U.P.B. Sci. Bull., Series B, Vol. 72, Iss. 3, 2010 ISSN 1454-2331

ETHYLENEDIAMINE FUNCTIONALIZATION EFFECT ON THE THERMO-MECHANICAL PROPERTIES OF EPOXY NANOCOMPOSITES REINFORCED WITH MULTIWALL CARBON NANOTUBES

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Funcţionalizarea nanotuburilor de carbon cu pereţi multipli (MWNT) poate îmbunătăţii proprietăţile termice şi mecanice ale compozitelor epoxidice în care sunt încorporate drept agenţi de ranforsare. Grupările aminice au fost alese în vederea funcţionalizării MWNT carboxilate datorită posibilităţii de deschidere a inelelor epoxidice a răşinii utilizate în obţinerea materialelor compozite. Ataşarea grupărilor etilendiaminice (EDA) a fost demonstrată prin TGA, FT-IR şi spectroscopie Raman. Temperatura corespunzătoare entalpiei maxime de reticulare a răşinii epoxidice, observată prin DSC, prezintă o deplasare spre valori mai mari, prin adăugarea a doar 0.3% MWNT funcţionalizate. De asemenea imaginile SEM au fost utile în demonstrarea dispersiei MWNT-EDA în compozite.

Functionalization of multiwalled carbon nanotubes (MWNTs) may improve the thermal and mechanical properties of the epoxy composites in which they are embedded as reinforcing agents. Amine groups were chosen to functionalize the carboxylated MWNTs due to their potential to form bonds with the epoxy resin used as polymeric matrix for composite materials. The attachment of the ethylenediamine (EDA) groups was proved by TGA, FT-IR and Raman Spectroscopy. The temperature at which the curing enthalpy is maximum, observed by DSC, was shifted to higher values by adding only 0.3% functionalized MWNTs. SEM images show the dispersion of the MWNT-EDA within the composites.

Keywords: functionalization, nanotubes, thermal properties, epoxy nanocomposites

1. Introduction

Much attention has been focused in recent works on carbon nanotubes (CNTs) due to their small size, unique properties [1-3], combined with a tubular morphology,

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having a huge potential in industrial applications [4-5] and also for biomedical devices [6-7].

There are two main drawbacks of the CNTs: the low reactivity of their graphitic structure and the agglomeration tendency due to the large specific surface. The potential of these new materials in composite materials can be fully explored when these disadvantages are solved, mainly by functionalization.

Chemical functionalization of CNTs is very important for most of their use in different applications. The attachment of functional groups or aliphatic carbon chains to the nanotubes can increase the solubility of nanotubes in organic solvents and compatibilize them with polymeric matrices [8].

It is known from many studies that the presence of different functional groups is the starting point for binding a variety of different chemical molecules on the nanotube surfaces [9].

Two ways are considered for surface modification of carbon nanotubes. One is noncovalent functionalization with molecules based on van der Waals forces [10] and the other one is covalent functionalization of the graphitic CNTs walls through direct bonding of different functional groups [11]. The advantage of the noncovalent functionalization is that the perfect structure of CNTs walls is not altered, thus their mechanical properties should not change. The disadvantage of the noncovalent functionalization is that the forces between the wrapping molecule and the CNTs are weaker than the covalent bonds. The covalent attachment of amine functional groups [12] to the surface of CNTs can improve the load transfer to epoxy matrices by forming a direct bond through opening the epoxy ring. However, it must be noted that the process for obtaining functional groups may introduce defects on the walls of the nanotubes [13], another way could be the obtaining the functional materials by direct synthesis [14].

Functionalization with amine groups usually lead to an improuvement of the mechanical properties. When the content of the MWNTs-NH_2 is 0.6%, the bending strength will increase by 100% and flexural modulus by 58% [15].

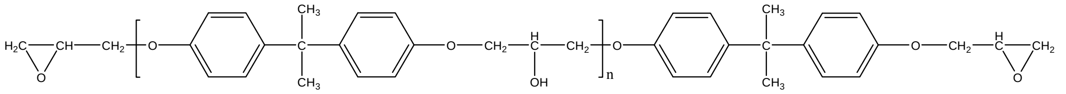
The aim of this study was the improvement of the dispersion state of the MWNTs reinforcing agent within the epoxy resin matrix and the properties of the nanocomposite materials obtained by diamine attachment on CNTs sidewalls.

2. Materials and methods

2.1. Materials

Multiwalled Carbon Nanotubes (MWNTs) were purchased from Sigma Aldrich having more than 90% carbon basis and D x L 10-15 nm x 0.1-10 µm, produced by Catalytic Chemical Vapor Deposition (CCVD). Oxidation was made using a mixture of 98% sulfuric acid (Merck) and 70% nitric acid (Merck). The ethylenediamine (EDA) modifier agent was supplied by Fluka. Epoxy matrix diglycidylether of bispfenol A

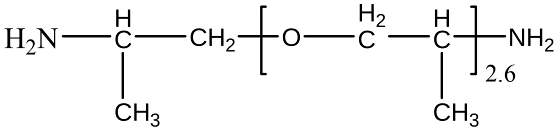
(DGEBA) and curing agent D230 were purchased from Huntsman. All reagents were used without further purification and their structures are presented in Scheme 1.



Diglycidyl ether of bisphenol A (DGEBA)

$H_2N{-}CH_2{-}CH_2{-}NH_2$

Ethylenediamine (EDA)



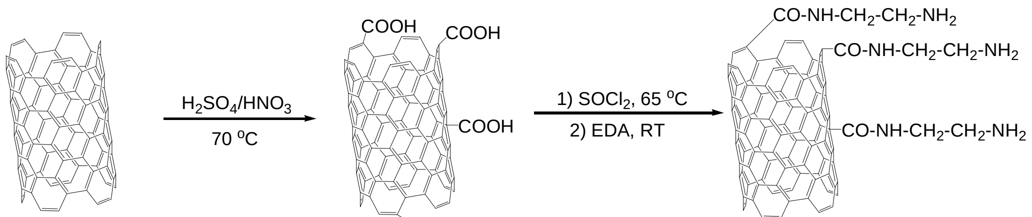
$$H_2N{-}\underset{CH_3}{\overset{H}{C}}{-}CH_2{-}\left[O{-}\overset{H_2}{C}{-}\underset{CH_3}{\overset{H}{C}}\right]_{2.6}{-}NH_2$$

Polyether amine (Jeffamine D230)

Scheme 1 Structural formulas of the reactants

2.2. MWNTs functionalization

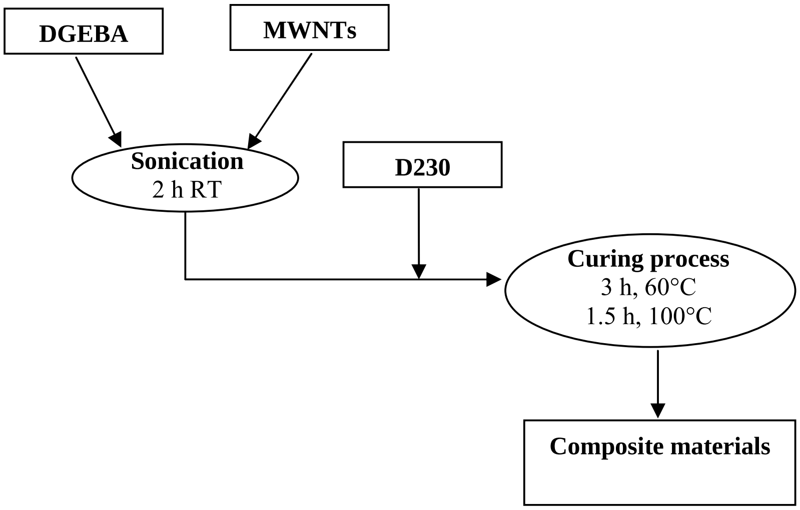
The reason for functionalization was the debundling and dispersion improvement of the nanotubes during composite processing. Thus, the functionalization process was made in two steps: firstly, the oxidation of MWNT using a 3:1 (vol.) mixture of H_2SO_4: HNO_3 in order to purify the raw material from catalyst traces, to obtain carboxylic groups on their surface, as well as at the end by capping the semispherical ends. Thus 100 mg of MWNTs was added to 12 ml H_2SO_4: HNO_3 mixture, heated at 70°C in silicon oil bath and kept under stirring for 12 h and then the product was filtrated on 0.22 μm pore Teflon membrane and washed until the pH reached neutral value. Carboxylated carbon nanotubes (MWNT-COOH) were dried under vacuum for 48 h at room temperature (RT). The second step have consisted in amine attachment at these nanotubes surface by acylation with thionyl chloride ($SOCl_2$) at 65°C for 24h, followed by amidation of the resulted MWNT-COCl with an excess of EDA at RT for 48 h to complete the functionalization process.



Scheme 2 Functionalization reaction of MWNT

2.3. Composite synthesis

Composite materials were obtained by mixing DGEBA resin with the reinforcing agents (MWNT, MWNT-COOH and MWNT-EDA) using ultrasounds bath, for 2 h at room temperature. The curing process was done with the flexible polyetheramine Jeffamine D230 following a two steps thermal treatment: one step for 3 h at 60°C and the second one for 1.5 h at 100°C to complete the reaction (named postcuring step). The method used to obtain the epoxy/MWNTs nanocomposite samples is illustrated in Scheme 3.



Scheme 3 Manufacturing steps for epoxy composites reinforced with MWNTs

2.4. Advanced characterization

FTIR spectra of functionalized MWNTs were registered on a Bruker Vertex 70 equipment in 400÷ 4000 cm^{-1} range with 4 cm^{-1} resolution and 32 scans. The samples were analyzed in KBr pellets. Raman spectra for functionalized MWNTs were recorded on a DXR Raman Microscope (Thermo Scientific) by a 633 nm laser line, with signal to noise ratio 100. The 10x objective was used to focus the Raman microscope. Thermogravimetry of the samples was done on Q500 TA equipment, using nitrogen atmosphere from 50°C to 800°C with 10°C/min heating rate. Dynamic mechanical analyses (DMA) of the composites were carried out on a TRITEC 2000 B instrument. Samples were analyzed in bending mode in the range of temperature 25-180°C using a heating rate of 5°C/min. Differential Scanning Calorimetry (DSC) curves were recorded on a Netzsch DSC 204 F1 Phoenix equipment. Samples were heated from 20 to 300°C using a heating rate of 10 °C/min, with a nitrogen flow rate of 40 mL/min.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

The enhancement of thermal stability for epoxy composites is desired for future applications. In figure 1, one can observe the thermal degradation of pristine and the two functionalized samples of MWNTs. It is well known that the graphitic structure of carbon nanotubes is stable up to 500-600°C, when thermal oxidative processes occur. The oxidation with strong acids of MWNTs introduces carboxylic groups at the nanotubes surface by creating defects in the hexagonal or pentagonal structures from the graphene sheet or by cutting the semispherical ends of the CNTs. The degradation process of MWNT-EDA exhibits two steps, one at ~173ºC assigned to the broken of amidic groups and another at ~538ºC normally attributed to graphite structures degradation.

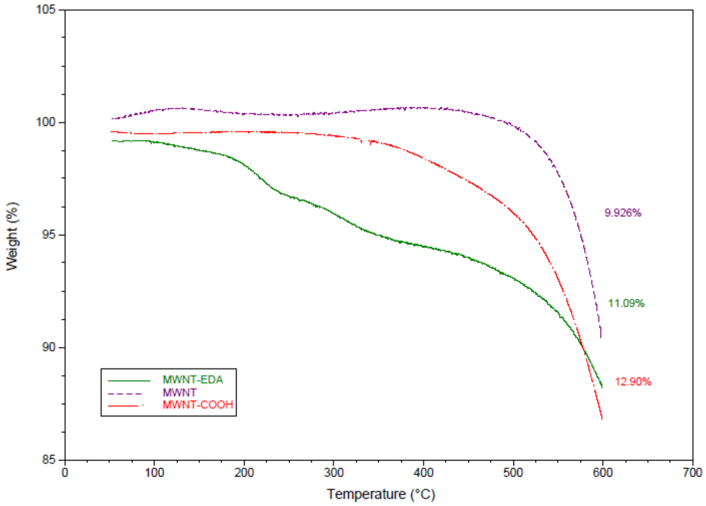


Fig. 1 TGA curves of pristine MWNTs and functionalized MWNTs

An increase in the mass loss of the samples subjected to TGA was observed because of the degradation of the functional groups bonded to the MWNTs surface as shown in Table 1, though the value for MWNT-EDA is lower than that for the oxidized MWNTs which means that the oxygenated functional groups influence also the nanotubes degradation.

Table 1

Mass loss values and degradation temperatures for MWNT samples

CNTs type	Mass loss, % (50÷600 °C)	T_d, °C
MWNT	9.9	554.5
MWNT-COOH	12.9	395.1
MWNT-EDA	11.1	172.8
		538.1

3.2. FT-IR measurements

The FT-IR spectroscopy is a very useful tool to show the presence of functional groups on the MWNTs surface, the bands assigned to C-H stretching symmetric and asymmetric vibrations at 2860-2920 cm^{-1} of the EDA chains can be noticed (Fig.2). In the figure 2 it can be also seen the appearance of the amide bands at 1576 cm^{-1} and 1459 cm^{-1}.

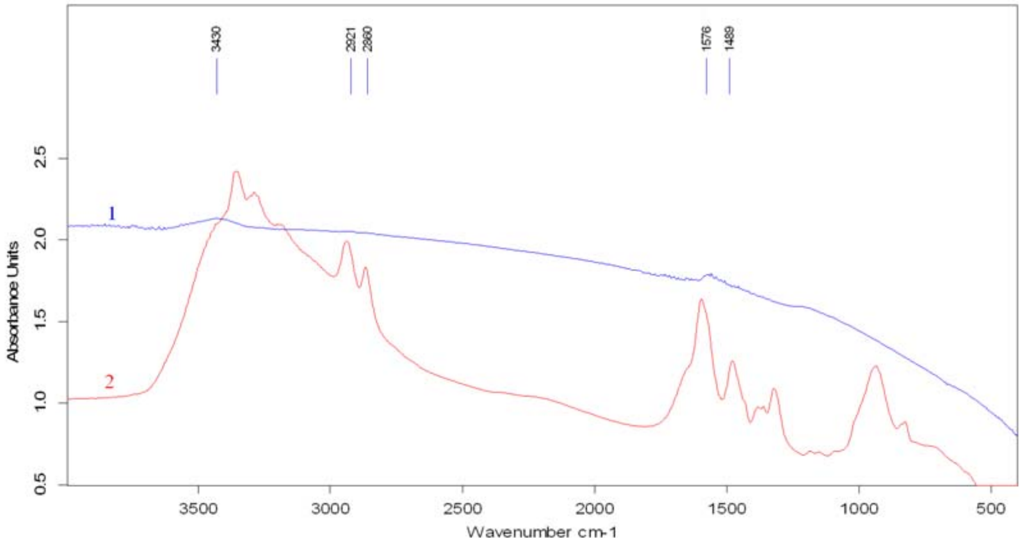


Fig 2 FT-IR spectra for MWNT-EDA (1) and EDA (2)

3.3. Raman spectroscopy

The disorder D band in MWCNTs is observed when the symmetry of hexagonal lattice is disrupted due to, for example, covalent side-wall functionalization. The G mode at ~ 1588 cm-1 represents the tangential vibration mode of the graphitic structure of the nanotubes [16]. As shown in the spectra from Figure 3, the form of these bands does not modify during functionalization, which means that the global structure of the graphene sheet does not suffer major damages during functionalization treatments. Still the ratio between the intensities of these two characteristic bands is a quantification of the functional groups introduction, by measuring the sp^3 carbon atoms introduced.

The Raman data from Table 2 show an increase of the I_D/I_G ratio value as the functionalization by oxidation and then amidation occurs. This tendency is maintained also for the shifting of the D and G bands positions.

Table 2

Raman data for the characteristic peaks of MWNTs

CNTs type	I_D	X_D , cm^{-1}	I_G	X_G , cm^{-1}	I_D/I_G
MWNT	56.9	1324.8	34.0	1576.4	1.6
MWNT-COOH	20.3	1327.3	11.7	1577.0	1.7
MWNT-EDA	9.3	1331.0	5.3	1585.5	1.8

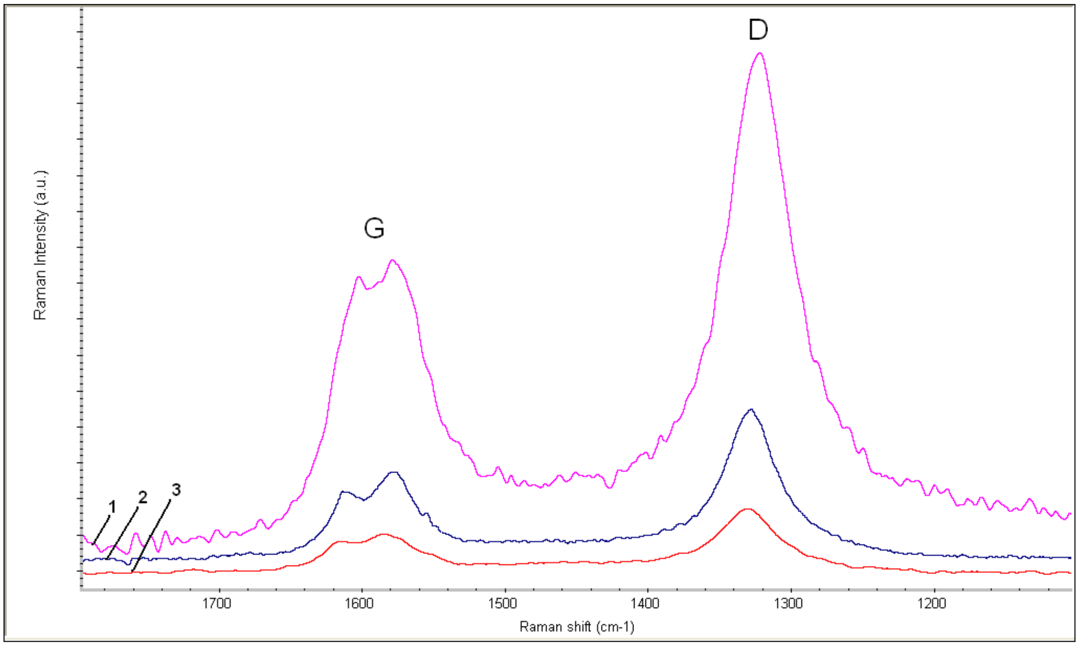


Fig. 3 Characteristic bands of Raman spectra for 1) MWNT; 2) MWNT-COOH and 3) MWNT-EDA

3.4. Composite characterization

TGA indicates a structural modification of the epoxy system when the reinforcing agents have compatible functional groups.

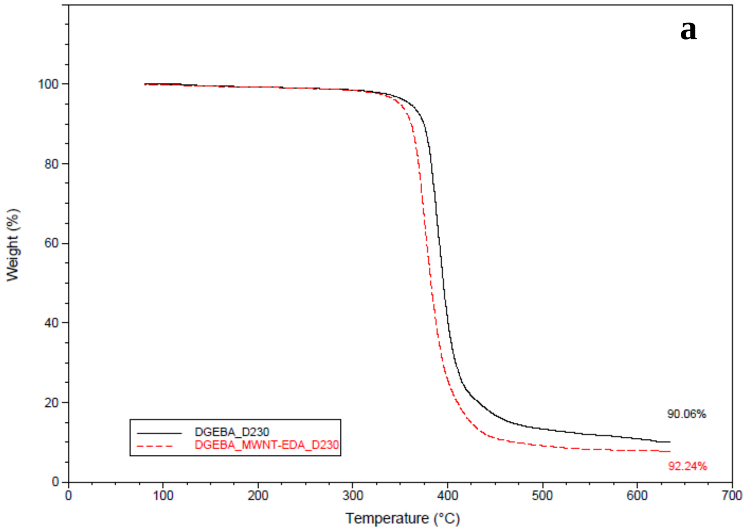


Fig. 4.a) TGA curves for the cured epoxy resin and the resin reinforced with MWNT-EDA

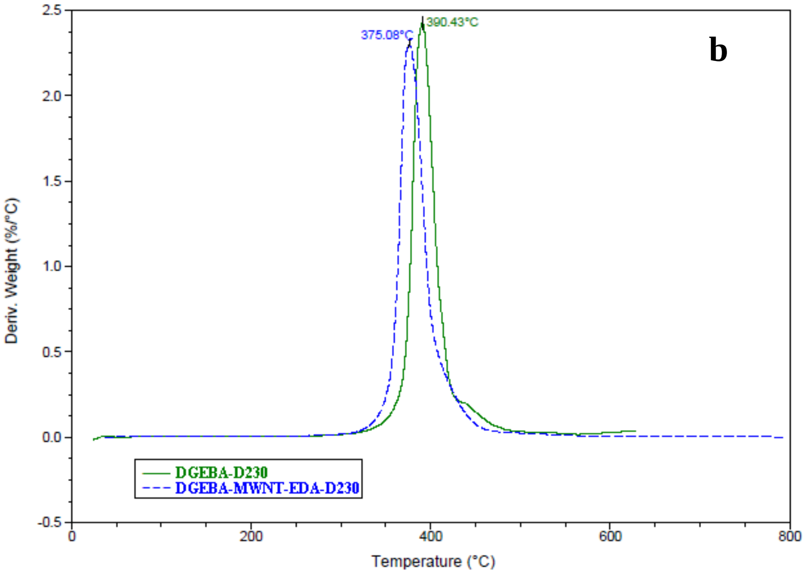


Fig. 4.b). DTG curves for the cured epoxy resin and the resin reinforced with MWNT-EDA

Figure 4 show the TGA (a) and DTG (b) curves for the neat resin and MWNT-EDA reinforced nanocomposite.

The carbon nanotubes influence the thermal degradation profile, particularly the temperature at which the degradation rate is maximum, which is lower for DGEBA/MWNT-EDA/D230 than for DGEBA/D230. This is probably due to the lower crosslinking degree obtained in the presence of MWNTs.

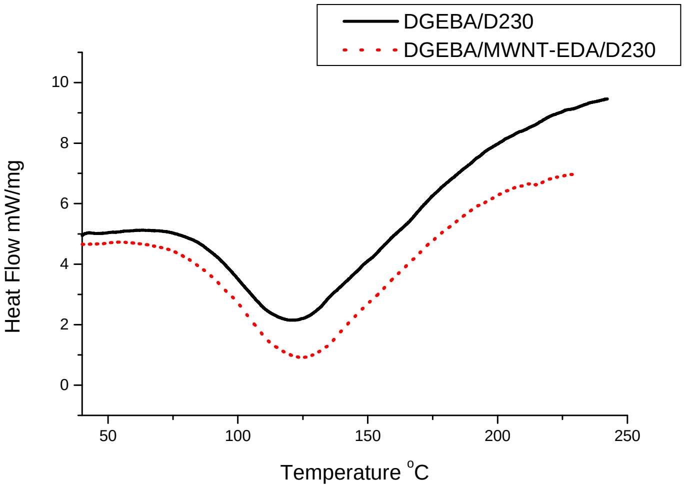


Fig. 5 DSC cure reaction curves for neat resin and epoxy reinforced with MWNT-EDA

Differential scanning calorimetry curves show an exothermic peak representing the cure process of the DGEBA with D230. Compared with the cured resin, the nanocomposite sample reinforced with MWNT-EDA shows a slight shift of the cure temperature from 120°C to 126°C, meaning that the presence of MWNT-EDA induces a lower reactivity in the crosslinking process.

A typical response from a DMA test shows both modulus and Tan δ. for the thermoset resins. The figure 6 a, b shows the dependencies of the storage modulus and the loss factor tan δ for the epoxy/MWNT-EDA nanocomposites. The value of *Tg* for DGEBA/MWNT-EDA/D230 is slightly lower (79.9 ºC) than for DGEBA/D230 which is probably due to the agglomerations formed by MWNT-EDA and thus the access of D230 to the molecules of epoxy resin DGEBA is hindered, which results in a lower degree of crosslinking and as a consequence a lower *Tg* value. This result is in good agreement with the DSC and TGA data.

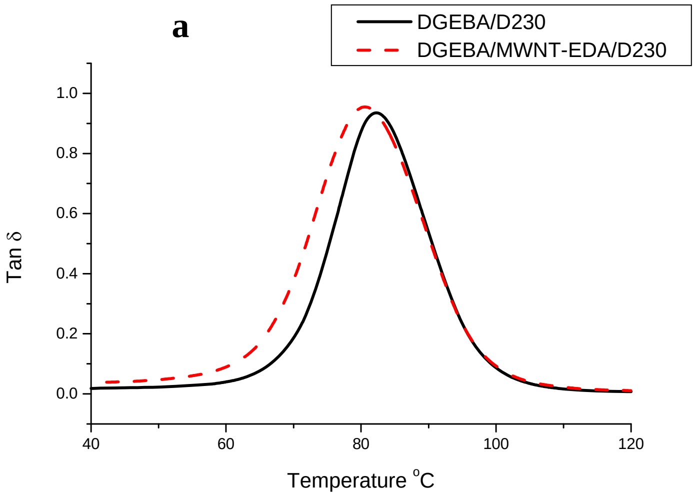


Fig. 6.a) DMA curves of Tan δ for cured epoxy resin and the sample reinforced with MWNT-EDA (at 1 Hz frequency)

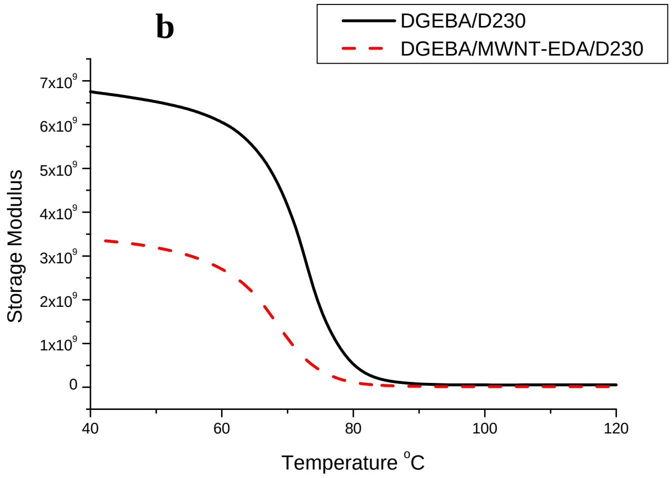


Fig. 6.b) DMA curves of Storage modulus for cured epoxy resin and the sample reinforced with MWNT-EDA (at 1 Hz frequency)

The surface morphology of DGEBA/MWNT-EDA/D230 was studied by SEM (Fig. 7). It is clearly observed that the amine functionalized MWNTs are quite uniformly dispersed in the polymer matrix due to the good compatibility between the two components. The few bright sticks observed in the figure are considered to be the broken ends of MWNTs pulled out from the matrix during fracture process, suggesting that not all the nanotubes are functionalized.

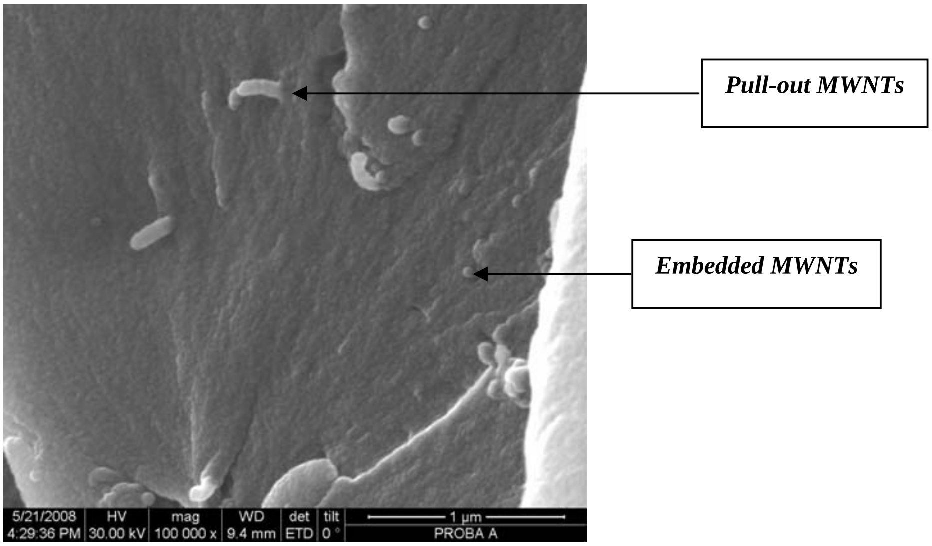


Fig. 7 SEM image of DGEBA/MWNT-EDA/D230

But most of the functionalized MWNTs are embedded into the epoxy resin, this being a strong evidence for the covalent bonding of MWNTs with the polymer matrix. The results demonstrate that, both the covalent bonds and the homogeneous dispersion play an important role in the improvement of thermal and mechanical properties.

4. Conclusions

Ethylenediamine groups were attached to MWNTs surface by chemical functionalization. Their presence was proved using TGA, FT-IR and Raman spectroscopy. Epoxy composites were obtained using the new functionalized MWNTs as reinforcing agents. The curing temperature, observed on DSC curve, increases in the presence of functionalized MWNTs, which means that a lower reactivity is obtained for DGEBA against D230 when MWNTs are added.

SEM images show the dispersion of the MWNT-EDA in the matrix and show the presence of the chemical bonding between MWNT-EDA and the epoxy matrix.

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