

The Influence of Different Types of Carbon Nanotubes on the Synthesis and Properties of Epoxy-based Nanocomposite Materials

CELINA-MARIA PETREA*, SORINA ALEXANDRA GÂREA, HORIA IOVU

Politehnica University of Bucharest, Department of Polymer Science and Technology, 149 Calea Victoriei, 010072, Bucharest, Romania

The incorporation of functionalized carbon nanotubes in a polymer matrix is expected to greatly enhance the physical and mechanical properties of the polymer due to inherent superior properties of carbon nanotubes (CNTs): high modulus and strength, high thermal stability and enhanced electrical conductivity. Nanocomposite materials based on epoxy polymer matrix and different types of functionalized carbon nanotubes were synthesized. The effect of CNTs on dynamic mechanical properties by DMA, on curing process by DSC and thermostability by TGA and DTG were studied. The system based on diglycidylether of bisphenol A (DGEBA) cured with a polyetheramine (D230) and reinforced with amino-functionalized double-wall carbon nanotubes (DWNT-NH₂) showed lower T_g values. SEM images reveal an enhance of dispersion if amino-functionalized CNTs are used.

Keywords: epoxy, nanotubes, nanocomposites, thermostability, glass transition temperature

Since their discovery in 1991 by Iijima, CNTs are intensively studied all over the world, because of their unique electronic, molecular and structural properties [1-3]. CNTs are nearly unidimensional, having the length (L) of few microns and the diameter (D) of few nanometer with a very high aspect ratio (sometimes over 1000). Due to these properties CNTs are studied for applications in hydrogen storage, Li intercalation, transistors, nanopores, nanosensors, but most of all they are used as reinforcing agent for nanocomposites synthesis with enhanced electrical and thermal properties [4-5]. The high axial electrical conductivity offers the potential for manufacturing conducting polymers. Thus CNTs could replace conventional conductive fillers for a range of applications like electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding [6].

CNTs are known as low reactivity materials, but however they form van der Waals interactions giving aggregates named bundles [7].

A number of researchers developed techniques to improve the dispersion of CNTs in epoxy polymers including ultrasonication, addition of surfactants and functionalization. The functional groups obtained after functionalization make possible a nanosized dispersion of CNTs in the polymer matrix [8].

Functionalized CNTs seem to solve two of the main problems in synthesis of nanocomposite materials from CNTs and epoxy resin matrix: 1) functional groups can prevent the aggregation of CNTs; 2) the attached functional groups can be used for subsequent links with epoxy groups from the matrix in order to improve the mechanical strength of nanocomposites [9-12].

Several synthesis methods are available for obtaining CNTs/polymer nanocomposites. All the techniques require to break the bundles and the aggregates, a better dispersion and obtaining a good interfacial bonding between the polymer matrix and the surface of CNTs. The effective use of CNTs in composite applications strongly depends on the ability to individually and uniformly disperse the CNTs within the polymer matrix without destroying their integrity or reducing their aspect ratio. The final architecture of the nanocomposite will determine its physical properties [13].

Melt mixing, *in-situ* polymerization and solution processing are the main methods in nanocomposite synthesis. However new techniques such as deposition using layer-by-layer assembly have been also successfully applied. Melt mixing of CNTs into thermoset polymers such as epoxy resins, is desirable because of the simplicity, solvent-free and absence of contaminants, which are regularly present in solution processing methods and *in-situ* polymerization. Another advantage of melt mixing is that the high L/D ratio of CNTs is kept constant [4,7,8,14].

The embedding of CNTs into polymer matrices giving nanocomposite materials, will also determine an increase of the mechanical properties such as the elastic modulus [15-19].

The aim of our study was to obtain nanocomposite materials with improved interfacial bonding based on epoxy resin as polymer matrix and functionalized CNTs as reinforcing agent.

Experimental part

Materials

The epoxy resin (DGEBA) was supplied by Dow-Chemical, with a low concentration of oligomers. The curing agent was a polyetheramine (Jeffamine D230) provided by Huntsman with a low amine index IA=60g/eq. These reactants were used as received.

Row CNTs were supplied by Sigma-Aldrich, one part of them being modified by oxidation with a (3:1 v/v) mixture of H₂SO₄ (98%) and HNO₃ (63%) at 60°C for 4 h, in our laboratory to obtain carboxylic functional groups on the surface, according to [15]. The other part was used as received.

Amino functionalized double-wall carbon nanotubes (DWNT-NH₂) were provided by Sigma-Aldrich.

The typical molecular structures of diglycidyl ether of bisphenol A (DGEBA) and the polyetheramine (D230) used, are shown in figure 1.

Synthesis of nanocomposites

The synthesis of polymer nanocomposites was done by melt mixing of DGEBA with different types of CNTs (1% wt.). Three nanocomposite types were obtained with

* email: petrea_celina@yahoo.com; Tel.: (+40) 0214022710

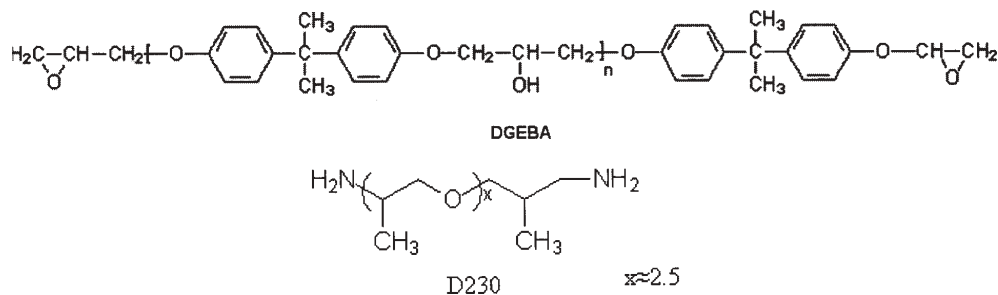


Fig. 1. Molecular structures of the epoxy resin and polyetheramine

unmodified CNTs (DGEBA/MWNT), oxidized CNTs having carboxylic functional groups (DGEBA/MWNT-COOH), amino functionalized CNTs (DGEBA/DWNT-NH₂). The reference was DGEBA without any CNTs.

The polymer matrix was heated at 50°C to diminish its viscosity. An appropriate amount of CNTs was added to epoxy, then the mixture was stirred and sonicated for 1 h to ensure good homogeneity. The calculated weight (7%) of hardener (D230) was added after cooling at room temperature, then the mixture was stirred and cast into a mold. The crosslinking process occurred at 60°C for 3 h followed by a heating sequence at 100°C for 30 min.

Characterization and measurements

FTIR measurements were performed on a SHIMADZU 8900 equipment. The FTIR spectra were recorded in 400 ÷ 4000 cm⁻¹ range with 4 cm⁻¹ resolution. The samples were analyzed from KBr pellets.

Thermogravimetical analysis (TGA) was done on a TA Instruments Q500 equipment, using nitrogen atmosphere from room temperature to 600°C with a rate of 10°C/min.

Differential scanning calorimetry (DSC) tests were done on a LINSEIS Pt 10 equipment using a rate of 10°C/min, from room temperature to 200°C.

Dynamic mechanical analysis (DMA) tests were carried out on a TRITEC 2000 B instrument. Samples were analyzed in bending mode in the range of temperature 25-200°C using a heating rate of 5°C/min.

Scanning electron microscopy (SEM) images of the nanocomposites samples surface were acquired using a HITACHI S 2600 equipment.

Results and discussion

The influence of CNTs type used as reinforcing agent on glass transition temperature (T_g) of nanocomposites was studied using DMA. Samples were analyzed at four frequencies: 0.316 Hz, 1 Hz, 3.16 Hz and 10 Hz. (fig.2-5). The T_g values of samples containing unmodified CNTs and MWNT-COOH are almost the same with the reference regardless of frequency. Therefore it may conclude that these types of CNTs do not exhibit any influence on T_g value of the nanocomposite. The samples with amino-functionalized nanotubes show lower values of T_g comparing to the other systems (table.1). A first explanation may be the modification of the tridimensional structure of the crosslinked epoxy resin due to the homopolymerization process catalyzed by the amino groups from the CNTs surface. In addition the ratio between curing agent and the epoxy resin is modified due to the homopolymerization/crosslinking process induced by the amino groups from the CNTs surface, not all epoxy functional groups from the resin being available for crosslinking reaction with the curing agent. Thus the unreacted quantity of polyetheramine (D230) acts as a plasticizer, leading to the T_g decrease.

In order to validate this assumption it is necessary to perform studies about the influence of CNTs type used as reinforcing agent on the crosslinking process of the epoxy resin matrix of nanocomposite samples using non-isothermal DSC method.

A second explanation takes into account the thermal degradation of C-N bonds formed between the epoxy groups and the amino groups from the functionalized CNTs surface. These bonds are the most unstable from the system.

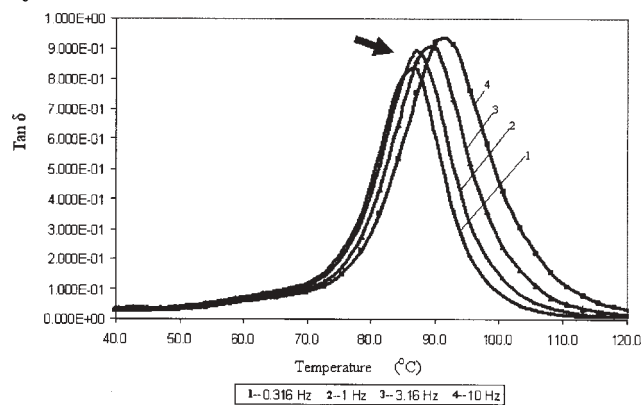


Fig. 2. The dependence of $\tan \delta$ against temperature for DGEBA / D230 system (reference) at different frequencies. [D230] = 7%wt

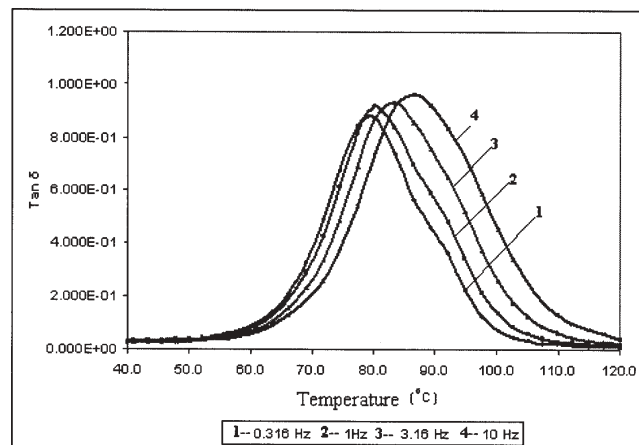


Fig. 3. The dependence of $\tan \delta$ against temperature for DGEBA / DWNT-NH₂ / D230 system at different frequencies. [D230] = 7%wt

To verify the first hypothesis which explains lower T_g value for the DGEBA/DWNT-NH₂/D230 system, non-isothermal DSC measurements were done onto three samples: reference, nanocomposite reinforced with DWNT-NH₂ and MWNT-COOH respectively (fig. 6). Because the unmodified CNTs exhibit no influence on the curing process, this was not analyzed by DSC.

From figure 6 it may be observed that the peaks are similar for all epoxy-based systems which means that the functional groups from CNTs exhibit no catalytic effect on

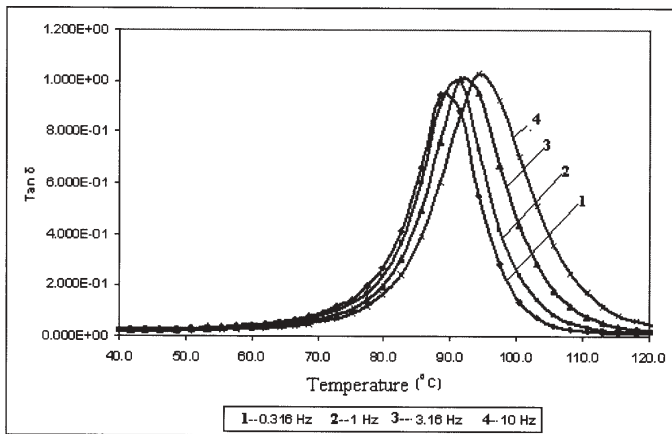


Fig. 4. The dependence of $\tan\delta$ against temperature for DGEBA / MWNT-COOH/D230 system at different frequencies. [D230] = 7% wt

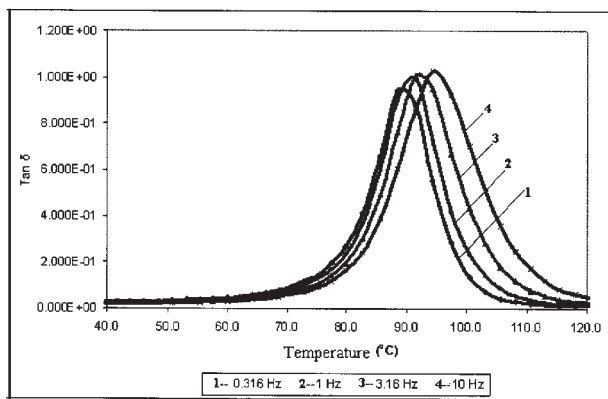


Fig. 5. The dependence of $\tan\delta$ against temperature for DGEBA / DWNT-MWNT / D230 system at different frequencies. [D230] = 7%wt

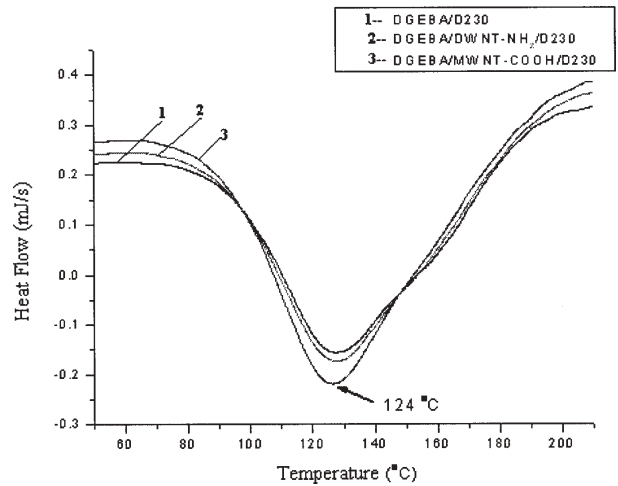


Fig. 6. The DSC curves for different epoxy-based nanocomposites

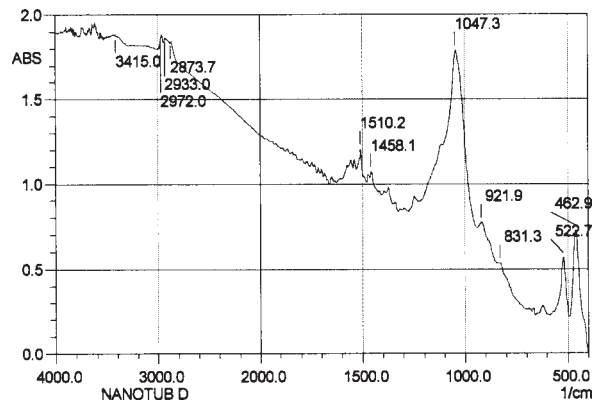


Fig. 7. FT-IR spectrum of DWNT-NH₂ in KBr pellet

Table 1
THE T_g VALUES FOR DIFFERENT NANOCOMPOSITES
BASED ON DGEBA REINFORCED WITH CNTs

System	Frequency (Hz)	Glass transition temperature (T _g) (°C)
DGEBA/D230	0,316	86
	1	87
	3,16	90
	10	93
DGEBA/DWNT-NH ₂ /D230	0,316	79
	1	80
	3,16	83
	10	87
DGEBA/MWNT/D230	0,316	86
	1	90
	3,16	91
	10	94
DGEBA/MWNT-COOH/D230	0,316	86
	1	90
	3,16	91
	10	94

curing process of the epoxy matrix. This is probably due to a low concentration of functional groups on the surface of CNTs. This fact was proved by FT-IR spectrum of DWNT-NH₂ (fig. 7)

From figure 7 one may notice the following bands: 1047 cm⁻¹ assigned to stretching vibration of C-H bond (ν_{C-H});

1458 cm⁻¹ assigned to the bending vibration (δ_{CH_2}) aliphatic or aromatic; 1510 cm⁻¹ assigned to the stretching vibration of aromatic ring (ν_{C-H}). The 2873 cm⁻¹ peak corresponds to symmetric stretching vibration bond of CH₃ (ν_{CH_3}); 2933 cm⁻¹ was assigned to asymmetric stretching vibration of CH₂ (ν_{CH_2}); 2972 cm⁻¹ band assigned to asymmetric stretching vibration of CH₃ (ν_{CH_3}); 3415 cm⁻¹ band assigned to the stretching vibration of N-H bond (ν_{N-H}). The peak corresponding to amino functional groups from 3415 cm⁻¹ exhibits a low intensity showing that the concentration of these groups is low.

The lack of catalytic effect of the functional groups from CNTs, points out that the first explanation regarding the decrease of T_g values is not valid. Therefore the shifting of T_g to lower values can not be explained by the modification of the tridimensional structure of the epoxy resin formed through homopolymerization /crosslinking.

In order to check the second explanation, the thermostability of samples was studied using thermogravimetric analysis (fig. 8).

The influence of different types of CNTs on nanocomposite thermostability was investigated using derivative thermogravimetric peaks from TGA analysis. As shown in figure 8, peaks for DGEBA/MWNT-COOH/D230 and DGEBA/MWNT/D230 systems are almost similar with the reference, meaning that unmodified MWNT and MWNT-COOH do not influence the thermostability of these systems. The shifting of the peak to lower values of degradation temperatures is typical for DGEBA/DWNT-NH₂/D230, due to new C-N bond which are weak and they will break first. These analysis confirm our second explanation and shows that between amino-functionalized CNTs and the epoxy matrix a good compatibility was obtained

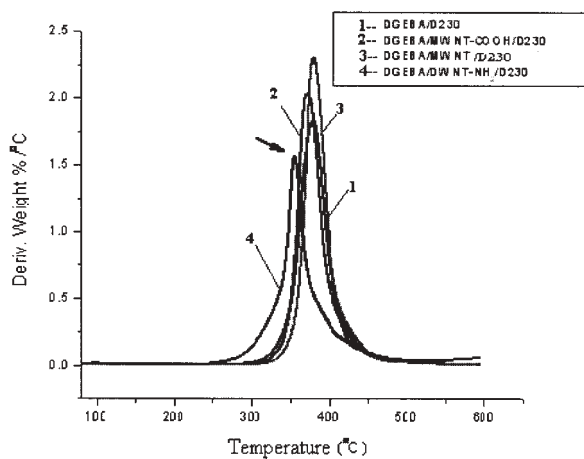


Fig. 8. The DTG curves for different nanocomposites based on DGEBA reinforced with CNTs

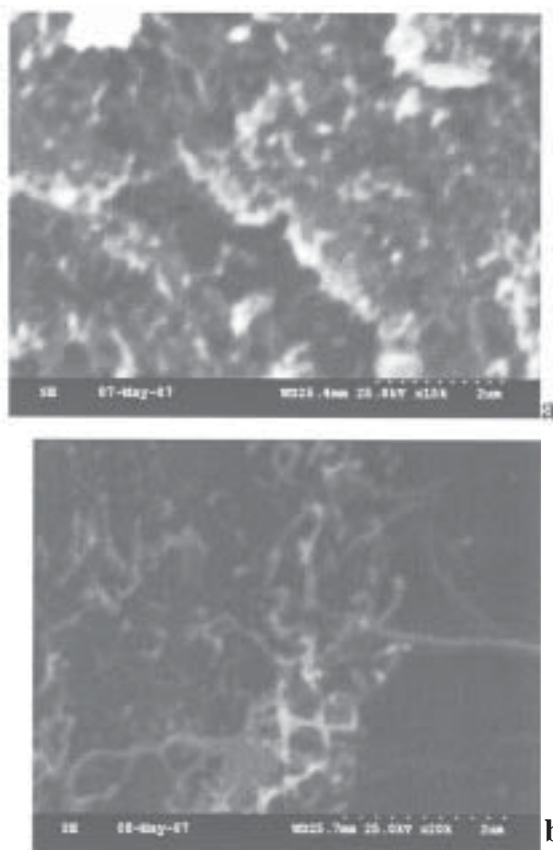


Fig. 9. SEM images of DGEBA / MWNT / D230 (a) and DGEBA / DWNT - NH₂ / D230 (b)

through chemical bonding between NH₂ functional groups and the epoxy groups from the resin.

The SEM images for the DGEBA/MWNT/D230 sample (fig.9 a) shows that the CNTs were still aggregated (the white zones) though the distribution of MWNTs is relatively homogeneous, the compatibility between MWNTs and epoxy resin being poor.

In the case of DGEBA/MWNT-COOH/D230 system, the SEM image shows that DWNT-NH₂ exhibit a good dispersion without aggregation (fig.9 b). This is due to the good compatibility between the epoxy matrix and the reinforcing agent, the amino groups prevent aggregation and allow chemical bonding with the polymer.

Conclusion

Three types of nanocomposites were obtained from DGEBA matrix, with MWNT, DWNT-NH₂, MWNT-COOH and using polyetheramine (Jeffamine D230) as a curing agent. Samples were analyzed using DMA, DSC, TGA and SEM. It

was shown that nanocomposites with amino functionalized CNTs exhibit a lower T_g value compared with the other systems due to the lability of the new C-N bonds formed. Amino functionalization leads to a better dispersion in the polymer matrix as shown in SEM images.

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