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MECHANICAL PROPERTIES OF MULTIWALL CARBON NANOTUBE-EPOXY COMPOSITES

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Composites containing epoxy resin and functionalized multiwall carbon nanotubes with different mass concentrations were preparedby ultrasonic homogenization followed by curing at room temperature.Mechanical characterizations of composites reveal a general improvement of the flexural strength at tensile stress and Young’smodulus at low concentrations of nanotubes, the enhancement of mechanical properties compared to pure epoxy resin being observed for carbon nanotube concentrations up to 4 wt. %. The tensile strength at tensile stress decreases slowly with increasing the concentration of nanotubes. Numerical simulations of flexural behavior agree with experimental data for a lower-than-unity polymerization degree, the un-completed curing process hypothesisbeing also supported by electrical measurements.Electrical measurements reveala strong decrease of the resistivity of the composites with the MWCNT content with no reproducible values above room temperature in heating-cooling cycles.

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1. Introduction

Epoxy resins areknown for their good insulating and mechanical properties,resistance to most chemicals, as well as for their thermal stability[1]. The special characteristics of this thermosetting polymersthat form a three-dimensional network of covalent bonds, recommend epoxy resins as adhesives, coatings or polymer matrices for composites with applications rangingfromelectronics to automotive.Applications in avionicsare also envisaged due to the relative low weight of these materials [1].

The properties of epoxy resins, especially their electrical conductivity, could be enhanced by adding conductive fillers, such asmulti-walled carbon nanotubes (MWCNTs).MWCNT-epoxy composites can then be used as antistatic composites [2] or transparent electrodes [3].In many cases, the thermal and mechanical characteristicsof epoxy composites improve as well with the

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addition of MWCNTs [4], making them suitable asreinforcement materials.The improvement of mechanical properties by addition of MWCNTs is influenced by many factors such as the bonding strength between MWCNTs and the polymer matrix, the dispersion and alignment of nanotubes in composites, the nanotube dimensions, and so on [5].

In this paper,the influence of the mass content of functionalized MWCNTs (fMWCNTs) on the mechanical properties of MWCNT-epoxy composites is investigated, both experimentally and theoretically. These investigations are of particular interest for avionics, previous tests on carbon fiber reinforced epoxy matrices [6-7] suggesting that the polymer matrix determines mainly the mechanical properties of composites. The experimental value of mechanical parameters could be retrieved by numerical simulations only by assuming that the polymerization of the composite is not complete. This result, supported also by electrical measurements, suggests that the curing degree can be monitored by mechanical investigations.

2. Preparation and characterization of MWCNT-epoxy composites

The composites were produced by ultrasonic homogenization of the P401 epoxy resin, the I3361 hardener and different mass concentrations of fMWCNTs. After mixing, the composites were deposited for about 7 days in air, at room temperature.

The P401 resin is basedon the diglycidyl ether of bisphenol A (DGEBA)and I3361is a mixture of TETA ethyleneamines with close boiling points, both components being acquired from Policolor – Romania.The fMWCNTs, with lengths of 10-30 μm, inner diameters of 5-10 nm and outer diameters of 10-20 nm, were purchased from Chinese Academy of Sciences. The fMWCNTs areproduced by chemical vapor deposition andfunctionalized with–COOH (carboxyl groups) in order toenhance their dispersion within the epoxy matrix and to strengthen the interconnections with the resin [5].

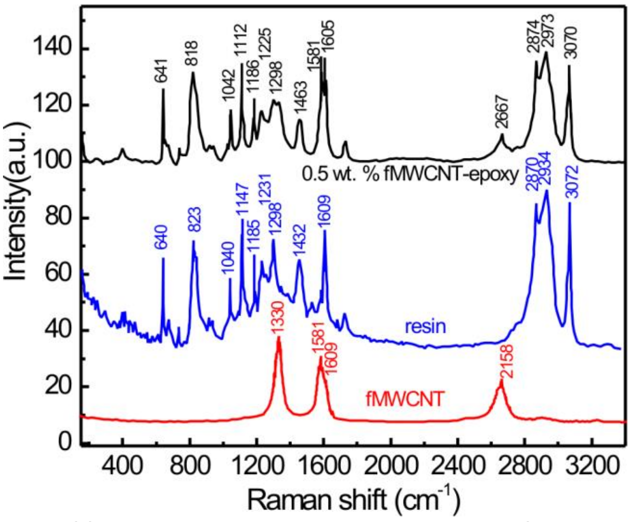


Fig. 1 Raman spectra of fMWCNT, epoxy resin and the 0.5 wt. % fMWCNT-epoxy composite.

The composites were characterized by Raman spectroscopy, at an excitation wavelength of 632.8 nm, the obtained spectra of fMWCNTs, epoxy resin and of the fMWCNT-epoxy composite with 0.5 wt. % fMWCNTs being presented in Fig. 1. The Raman spectrum of fMWCNT shows the characteristic D band at about 1330 cm^{-1}, G band at 1580 cm^{-1} and 2D band at about 2658 cm^{-1}, the presence of the –COOH groups being indicated by the peak at 1605 cm^{-1}. The large intensity ratio between the D and G bands suggests a large number of defects introduced during the functionalization process [8-9]. The radial breathing mode (RBM) associated to radial vibrations of C atoms and positioned in the low-frequency range of the Raman spectrum(generally, below 250 cm^{-1}), is not observable because of the large diameters of fMWCNTs [10]. In the 0.5

wt. % fMWCNT-epoxy composite, the presence of fMWCNTs is indicated by the peaks at 1331 cm^{-1}, 1581 cm^{-1} and 2667 cm^{-1}, the shift in the peak positions of some lines compared to fMWCNTs or epoxy resin (especially the 2D band) suggesting a strong interaction between the constituents of the composite material. The assignment of the Raman peaks in all samples is given in Table 1.

Table 1.Assignment of Ramanpeaks for fMWCNT, epoxy resin and the composite with 0.5 wt. % fMWCNT (ν – stretch; α – in plane; γ – out of plane bend; δ – deformation; W – wagging)

fMWCNT	Epoxy resin	0.5 wt. % fMWCNT-epoxy composite	Assignment of Raman peaks
–	640.4	641.1	γ Epoxy (p-sub. Benzene)
–	737	737	α-Epoxy
–	823.5	818.8	W C-H
–	916.5	916.6	γ Epoxy
–	937	937	W C-H
–	1014	1013,8	ν aromatic ring
–	1040.8	1042.3	aromatic ring ; p-sub. Benzene ring
–	1114.7	1112.5	α Epoxy (in plane ring deformation)
–	1185.1	1186.9	W C-H
–	1248	1249	Epoxy ring breathing and C-O stretching
–	1298.1	1298.1	CH_2 deformation
1330	–	1331.5	MWCNT (D band)
–	1452.2-1463	1463.5	δ CH_2 (aromatic ring breathing)
1580	1581.2	1581	ν aromatic ring and MWCNT (G band)
1605	1609.4	1605.4	ν aromatic ring
2658	–	2667	MWCNT (2D band)

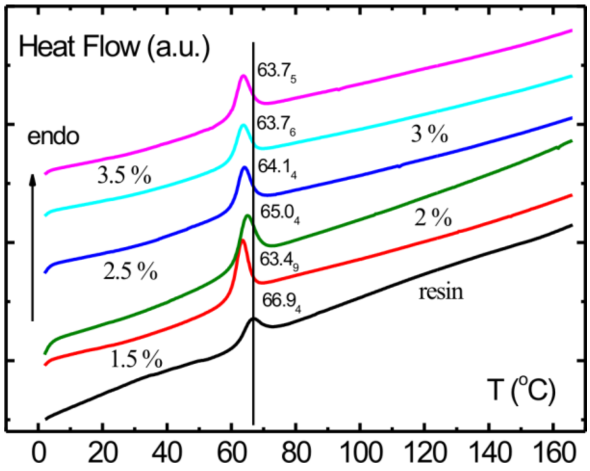


Fig. 2 DSC analyses of the epoxy resin and its composites with different fMWCNTmass contents.

Differential Scanning Calorimetry (DSC) investigations of the epoxy resin and composites with different fMWCNT mass content, shown in Fig. 2, reveal an endothermal peak that could correspond to the glass transition temperature T_g. This temperature, slightly shifted at lower values as the fMWCNT mass content increases, separates the glassy state existing below T_g, in which only vibrational motion of molecular segments is allowed, from the rubbery state above T_g, when relative motion between these segments can take place.The glass transition temperature is an indication of the operational limit, a significant change in mechanical properties occurring above it

[11]. The T_g parameter ranges between few degree Celsius and more than 200 ^{o}C depending on the curing conditions, resin and hardener [1,12], but values comparable to those in Fig. 2 have been obtained in DGEBA-based adhesives [11].

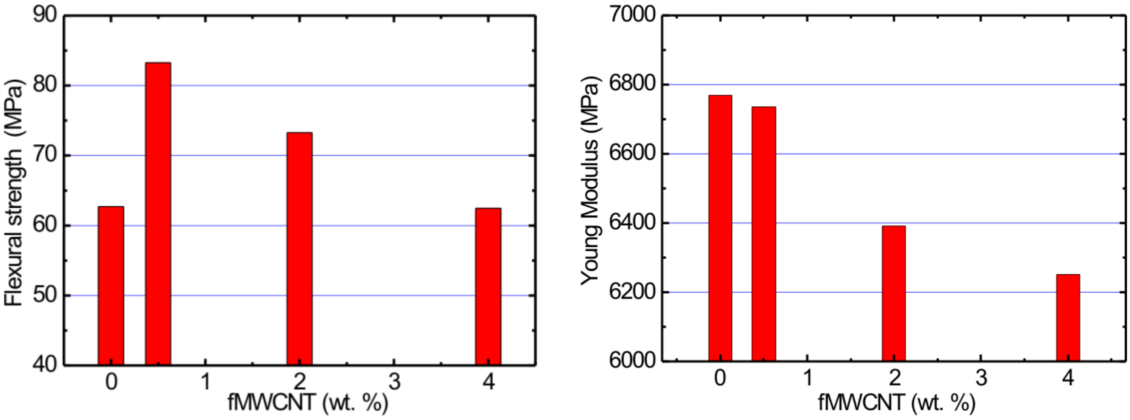
The low values of T_g in the epoxy resin and its fMWCNTscomposites observed in Fig. 2 suggest an un-complete curing process [13, 14], supported by the fact that the samples were not subjected to a post-curing treatment after being cured at room temperature. The shift of the endothermal peak towards lower temperatures as the fMWCNT concentration increases, also evidenced in composites containing DGEBA resins, anhydride hardeners and MWCNTs [15], or bisphenol A resins, triethylenetetramine hardeners and low concentrations of Al_2O_3 and TiO_2nano-fillers [16], indicates strong interaction at the interface between the epoxy matrix and fMWCNTs. These results supportthe finding of the Raman investigation.

3. Mechanical characterization of fMWCNT-epoxy composites

The mechanical tests were designed to measure severalstandard parameters: flexural strength at tensile stress at a transverse deflection of 6 mm and up tobreaking point, and tensile strength at tensile stress. TheYoung modulus was determined in all experiments. The measurements at room temperature and at a constant speed of 5 mm/min were performed with anInstron3382 equipment, which allows uniaxial load application. Three samples were used for each measurement, and the results were averaged over the obtained values.

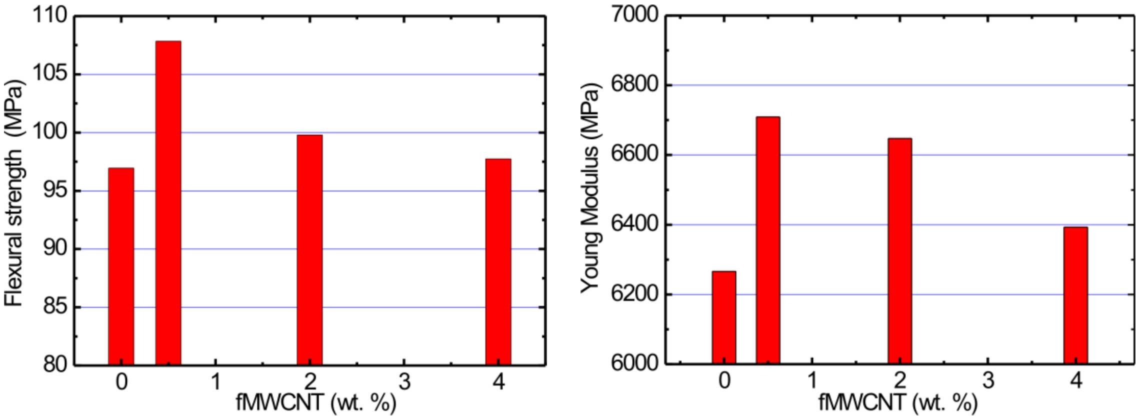
For flexural strength investigations, samples from epoxy resin and composites with different fMWCNT mass concentrations were prepared as plates with length l = 110 mm, width w = 10 mm and thickness t = 3.5-4 mm, and a 3-point loading method was used. The flexural strength for a transverse displacement of 6 mm, and the corresponding Young's modulus, are presented in Figs. 3(a) and 3(b), respectively, while the same characteristics up to breaking point are displayed in Figs. 4(a) and 4(b).

The Young's modulus is calculated from the relation $E = F/(S \cdot \delta l)$ where F is the applied load, $S = w \cdot t$ is the cross-section, and δl is the relative elongation of the sample.



(a) (b)

Fig. 3 (a) Flexural strength and (b) Young modulus at tensile stress for a transverse deflection of 6 mm.



(a) (b)

Fig. 4(a) Flexural strength and (b) Young modulus at tensile stress at the breaking point.

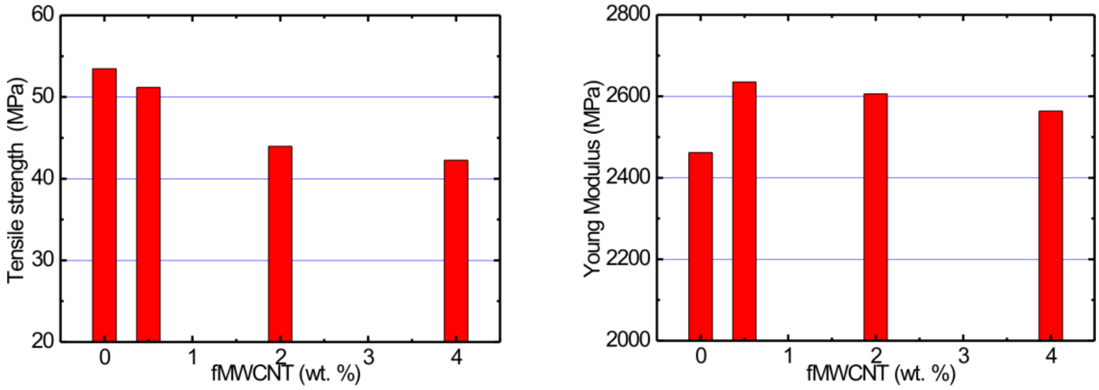
Because MWCNTs have a large elastic modulus, of about 0.2 TPa for nanotube diameters similar to those used in our experiments [17], it is expected that the mechanical properties would be enhanced by addition of fMWCNTs. Indeed, in DGEBA-based resins with high loading of well dispersed MWCNTs, the tensile strength and Young's modulus were found to increases with respect to pure resin [18].

In our experiments, the flexural strength increases with 24% for a transverse displacement of 6 mm and 11% up to breaking point, relative to the values in epoxy samples, after addition of 0.5 wt. % fMWCNTs. However, the enhancement in flexural strength values in both types of measurement, relative to epoxy resin samples, decreasesfor larger values of the fMWCNT mass content. Indeed, in the 4 wt. % fMWCNT-epoxy composite the flexural strength decreases with 0.4 % for a transverse displacement of 6 mm and is only with 0.8 % larger than in the epoxy resin up to breaking point. After an almost constant value of the Young's modulus (decrease with only 0.4 %) in the 0.5 wt. % fMWCNT-epoxy composite with respect to the epoxy resin at a transverse displacement of 6 mm, and an increase with 4 % of this parameter up to breaking point, the Young modulus decreases with a further increase of fMWCNTs mass content. In the 4 wt. % fMWCNT-epoxy composite this parameter is lower than in the epoxy resin with 7.6% at a transverse displacement of 6 mm and is higher with only 2 % up to breaking point.

Although, according to [19], an aspect ratio of fMWCNTs larger than 500 (as in our case) assures an optimum load transfer betweenthe epoxy matrix and nanotubes at tensile load, the generalenhancement of mechanical properties infMWCNT-epoxy composites still does not take full advantage of the MWCNT characteristics.Among the reasons, we mention the defects induced by –COOH functionalization and the random orientation of nanotubes [20]. The mechanical properties are influenced by the alignment of MWCNTs; in epoxy-based composites withalignedMWCNTs the mechanical properties are highly anisotropic [21, 22].

At large tensile strengths, for example in mechanical testing up to breaking point, MWCNTs undergo permanent damage, known as plastic deformation or yielding. At room temperature, MWCNTs could yield within 5-10% tensile strain [19], the plastic deformation that releases the strain energy in the system being associated to the formation of Stone-Wales defects. At increasing tensile stress the nanotubes can neck and break.

The measured results for tensile strength and Young's modulus at tensile stress applied on a dog bone sample with dimensions l = 150 mm, t = 4 mm, w = 10 mm (w = 20 mm at the ends) are represented in Figs. 5(a) and 5(b), respectively.



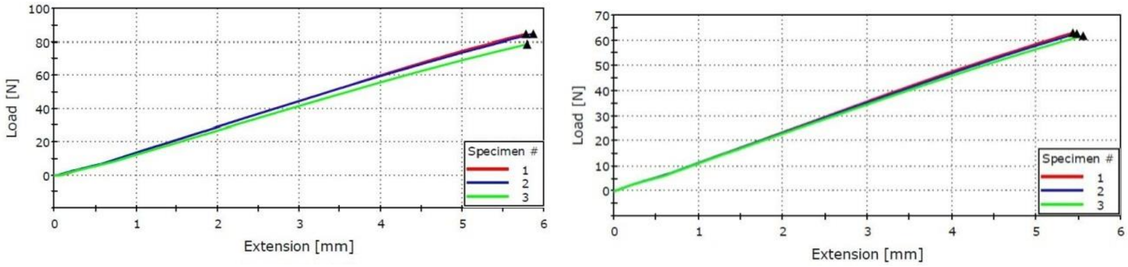
(a) (b)

Fig. 5 (a) Tensile strength and (b) Young modulus at tensile stress at the breaking point.

The tensile strength in this case is found to decrease constantly with the fMWCNT mass content, being smaller with 4 % than in theepoxy resin for the 0.5 wt. % fMWCNT-epoxy composite and with 21 % for the composite with 4 wt. % fMWCNT. The Young's modulus, after an initial increase with 7 % compared to the epoxy resin in the composite with 0.5 wt. % fMWCNT, decreases with a further increase in fMWCNT mass content, being only 4 % higher than in the resin in the 4 wt. % fMWCNT-epoxy sample.

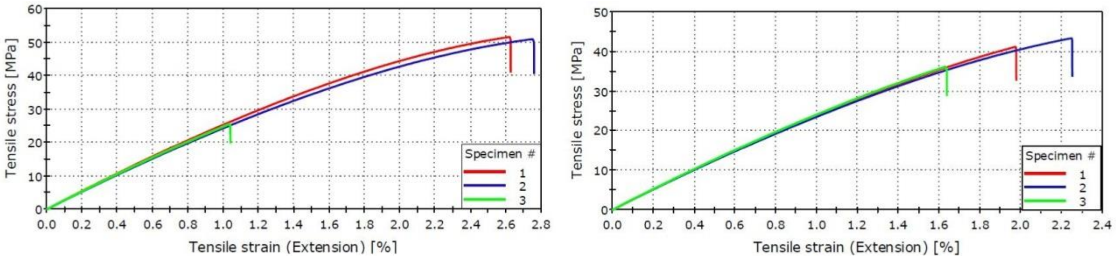
Previous studies on mechanical properties of DGEBA-based composites containing an amine-based hardener and single-walled carbon nanotubes showed an increasing trend for tensile strength and Young's modulus with the addition of small amounts of nanotubes, up to 0.25 %, the flexural strength being almost unaffected by increasing the concentration of nanotubes [23]. Similar enhancements in tensile strengths of bisphenol F epoxy resin-based composites containing carbon nanotubes functionalized in ionized liquids with different anions were reported in [24].However, non-uniform variations of mechanical properties of MWCNT-polyester composites with the filler mass content, as in our case, with an optimum tensile strength at 0.05 wt. %, were observed in [25] and explained by the increased agglomeration tendency of MWCNTs as their mass content increases.

Flexural testing (for details, see [26]) were also performed on three samples for the epoxy resin and fMWCNT-epoxy composites with fMWCNTconcentration values of 0.5 wt. %, 2 wt. %, and 4 wt. %.Typical results for a transverse deflection of 6 mmare shown in Figs. 6(a)-6(b),while examples of stress-strain curves at tensile stress are given in Figs. 8(a)-8(b). The overall behavior of the fMWCNT-epoxy composites is in agreement with the other mechanical testing results presented above, small loadings of fMWCNTs improving the mechanical characteristics of epoxy composites. In addition, the introduction of fMWCNTs in the epoxy matrix seems to improve the linearity of the stress-strain curves. As reported in [26], the flexural testing results were found to be in agreement with simulations performed with theNASTRAN/PATRAN program, where NASTRAN is the acronym forNAsaSTRuctureANalysis and PASTRAN stands for patches of NASTRAN.



(a) (b)

Fig. 6 Mechanical measurements for a deflection of 6 mm forfMWCNT-epoxy composites withfMWCNT mass concentration of (a) 0.5%, and (b) 4%



(a) (b)

Fig. 8 Stress-strain curves at tensile stress forepoxy composites with (a) 0.5 wt. % fMWCNTs, and(b) 4 wt. % fMWCNTs

4. Numerical simulations of mechanical deformations

The commercially available ANSYS (ANalysisSYStem) programbased on the finite-element model was used to simulatethe mechanical traction results. The parameters of the equivalent homogeneous viscoelastic material, which is simulated by ANSYS, were assumed to be those in the experiment. In particular, the Young modulus was taken as the experimental mean value obtained from the three samples at each fMWCNT mass concentration, and the Poisson ratio was taken as 0.33, which is a typical value for non-metallic materials. The ANSYS program offers the possibility to account for the polymerization degree of the sample via the viscosity coefficient [27]. As shown in Tables 2 and 3, the experimental data are consistent with the simulations of the ANSYS program, only if a 55-65% polymerization degree of the sample is assumed; higher polymerization degrees lead to unrealistic ANSYS results for stresses and displacements. These simulations confirm the hypothesis of an un-complete cured sample, suggested by DSC data.

Table 2 Results of ANSYS simulations for a 55-65% polymerization degree

fMWNCNT content (wt. %)	Young modulus *E* (Mpa)	Poisson ratio	Applied forces (daN)	Stresses (MPa)		Displacements (mm)	
				Lab tests	Numerical results	Lab tests	Numerical results
2	2605	0.33	165.792	43.96	45.4	2.18	1.63
4	2563	0.33	148.777	40.21	41.2	1.99	1.50

Table 3 Results of ANSYS simulations for a polymerization degree higher than 75%

fMWNCNT content (wt. %)	Young modulus *E* (MPa)	Poisson ratio	Applied forces (daN)	Stresses (MPa)		Displacements (mm)	
				Lab tests	Numerical results	Lab tests	Numerical results
2	2605	0.33	165.792	43.96	79.2	2.18	3.98
4	2563	0.33	148.777	40.21	75.2	1.99	3.62

5. Experimental data analysis and discussions

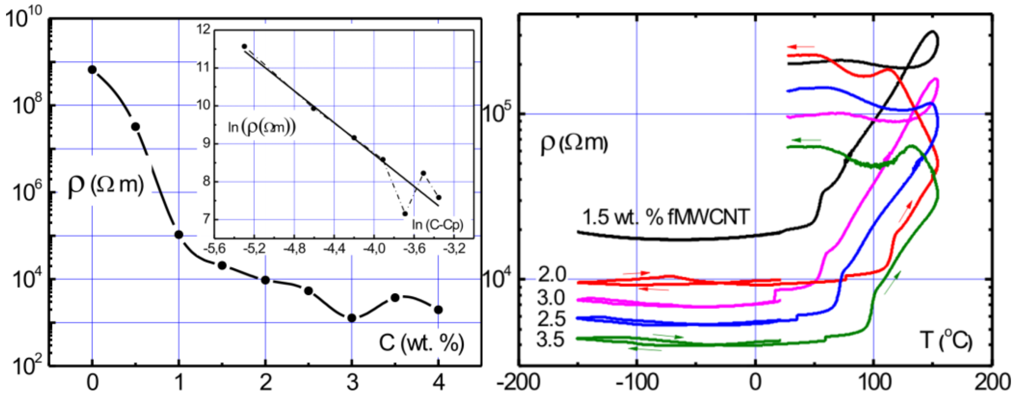
To explain the obtained results one should look closer to the load transfer from the matrix polymer to the fMWCNTs. The results of Raman and DSC analyses suggest a strong interaction at the epoxy-fMWCNT interface and hence a significant load transfer. This finding seems to be supported by the increase in modulus of elasticity for small nanofiller content, up to 0.5 wt. %. On the other hand, in composites with larger fMWCNT mass contents, the mechanical properties degrade with respect to the 0.5 wt. % fMWCNT-epoxy sample, suggesting a decrease in the load transfer effectiveness.

In composites containing MWCNTs, only the outermost nanotube is loaded at tension, because the MWCNT shells have low interlayer adhesion [28].In insulating polymers containing conductive nanotubes, an interfacial interaction zone surrounding the MWCNTs appear, which dictates the composite characteristics. This interaction zone is composed of an inner layer in the immediate neighborhood of MWCNTs, in which the mobility of the surrounding polymer molecules is highly reduced,andan outerlayer, in which the polymer molecules are more loosely bound [29].In particular, a modification of chain kinetics of the strongly immobilized epoxy molecules in the inner layer leads to a T_g shift towards higher temperatures, whereas an increase of the free volume of the more loosely bound polymer chains in the outer layer, determines a shift of the glass transition temperature towards smaller temperatures, the observed shift of the endothermal peak in fMWCNT-epoxy composites in Fig. 2 being a result of these two competing mechanisms [14].

As the fMWCNT mass content increases, the inter-nanotube distance decreases and the immobile polymer regions can overlap. On the other hand, as the fMWCNT mass concentration increases the tendency of nanotube agglomeration is enhanced and the interfacial effects become less pronounced.

The experimental results of fMWCNT-epoxy composites with low nanofiller concentrations (up to 0.5 wt. %) presented in Section 3 seem to suggest that the inner layer of the interfacial interaction zone dominates the mechanical properties. More precisely, the stiffer fMWCNTsimpart higher flexural strengths to the epoxy matrix via the inner layer of highly immobilized polymer chains; the load transfer effectiveness is optimum in polymer matrices with low stiffness [5]. The efficient load transfer mechanism breaks down at fMWCNT concentrations $C>$ 0.5 wt. % because the nanotubes begin to form a three-dimensional network inside the epoxy matrix.Numerical coarse-grained molecular dynamics simulations validate also the correlations between stress at failure, filler size and loading, and network structure [30]. These simulations show that for strong filler-polymer interactions the largest stress at failure occurs for small loadings, when there is no filler-filler contact and the relative mobility between the filler and the polymer matrix is reduced. At increased loading, when filler-filler contact become numerous, the relative filler-polymer matrix mobility is enhanced and the stress at failure decreases.

The appearance of such afMWCNT network above 0.5 wt. % is indicated also by the percolation threshold of fMWCNT-epoxy composites observed in DC electrical measurements. These measurements were performed in a Faraday cage equipped with a heater/cooler system such that the temperature could be varied from –150 °C to 150 °C. The current-voltage characteristics for applied voltages between –10 ÷ + 10 V were linear in all samples at room temperature, the resistivity of composites with differentwt. % fMWCNT contents, denoted by C, being shown in Fig. 14(a).



(a) (b)

Fig. 14 (a) Dependence of the resistivity of epoxy composites on the fMWCNT concentration at room temperature. (b) Temperature dependence of the resistivity of fMWCNT-epoxy composites.

The decrease of resistivity with increasing the fMWCNTmass concentration C, observed in Fig. 14(a),can be fitted with the expression $\rho(C) = \rho_0 (C - C_p)^{-t}$ above the percolation threshold C_p = 0.5 wt. %, which indicates the transition from an insulating to a conductive material. In this expression the critical exponent is found to be t = 2.1, which indicates the appearance of a three-dimensional network of conducting fMWCNTs [31]. The not-so-good fit of the resistivity formula with the experimental point C = 3 wt. % in Fig. 14(a)can be assigned toa more conducting network, which probably extends from one electrode to the other,and originates in the sample synthesis process.On the contrary, for C = 3.5 wt. % in Fig. 14(a), the resistivity is higher than the general trend, which can be attributedprobably to the formation of aggregates in the sample. Aggregation is a serious problem in polymer composites with high MWCNT mass contents, in which the homogenization is impeded by an increased viscosity [32].

The electrical measurements identify the threshold for insulating-to-conducting transition C_p = 0.5 wt. % as the same fMWCNT mass concentration at which the mechanical behavior changes with C. Similar connections between the percolation threshold for electrical conduction and mechanical properties have been evidenced in soft, rubbery epoxy resins containing randomly distributed MWCNTs, in which the enhancement in mechanical properties due to addition of MWCNTs to the polymer matrix tends to saturate above C_p [32]. Moreover, investigations of suspensions of MWCNTs in an uncured DGEBA-based epoxy resin revealed a connection between the percolation threshold and the fluid-to-solid rheological transition as the MWCNT mass content increased, both transitions requirements improved contacts between CNTs [33]. In our case, mechanical measurements suggest a decrease in the load transfer effectiveness as the fMWCNT network forms, process associated with increased separation/weaker interaction between the stiff fMWCNT network and the less stiff resin.

Electrical measurements performed at a constant bias voltage of 5 V in cooling-heating cycles also support the finding of numerical simulations regarding the un-complete curing of composites. Figure 14(b), which illustrates the temperature dependence of several fMWCNT-epoxy composites cooled from room temperature to –150 ^{o}C, heated afterwards to 150^{o}C and then cooled again at room temperature, reveal a strong hysteretic behavior. This non-reproducibility of resistivity values in cooling-heating cycles that extend beyond the glass transition temperature could be associated with spatial rearrangements of polymeric chains and nanotubes in the samples, as well as with the different thermal expansion coefficients of these composite constituents. In epoxy resins the thermal expansion coefficient is typically about $3\times10^{-5o}C^{-1}$, whereas for nanotubes this parameter is only $7.5\times10^{-6o}C^{-1}$ [34].

On the other hand, large hysteretic behaviors of many parameters, for instance refractive index [35] and density [13], were observed during curing of thermosetting resins, such as DGEBA, when the curing temperature differs from the glass transition temperature of the fully cured resin. These parameters change because the chain packing is increasingly restricted as the epoxy network forms in the curing process [13]. The large thermal hysteresis in resistivity observed in Fig. 14(b)could be caused by the post-curing process. Indeed, as the temperature increases,the post-curing is favored, and the increased conductivity could result from a reduced separation between fMWCNT, similar to the observations in MWCNT-SU8 epoxy composites [36], or from a change in the molecular structure, which would involve a further cross-linking of the unreacted epoxy resin with the hardener and an increased participation of fMWCNTs in the crosslinking mechanism [14]. The last behavior becomes more important as the fMWCNT mass content increases.Because the thermal conductivity of MWCNT is much larger than that of epoxy (of 1000 W/mK [37]for MWCNTs with similar diameters as those used in our samples compared to 0.2 W/mK [38] in the epoxy resin), the nanotubes can increasingly act as local heaters when their mass concentration increases. Indeed, the ratio between the high resistivity value at the end of the thermal cycle and the low resistivity at the beginning of the cycle (at room temperature) increases from 10 to 24 as the fMWCNT concentration increases from 1.5 wt. % to 2.5 wt. %. For C = 3 wt. % this ratio decreases to about 13 because of a more efficient heat dissipation trough the fMWCNT network that extend between the electrical contacts. For C = 3.5 wt. % the ratio between the resistivity values at the end and the beginning of the thermal cycle increases again to about 15 due to aggregation of nanotubes.

5. Conclusions

Composites containing epoxy resin and fMWCNTswith different mass concentrations were prepared. These composites were characterized by Raman spectroscopy and DSCbefore performing mechanical measurements which reveal a strong interaction between resin and fMWCNTs. It was found that the addition of fMWCNT to the polymer matrix generally increases the mechanical behavior for small mass concentration of fMWCNTs, up to 0.5 wt. %, further nanotube addition having a detrimental effect. This mass concentration value was found to correspond also with the percolation threshold in electrical measurements, which suggests a change in the load transfer effectiveness as fMWCNT networks form in the epoxy matrix.

Numerical simulations reveal that experimental data could only be reproduced if the curing process is not complete. Electrical measurements validate also this result, the observed thermal hysteresis of resistivity in cooling-heating cycles indicating major changes in the epoxy network, consistent with a post-curing process. These results suggest that, besides density, refractive index or resistivity, mechanical measurements can be used as well to monitor the curing process/polymerization degree of fMWCNT-epoxy composites.

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