristine MWCNTs (a) and MWCNT-SP135 (b)

2 Materials and testing methods

Fluorinated epoxy resin: diglycidylether of hexafluorinated bisphenol A (DGEFBA) was synthesized from epichlorhydrine and 4,4′-(Hexafluoroisopropylidene)diphenol by a method described in the literature [1]. Surfactant modified CNTs have been functionalized by a noncovalent method, using two different polyether nonionic surfactants (Triton X100 and Triton SP-135) in order to reinforce the fluorinated epoxy resin. Surfactant functionalized MWCNTs were prepared via ultrasonication in acetone solution to obtain surfactant coated nanotubes. Functionalization was proved by Thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Photoelectron Spectrocopy (XPS) analysis. The modified CNTs were dispersed in DGEFBA by tip sonication, cured with an aromatic polyamine (Poly(m-xylylenediamine-alt-epichlorohydrin) diamine terminated) by a two step temperature schedule to obtain the final composites. Composite samples were characterized by TGA and Scanning Electron Microscopy (SEM) analysis.

References

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