Advanced Characterization of Modified Carbon Nanotubes Epoxy-based Composites

CELINA-MARIA PETREA*, CORINA ANDRONESCU, ANDREEA MĂDĂLINA PANDELE, SORINA ALEXANDRA GÂREA, HORIA IOVU
University Politehnica of Bucharest, Department of Polymer Science and Technology, 149 Calea Victoriei, 010072,
Bucharest, Romania

Epoxy-based composites with modified carbon nanotubes (CNTs) were synthesized using different types of CNTs. These were first modified by amidation of the carboxylic groups from the CNT's surface and then embedded into the epoxy matrix. The modified CNTs and the corresponding composites were analyzed by FTIR, TGA, DMA and Raman Spectroscopy. The influences of CNT type and the nature of the organic modifier were pointed out in connection with the composites structure.

Keywords: functionalization, carbon nanotubes, polymer nanocomposites, thermostability, Raman Spectroscopy

Carbon nanotubes were discovered in 1991 [1], and due to their unique properties they have been investigated by many researchers [2]. CNTs exhibit an unique structure, with a large length and a small diameter, so they can be considered as nearly one dimensional structure. They show high electrical conductivity [3], high modulus, high mechanical strength and chemical stability. The low reactivity of CNTs is the reason for the low solubility and the low compatibility in composite materials. To improve the dispersion of the CNTs it is required to functionalize them in order to obtain a uniform dispersion in the final composite material. The functionalization may be achieved by chemical bonding of the modifying agent on the surface of the CNTs or by an ionic bonding between the CNTs and the modifying agent. Even if the chemical bonding is stronger that the ionic bonding, the chemical functionalization may disturb the bonding of the graphene sheet, so the mechanical properties of the functionalized CNTs in the final composite may be reduced [4].

An improvement of the dispersion of CNT in polymer matrices may be achieved by amidation [5] of the carboxyilic groups, obtained on the surface of CNT by the oxidation methode [6, 7]. In order to obtain amidic groups on the CNT's surface there are two different routes: either by using thionyl chloride and then reacting with an amine or by using dicyclohexylcarbodiimide (DCC) as a catalyst for the direct reaction between the carboxylic groups and the amine [5, 8].

Our purpose was first to modify the carboxylic group already existed on the surface of different types of CNT into amidic group by using different amines, and then, with this new modified CNT to achieve different nanocomposites based on epoxy resin matrix. Also we performed DMA, TGA, FTIR analyses in order to achieve an advanced characterization of the nanocomposites and therefore to explain the influence of CNT and organic modifier type on the final composite properties. The nanocomposites structure was revealed by Raman Spectroscopy which gives the required information regarding the CNT content within the composites.

Experimental part

Materials

Carboxylated Single Wall Nanotubes (SWNT-COOH) and Multi Wall Nanotubes (MWNT-COOH), ethylenediamine (EDA), octadecylamine (ODA), chloride thionyl($SOCl_2$) and tetrahydrofurane (THF) were supplied by Sigma Aldrich.

Surfonamine B100 used as organic radical modifier for functionalization and the curing agent, a polyetheramine (Jeffamine D230) were provided by Huntsmann Corporation.

The epoxy resin diglycidyl ether of bisphenol A (DGEBA) was purchased from Dow Chemical.

All the materials were used without any purification.

The chemical structures for the organic modifiers, the polymer matrix and the crosslinking agent are shown in scheme1.

CNTs functionalization

In order to obtain amide groups on CNT's surface, the first step was to modify the carboxylic groups through acylation with thionyl chloride at 65 °C for 24 h under stirring and purified by washing on teflon membrane (d=0.2μm) several times with THF. In the second step, the organic modifiers (EDA, B100) were added in excess to react with acyl-chlorinated CNTs at room temperature for 48 h. In case of ODA the reaction was carried out at 55°C also for 48 h. The same purification method was applied after each step. The resulted products are functionalized CNTs for example SWNT-EDA. The reaction steps are presented in scheme 2.

Composites sythesis

The synthesis of polymer nanocomposites was done by melt mixing of DGEBA with the modified CNTs (0.3% wt.). As reinforcing agent SWNT-EDA, SWNT-ODA, SWNT-B100, MWNT-EDA, MWNT-ODA and MWNT-B100 were used. The reference was DGEBA without any CNTs.

The polymer matrix was heated at 50°C to diminish its viscosity. The calculated amount of CNTs (0.3%) was added to epoxy, then the mixture was stirred and sonicated for 1 h to ensure good homogenity. The curring agent (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 process at 100°C for 1.5 h for postcuring.

Advanced characterization

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.

Thermogravimetrical analysis (TGA) was done on a Q500 TA Instruments equipment, using nitrogen

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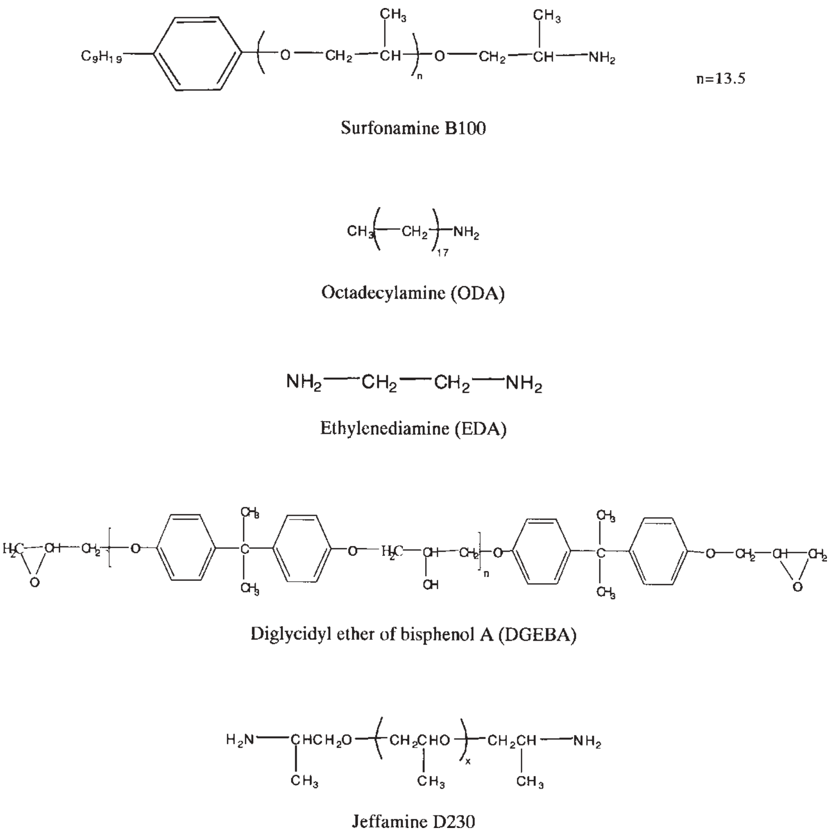
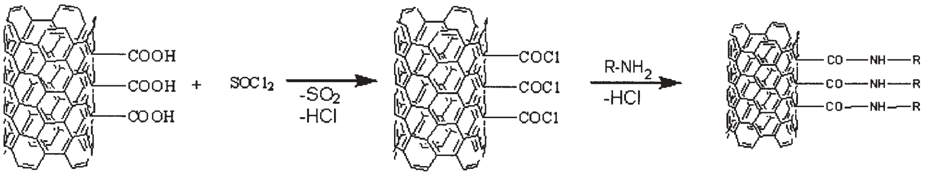
* email: petrea_celina@yahoo.com



Scheme 1. Chemical structures of organic modifiers, DGEBA and Jeffamine D230



Scheme 2. Modifying reactions of carboxylic groups

atmosphere from room temperature to 800°C using a heating rate of 10°C/min.

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 25-180°C using a heating rate of 5°C/min.

Raman spectra were registered on a DXR Raman Microscope from Thermo Scientific using a 532 nm laser line and a number of 50 scans. The laser beam was focused with the 10x objective of the Raman microscope.

Results and discusion

FTIR Analysis

From figure 1 it can be seen that the spectrum of MWCNT functionalized with B100 exhibits two peaks in the 2800-2900 cm^{-1} region, which may be assigned to the vibration of C-H bonds from the organic radicals bonded on the nanotubes surface. This is a good proof that the functionalization occurs with the formation of MWCNT-B100 compound.

TG Analysis

The thermostability of the functionalized CNTs and the corresponding nanocomposites is estimated from TG analysis. One may notice from table 1 and figure 2 that DTG curve of the reference (unmodified MWNT) exhibits only one maximum at 637°C which was assigned to degradation of the C-C bonds from the nanotubes structure. All the other systems with functionalized CNTs exhibit two peaks in DTG, the first one being assigned to the degradation of the organic modifier and the second one to the CNT's degradation. The ratio between these two peaks is strongly influenced by the nature of the organic modifier.

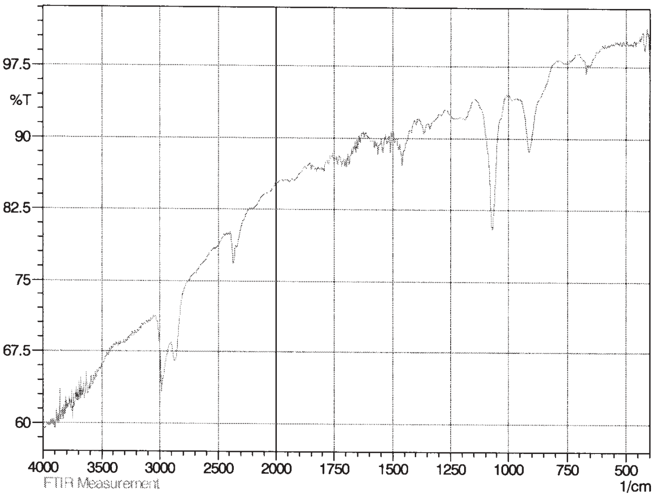


Fig. 1. FTIR spectrum of MWNT functionalized with B100

Thus in the case of SWNT-B100 (fig. 3. a) the first peak is predominant which means that the conversion of carboxylic groups modified with B100 is very high and therefore the quantity of B100 included into the functionalized SWNT-B100 is increased. The same result was obtained for MWNT-B100 (fig. 3. b).

Despite of these systems, for all the other functionalized CNTs the second peak assigned to C-C degradation, is much higher than the first one. This may be a result of a

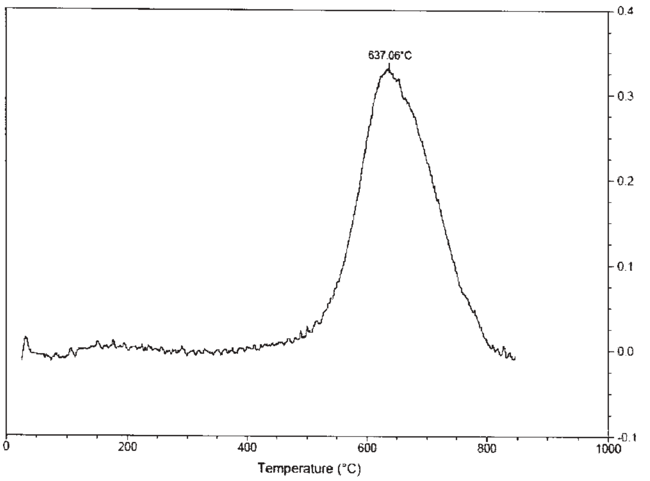


Fig. 2. DTG curve for the reference (MWNT)

Table 1

MAXIMUM TEMPERATURES FROM DTG ANALYSIS FOR FUNCTIONALIZED CNTs WITH DIFFERENT ORGANIC MODIFIERS

Carbon nanotubes	T_{max1}, °C	T_{max2}, °C
MWNT	-	637
MWNT-B100	266.6	582
MWNT-ODA	196.5	683
MWNT-EDA	216	660.7
SWNT-B100	286	693.8
SWNT-ODA	190.5	567.9
SWNT-EDA	240	603.2

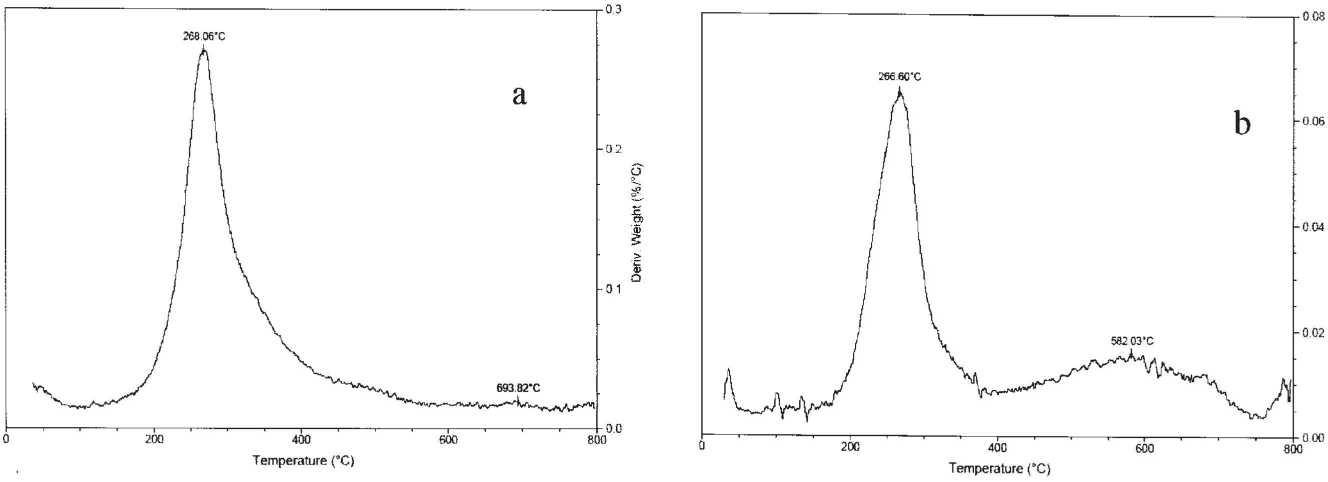


Fig. 3. DTG curves for : a) SWNT-B100 and b) MWNT-B100

lower conversion for the modification of CNT-COOH with organic modifiers (fig. 4.).

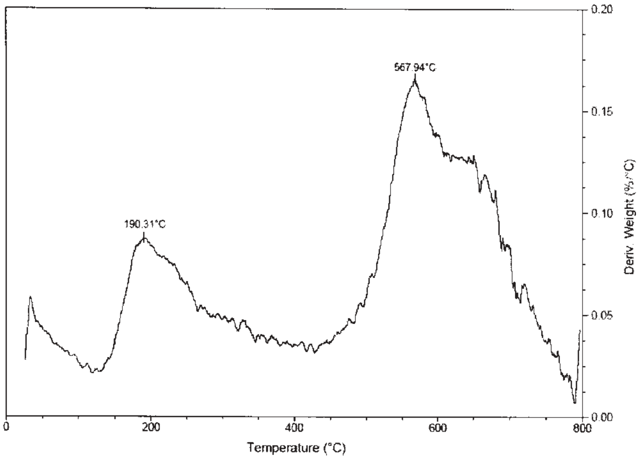


Fig. 4. The DTG curve for SWNT-ODA

The influence of the CNTs type against the mass loss in TGA may be observed from table 2. Thus the mass loss is higher for all the functionalized SWNT systems than for the MWNT systems as it was expected due to the ratio between the organic modifier and the mass of CNTs.

Table 2

MASS LOSS OF FUNCTIONALIZED CNTs WITH DIFFERENT ORGANIC MODIFIER

Carbon Nanotubes	*Mass loss, %*
MWNT-B100	11
MWNT-ODA	6.7
MWNT-EDA	28.6
SWNT-COOH	48.29
SWNT-B100	37.7
SWNT-ODA	50.3
SWNT-EDA	34.14

The TG and DTG analyses were done also for the composites based on DGEBA and functionalized CNTs. From table 3 it may be noticed that a single value for the temperature at which the mass loss rate is maximum is significant (374÷390°C), which is normal considering the very high weight ratio between the polymer matrix (DGEBA) and the reinforcing agent (functionalized CNTs) (fig. 5.).

Dynamic mechanical analysis (DMA)

To better understand the influence of CNTs embedded in the epoxy matrix on the thermal and mechanical properties, DMA analysis was performed. The glass transition temperature (Tg) was influenced both by the type of organic radical of the amine used for functionalization of CNTs and the type of CNTs (SWNT or MWNT).

Table 3
MASS LOSS AND MAXIMUM TEMPERATURES FROM TG AND DTG ANALYSIS FOR THE COMPOSITE SYSTEMS

Composite System	*Mass loss, %*	*T_{max}, °C*
DGEBA/D230	90	390.4
DGEBA/MWNT/D230	90.4	385.5
DGEBA/MWNT-B100/D230	92.7	376.5
DGEBA/MWNT-ODA/D230	90.2	374.1
DGEBA/MWNT-EDA/D230	92.8	375.1
DGEBA/SWNT-B100/D230	90.7	375.1
DGEBA/SWNT-ODA/D230	92.2	376.5
DGEBA/SWNT-EDA/D230	92.8	376.6

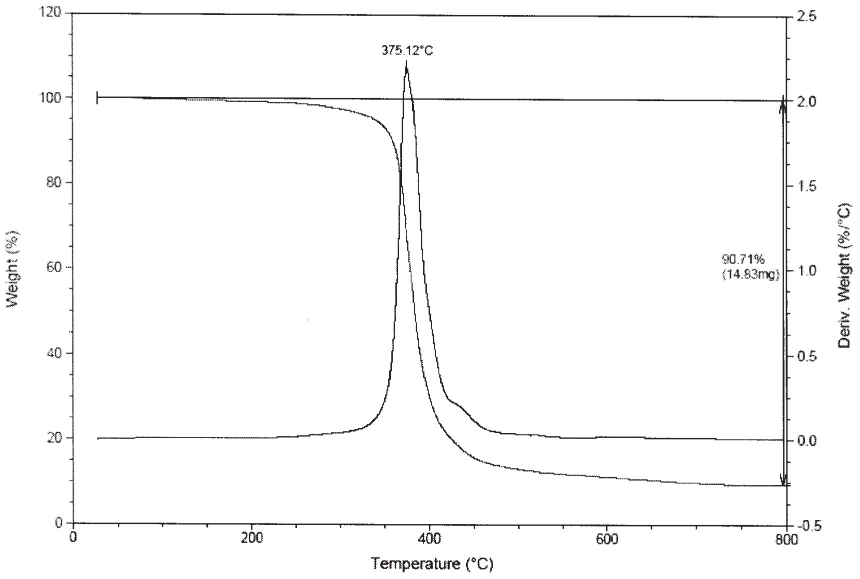


Fig. 5. TG and DTG curves for DGEBA/SWNT-B100/D230 system

Table 4
Tg VALUES FOR COMPOSITES BASED ON FUNCTIONALIZED CNTS FROM DMA (FREQUENCE=0.316 Hz); [CNTs]=0.3%

Composite System	*Temperature, °C*
DGEBA/D230	80.4
DGEBA/MWNT-B100/D230	80.8
DGEBA/MWNT-ODA/D230	76.3
DGEBA/MWNT-EDA/D230	79.7
DGEBA/SWNT-B100/D230	70.9
DGEBA/SWNT-ODA/D230	79.8
DGEBA/SWNT-EDA/D230	81.9

As one may see in table 4 the general behaviour is the decrease of Tg for the systems containing amino functionalized CNTs compared with reference (cured epoxy resin without any CNTs), but also an increase of Tg for ethylenediamine (EDA) functionalized SWNT system.

The reason may be the organic radical of EDA which is shorter than the other radicals and it includes amino functional group at the end, which reacts with the epoxy matrix making the composite structure more rigid, therefore it needs more energy to destroy the crosslinked structure. However if the functionalized CNTs are done with EDA based on MWNT, the Tg value shows a small decrease in comparison with the reference, which means that the CNTs type exhibits a significant influence on the thermo-mechanical properties (fig. 6.).

Therefore the systems based on functionalized MWNT usually exhibit lower Tg values than those based on SWNT regardless of the nature of organic modifier used for functionalization. Only in one case (SWNT-B100) the Tg exhibits a lower value probably due to the longer and

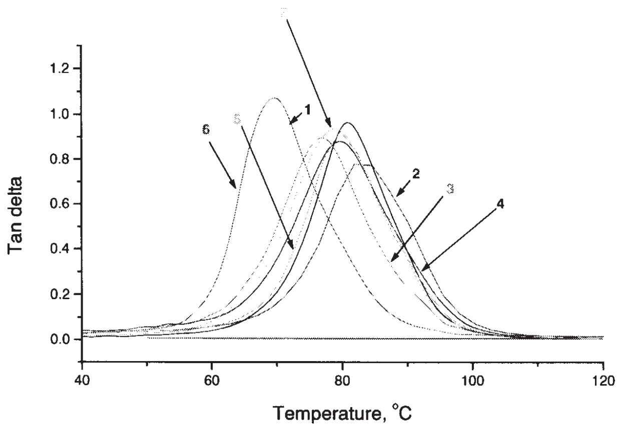


Fig. 6. DMA curves for composite systems :
1-Reference (DGEBA/D230);
2-DGEBA/SWNT-EDA/D230;3-DGEBA/MWNT-ODA/D230;
4-DGEBA/MWNT-B100/D230;
5-DGEBA/SWNT-ODA/D230; 6-DGEBA/SWNT-B100/D230;
7-DGEBA/MWNT-EDA/D230

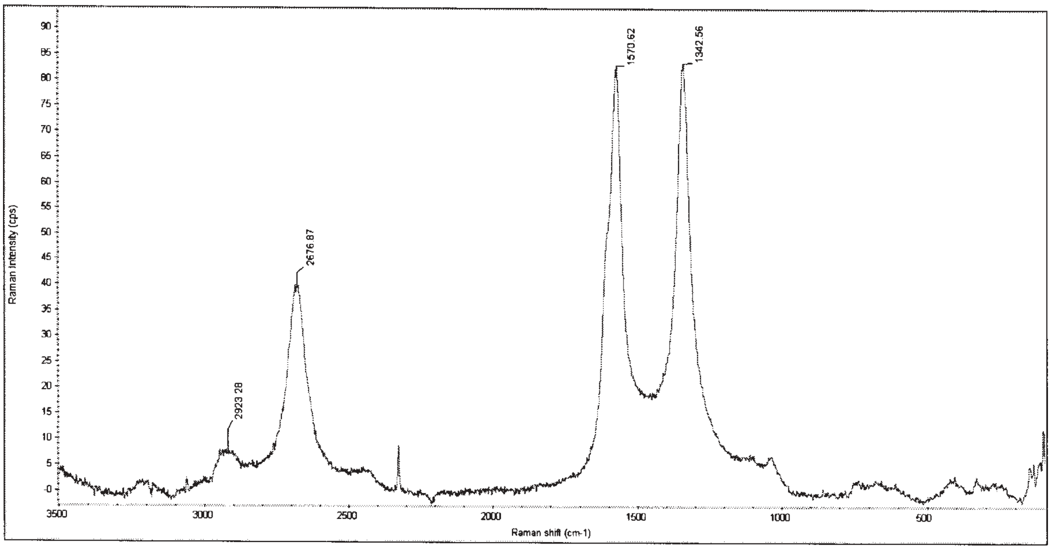


Fig. 7. Raman spectrum of MWNT-B100

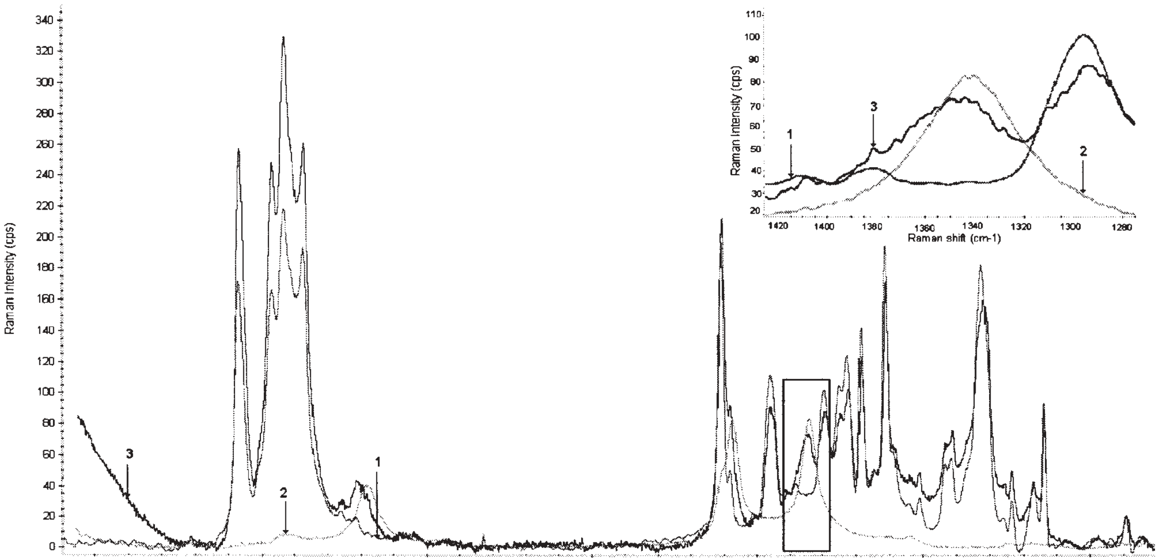


Fig. 8. Raman spectra of reference system (1), MWNT-B100 (2), and related composite (3)

flexible chain of B100 which leads to a less rigid nanocomposite.

Raman Spectroscopy

The functionalized CNTs and the coresponding composites were also analyzed by Raman Spectroscopy. For the modified MWNT with B100, besides the FTIR proof, the Raman spectrum (fig. 7.) shows also the presence of C-H bond by the signal at 2923 cm^{-1}. This spectrum gives also the main signals assigned to MWNT structure. Therefore the following characteristic bands occur: D band at 1342 cm^{-1}, G band at 1573 cm^{-1}, G' band at 2676 cm^{-1} (according to [9]). The normal RBM band does not occur in the spectrum of MWNT-B100 which is not unusual for MWNT [10]. By comparing the Raman spectra for MWNT-B100, the cured resin (DGEBA/D230) and the composite (DGEBA/MWNT-B100/D230) (fig. 8.), one may notice the presence of D band in the composite spectrum which gives the proof of the reinforcing agent within the composite. The G band is not detectable alone due to the superposition with a band from the resin. The ratio between the intensities of D band and G band may give information about the quality of the MWNT-B100 as reinforcing agent within the polymer matrix. Thus, due to the high intensity of D band one may conclude that the reinforcing agent exhibits a lot of stuctural deffects on the MWNT surface probably due to the initial step of MWNT oxidation to MWNT-COOH.

Conclusions

Carboxylated SWNT and MWNT were modified by functionalization with different types of amines (EDA, ODA, B100) in order to increase the compatibility with the polymer matrix (DGEBA) within the obtained nanocomposites.

The type of CNTs significantly influences the Tg value of the final nanocomposite and especially the nature of the organic modifier will cause variations in the Tg value and also important differences between the thermostability of the modified CNTs.

The best results were obtained for CNTs modified with B100 so that the obtained composite exhibits the highest Tg value.

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