

# Dielectric properties of multiwall carbon nanotube-epoxy composites

S. PALADE<sup>a</sup>, A. PANTAZI<sup>a</sup>, C. BERBECARU<sup>a,e\*</sup>, E. VAJAIAC<sup>a,b</sup>, A. STEFAN<sup>b</sup>, A. MATEI<sup>c</sup>, V. MELTZER<sup>d</sup>, E. PINCU<sup>d</sup>, D. DRAGOMAN<sup>a,f</sup>

<sup>a</sup>Faculty of Physics, University of Bucharest, P.O. Box MG-11, 077125 Bucharest, Romania

<sup>b</sup>National Institute for Aerospace Research and Development „Elie Carafoli”, 061126 Bucharest, Romania

<sup>c</sup>National Research and Development Institute in Microtechnologies, Str. Erou Iancu Nicolae 126 A, 077190 Bucharest, Romania

<sup>d</sup>Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta 4-12, 030018 Bucharest, Romania

<sup>e</sup>Romanian Materials Science - Crystal Growth Society, Bucharest-Magurele, 077125, Romania

<sup>f</sup>Academy of Romanian Scientists, Splaiul Independentei 54, 050094 Bucharest, Romania

Resin and functionalized multiwall carbon nanotubes (fMWCNT) were used to obtain composites, cured at room temperature (RT). Dielectric measurements show changes of permittivity and losses in cooling-heating cycle with non-reproducible values above 50 °C. Interplay of segments with increased mobility due to increasing resin temperature, the differences between thermal expansion coefficients between resin and fMWCNT, spatial rearrangements in samples and post curing effects could explain the evolution of dielectric parameters versus temperature. Permittivity and losses show strong frequency dependence associated with reducing contributions of different polarization mechanisms at increasing frequencies. Permittivity, losses and electrical conductivity of the samples reveal a tremendous increase with nanotubes concentration at the percolation threshold. Percolation and tunneling mechanisms at RT and thermally activated mechanisms, which dominates the electrical conduction at high temperatures, can explain the temperature dependence of samples' conductivity. Electrical measurements also showed non-reproducible values at heating and cooling beyond 55 °C.

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## 1. Introduction

Epoxy resins, which are thermosetting plastics, consist of a three-dimensional network of covalent bonds that confer to these materials good mechanical and insulating properties, thermal stability and resistance to most chemicals [1]. Epoxy resins are used as coatings and adhesives, as well as polymer matrices for composites with a wide range of applications [1], including electronics, automotive and avionics.

Conductive fillers, in particular multi-walled carbon nanotubes (MWCNTs), were shown to improve the electrical conductivity of epoxy resins, rendering these materials suitable as transparent conducting electrodes [2] or antistatic composites [3]. MWCNTs have not only excellent electrical properties, but also excellent mechanical and thermal characteristics [4].

This paper investigates the temperature and frequency dependences of the dielectric properties of the MWCNT-epoxy composites for different MWCNT mass concentrations, as well as the temperature dependence of the samples' conductivity. The aim is to study the changes in complex permittivity and conductivity with the MWCNT concentration and to reveal the mechanisms responsible for these changes.

## 2. Preparation and structural characterization of MWCNT-epoxy composites

The composites were prepared using high-purity MWCNTs purchased from the Chinese Academy of Sciences (CAS), with outer diameters of 10-20 nm, inner diameters of 5-10 nm, and lengths of 10-30 μm. MWCNTs were obtained by chemical vapor deposition and were functionalized with carboxyl groups (-COOH); they are further denoted as fMWCNT. The -COOH functionalization of MWCNTs improves their dispersion within the epoxy matrix and allows the formation of an interface between MWCNTs and the resin, with stronger interconnections [5].

The epoxy resin P401 is based on the diglycidyl ether of bisphenol A (DGEBA), while the triethylenetetramine I3361 hardener is a mixture of TETA ethyleneamines with close boiling points, including linear, branched, and two-cyclic molecules.

The fMWCNT-epoxy samples were prepared by mixing the P401 resin and the I3361 hardener (both purchased from Policolor – Romania) with different mass concentrations of fMWCNTs. Samples with 0 ÷ 4 wt. % fMWCNT mass content, in steps of 0.5 wt. % fMWCNT, were prepared.

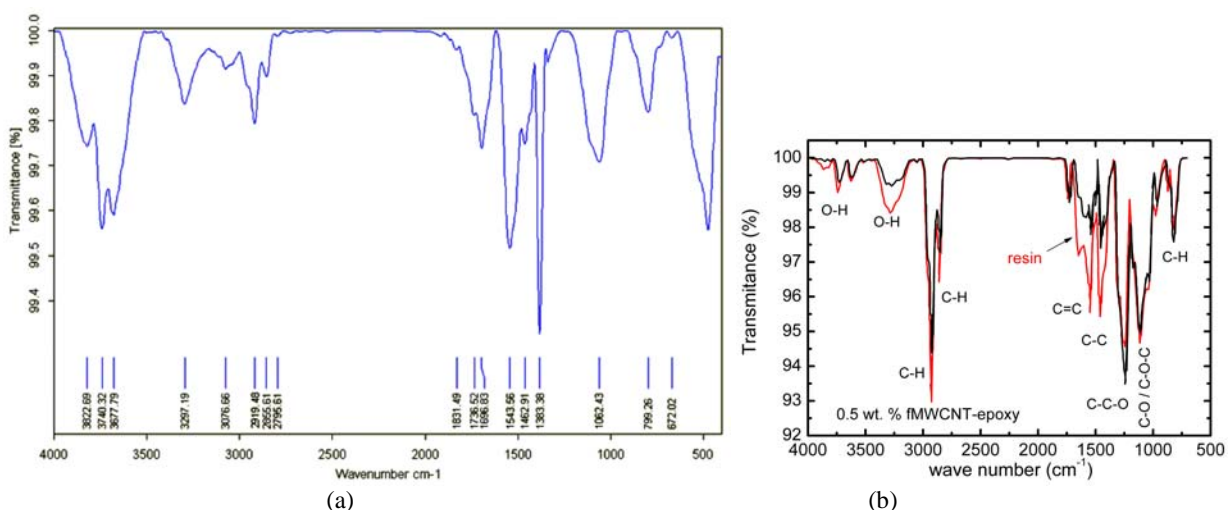


Fig. 1 FTIR spectra of: (a) fMWCNT and (b) P401 resin and the 0.5 wt. % fMWCNT- P401 resin composite.

Table 1. IR active functional groups for fMWCNT, epoxy resin and the 0.5 wt. % fMWCNT-epoxy composite

fMWCNT		Epoxy resin		0.5 wt. % fMWCNT-epoxy	
Wavenumber (cm <sup>-1</sup> )	IR active group	Wavenumber (cm <sup>-1</sup> )	IR active group	Wavenumber (cm <sup>-1</sup> )	IR active group
3823	O-H	3737	O-H	3734	O-H
3740	O-H	3621	O-H		
3678	O-H	3284	O-H	3284	O-H
3297	O-H	2923	C-H from -CH <sub>2</sub> and -CH <sub>3</sub> groups	2924	C-H from -CH <sub>2</sub> and -CH <sub>3</sub> groups
3077	O-H	2855	C-H from -CH <sub>2</sub> and -CH <sub>3</sub> groups	2856	C-H from -CH <sub>2</sub> and -CH <sub>3</sub> groups
2919	C-H	1739	C=O	1732	C=O
2856	C-H	1546	C=C from the benzene ring	1544	C=C from the benzene ring
2796	C-H	1459	C-C from the benzene ring	1458	C-C from the benzene ring
1831	C=O	1243	C-C-O	1241	C-C-O
1737	C=O	1114	C-O / C-O-C	1119	C-O / C-O-C
1697	C=O	871	C-H	971	C-H
1544	O-H/COO-	819	C-H	829	C-H
1463	C-H/COO-				
1383	C-H				
1062	C-O				
799	C-OH				
672	C-H				

The as obtained mixtures, produced using an ultrasonic homogenization technique, were left at room temperature (RT) in air for about 7 days to complete the curing process.

The fMWCNT, the pure P401 epoxy resin, as well as the 0.5 wt. % fMWCNT-epoxy composite were characterized by Fourier Transform Infrared (FTIR)

spectroscopy, as shown in Figs. 1(a) and 1(b). The main peaks in Figs. 1(a) and 1(b) were identified according to Table 1. The main peaks of the FTIR spectrum of fMWCNTs fall almost in the same spectral regions as those of the resin, and have smaller amplitudes. As a consequence, the peaks of fMWCNT are covered by those of the resin. However, as can be seen from Fig. 1(b), the

peak positions and some of their amplitudes are significantly changed in the 0.5 wt. % MWCNT-epoxy composite in comparison to the raw materials. In Fig. 1(b),

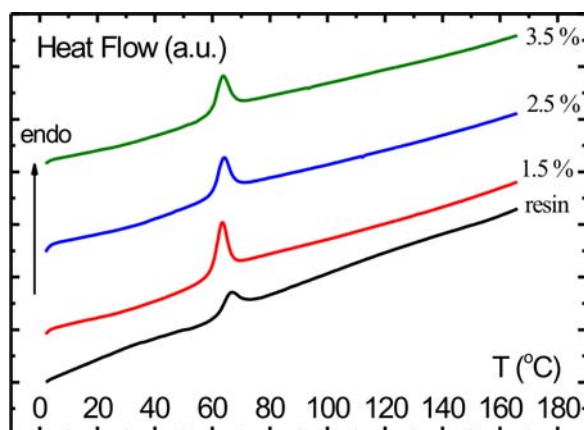


Fig. 2 DSC analyses of the P401 resin and composites with different fMWCNT mass contents.

Table 2 Shift of the endothermal peak with the MWCNT's concentration.

MWCNT Concentration (wt. %)	Temperature (°C)
0	66.9
1.5	63.5
2	65.0
2.5	64.1
3	63.8
3.5	63.8

it is clearly seen that 0.5 wt. % fMWCNT in the resin matrix heavily affects the bonds, especially in the 1350 – 1700  $\text{cm}^{-1}$  and 3100 – 3500  $\text{cm}^{-1}$  regions of FTIR spectra, which include the fingerprints of the resin. More affected are the simple and double bonds of carbon from benzene rings, and the OH bonds. This behavior suggests a strong interaction between fMWCNTs and the resin.

As illustrated in Fig. 2, Differential Scanning Calorimetry (DSC) analyses of the epoxy resin and fMWCNT-epoxy composites show an endothermal peak at about 67 °C, which slowly shifts at lower temperatures when fMWCNTs are added in the epoxy matrix, table 2. This peak can be associated with the glass transition temperature  $T_g$  that separates the glassy state, which exists at lower temperatures and in which only vibrational motion occurs, from the rubbery state at higher temperatures, in which individual molecular segments can move relative to each other. Depending on the base resin, the hardener and curing conditions, glass transition temperatures can vary between some degrees Celsius and over 200 °C [1]. The temperature shift of the endothermal peak as the fMWCNT concentration increases is an indication of significant interactions at the interface

between fMWCNTs and the epoxy matrix, and supports the finding of FTIR analyses.

A similar shift of the endothermal peak has been observed also in bisphenol A resins with triethylenetetramine hardener and  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  nanofillers [6], and in DGEBA resins with anhydride hardeners and MWCNTs fillers [7].

Unlike in MWCNT-DGEBA composites with a 4, 4'-(diaminodiphenyl) sulfone hardener, no homopolymerization of the resin induced by MWCNT functionalization is observed in the DSC analysis, this process being characterized by the appearance of a small peak at temperatures higher than the main endothermal peak [5].

### 3. Dielectric characterization of MWCNT- epoxy composites

A specially designed sample holder was used to investigate the variation of electrical parameters with temperature and frequency. Dielectric measurements using a Hioki 3532-50 type automatic RLC bridge were performed in a wide range of frequencies, between 300 Hz and 5 MHz, and on an extended temperature interval, between  $-120 \div +155$  °C. All samples were cleaned up in an  $\text{N}_2$  flow for at least 30 min before measurements, inside the sample holder. The dielectric constant was computed from capacitance measurements using the formula  $\epsilon = Cd / \epsilon_0 S$ , where  $d$  is the thickness and  $S$  is the surface of the sample. A Kethley 2010 multimeter and a chromel–alumel thermocouple were used for temperature measurements. Both instruments were controlled by a computer through GPIB interfaces for automatic data registration and subsequent analysis. Some samples were cooled from RT up to  $-120$  °C, heated up to  $+150$  °C and cooled again at RT, at a speed of about 1.5 °C/min and at a measuring electrical field of 0.6 V.

Fig. 3(a) ÷ 3(d) show typical temperature dependences of dielectric permittivity and losses at three selected frequencies, for the P401 resin and fMWCNT-epoxy composites with different fMWCNT concentrations. All electrical parameters were measured in a cooling/heating cycle, in which the temperature was modified with a constant rate of 1.5 °C/min. Typically, the samples, initially at RT, were cooled, then heated above RT, and cooled down again up to RT. From Figs. 3(a) ÷ 3(d) it follows that the permittivity is strongly dependent on the fMWCNT concentration, increasing drastically and then decreasing as the fMWCNT concentration increases.

The temperature dependence of  $\epsilon$  for the epoxy resin, represented in Fig. 3(a), is not uniform in the heating process: it increases, reaches a maximum value that depends on frequency, and then decreases. The maximum permittivity values also show a shift with the frequency toward higher temperatures, as indicated by the vertical arrows in Fig. 3(a). On the contrary, in the cooling process the dielectric constant has a decreasing trend, the maximum value being attained at 150 °C.

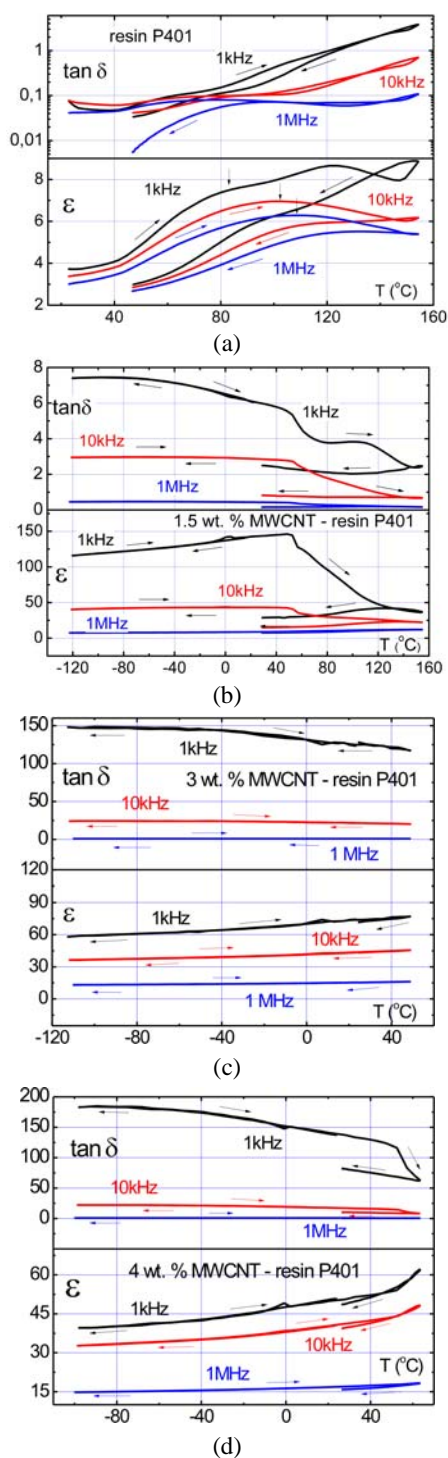


Fig. 3 Temperature dependence of the permittivity and losses of the epoxy resin and fMWCNT-epoxy composites with different fMWCNT wt. % concentrations.

In fMWCNT-epoxy composites, a monotonous increase of  $\varepsilon$  until about 50 °C is observed in Figs. 3(b) ÷ 3(d), followed by a pronounced decrease up to 155 °C in Fig. 3(b). Reproducible values of permittivity

were registered in the  $-120 \div +50$  °C temperature ranges for all samples in a heating/cooling process, as shown in Fig. 3(c). Large differences can be observed for temperatures higher than 50 °C, i.e. a decrease of permittivity values from almost 150 (heating) to less than 50 (cooling), as illustrated in Fig. 3(b), for 1 kHz frequency, as example.

The dielectric losses also depend strongly on the fMWCNT content of the samples and the temperature range of investigation. Dielectric losses increase with temperature for the epoxy resin, especially at low frequencies, increasing with about two orders of magnitude in the investigated temperature range at 1 kHz. The losses show a large thermal hysteresis in the 50 ÷ 155 °C interval. The relative maxima of losses could be correlated with those of the permittivity.

As shown in Figs. 3(b) ÷ (d), the composite shows a decreasing trend of losses as the temperature increases, with reproducible values at heating/cooling cycles at temperatures up to 50 °C. This last behavior is confirmed in the sample with 3 wt. % fMWCNT, where thermal hysteresis effect was not observed when the maximum temperature was lower than 50 °C. In all composites, the losses decrease strongly at temperatures higher than 50 °C, temperature at which  $\varepsilon$  attains its maximum value. In addition, the dielectric losses show a large difference at temperature cycling, e.g. 5.8 (heating) to 2.4 (cooling) for the composite with 1.5 wt. % fMWCNT around RT.

The temperature dependence of the dielectric constant and losses can be understood as the interplay of several mechanisms. One of them implies an increase of the segments' mobility in epoxy resin as the temperature increases, which also leads to an increase in  $\varepsilon$ . On the other hand, the differences of thermal expansion coefficients of MWCNT and epoxy resin could lead to a decrease of  $\varepsilon$  [8]. The post curing effect at heating can contribute also to a reduction of permittivity value due to the reaction between hardener and epoxy. Otherwise, the decreasing trend of losses with increasing temperature could be seen as a consequence of the reduced mobility of the large units formed in the post curing process. Our samples have been cured at RT without a post curing treatment. This procedure also influences the thermal stability of materials [9], especially the low value of  $T_g$  evidenced by DSC measurements [10]. The residual exothermic peak evidenced by DCS analysis in Fig. 2 indicates that the curing reaction is not complete [11].

Thermal stability of the resin is expected to have a significant influence on the properties of composites, including the electric ones. In particular, the observed non-reproducibility of  $\varepsilon$  and  $\tan \delta$  values at cooling/heating cycles exceeding 50 °C can be accounted for by spatial rearrangements in the samples as the temperature approaches the glass transition temperature, and/or by the differences between thermal expansion coefficients of MWCNT and epoxy matrix. Typical thermal expansion coefficients of epoxy resins are about  $3 \times 10^{-5}$  °C<sup>-1</sup>, while for the CNT the measured value of this parameter is of only  $7.5 \times 10^{-6}$  °C<sup>-1</sup> [12]. In fact, theoretical and experimental studies of the MWCNT-bisphenol F epoxy

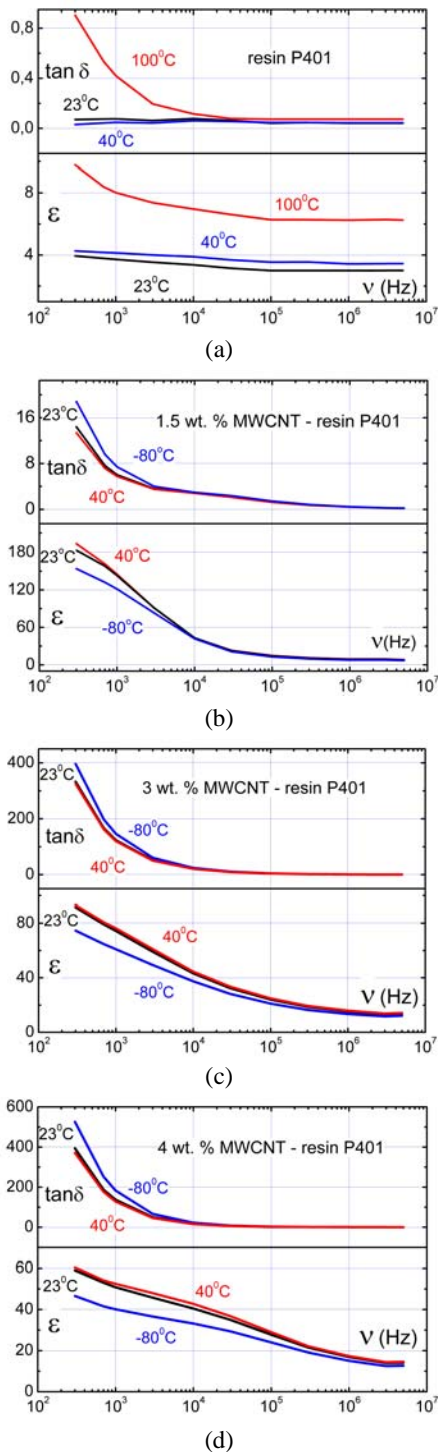


Fig. 4 Frequency dependence of permittivity and losses of the epoxy resin and fMWCNT- epoxy composite s with different fMWCNT wt. % concentrations.

resins and an amine hardener showed that the composites undergo thermal contraction at temperatures comparable to and higher than RT, up to 62 °C, whereas thermal expansion takes place at still higher temperatures, up to 120 °C [13].

Fig. 4(a) ÷ 4(d) illustrate the frequency dependence of permittivity and losses for fMWCNT-epoxy composites with different fMWCNT concentrations, at selected temperatures. The dielectric constant  $\epsilon$  of all composites is much higher than in the pure epoxy resin, increases abruptly for low fMWCNT concentrations, and then decreases steadily as the fMWCNT concentration increases further.

In general, the dielectric constant decreases with increasing frequency for all samples, this trend being particularly pronounced for fMWCNT-epoxy composites. This behavior was also observed in the 1 MHz ÷ 1 GHz frequency range, for the same epoxy resin, and attributed to the reduced contributions of dipolar groups at the permittivity value [6]. Otherwise, in the investigated frequency range we may take into account the contributions of space charge, dipoles and charge carriers to the permittivity. The strong decrease of permittivity is associated with the reduced contributions of different polarizations mechanisms at increasing frequencies values. The increase of the frequency for which the dielectric permittivity attains almost constant and small values with increasing fMWCNT concentration ( $C$ ) is consistent with the mechanism suggested in [14], according to which the potential energy at the interface between the insulating epoxy resin and the conductive fMWCNTs decreases with increasing  $C$ , such that the localized charge carriers can hop easier, and the polarization decreases at higher frequencies.

In fMWCNT-epoxy composites  $\tan \delta$  decreases with increasing frequency, since the AC conductivity in conducting samples is almost independent of frequency, while in insulating samples (the epoxy resin, for example) the AC conductivity increases as the frequency increases and so  $\tan \delta$  has a weak (if, at all) frequency dependence (see, for example, [15]). The significant decrease of losses with frequency for composites with fMWCNT concentration as low as 0.5 wt. % suggests a percolation threshold around this concentration value (see next Section). Dielectric losses in fMWCNT-epoxy composites show a dramatic increase compared to the pure epoxy resin, caused mainly by an increase of conductivity with several orders of magnitudes above the percolation threshold.

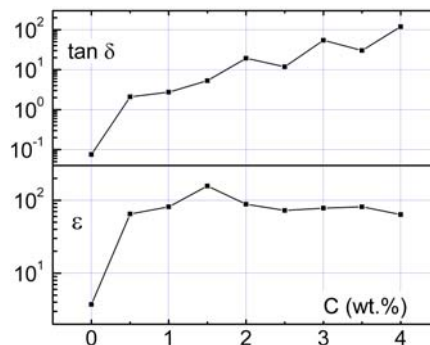


Fig. 5 Concentration dependence of dielectric losses and dielectric constant at RT and at a frequency of 1 kHz.

The increase in dielectric losses with the concentration  $C$  of fMWCNTs, due to an increase in conductivity is confirmed also by Fig. 5. This figure shows that the dielectric constant increases near the percolation threshold and then decreases, in agreement with the results in Fig. 4. This behavior is due to the so-called minicapacitor effect caused by clusters of conductive fMWCNTs separated by very thin epoxy layers [14, 16].

Above the percolation limit,  $\varepsilon$  decreases because the interfacial polarization effect decreases, and the conductivity is determined by electron flow through the continuous network of conductive fMWCNTs.

#### 4. Electrical characterization of MWCNT-epoxy composites

DC electrical measurements were performed from RT up to about 155 °C using a Faraday cage equipped with a heater. At RT, for applied voltages in the range  $-10 \div +10$  V range, the current-voltage characteristic was linear for all composites, the conductivity being dependent on the fMWCNT mass concentration, as illustrated in Fig. 6(a).

The linear current-voltage characteristic indicates that Fowler-Nordheim-type tunneling mechanisms, with voltage-dependent barriers, are not involved in electrical transport [17]. Moreover, the applied electric fields are sufficiently small to not induce the formation of fMWCNT networks [18].

As can be seen from Fig. 6(a), the conductivity increases abruptly with  $C$ , which indicates the transition from an insulating to a conductive material, in which electrical transport is of a percolative nature. The percolation threshold corresponds to an fMWCNT concentration of  $C_p = 0.5$  wt. %, as suggested by Fig. 6(b). The critical exponent  $t$  in the expression of conductivity  $C_p$ :

$$\sigma(C) = \sigma_1 (C - C_p)^t, \quad C > C_p \quad (1)$$

is  $t = 2.1$ , suggesting the formation of a three-dimensional network of conductive MWCNTs [18]. This exponent depends only on the dimensionality of the system.

The higher conductivity value for  $C = 3$  wt. % fMWCNT in Figs. 6(a) and 6(b), which does not fit the expression in (1), could have been caused by fMWCNT aggregation. Indeed, serious aggregation problems are known to appear in polymer composites with high CNT concentrations, these problems being however associated with a decrease in conductivity [17, 19]. In particular, in a rubbery epoxy matrix consisting of bisphenol A epichlorohydrine and a triethylenetetramine hardener, the samples with 4 wt. % MWCNT were found to be very viscous, such that MWCNT aggregates form due to an increasing difficulty of homogenization [15]. On the other hand, for  $C = 3$  wt. % MWCNT content the nanotubes could form a more conductive network between the electrodes due to a better dispersion in the matrix. This effect leads to the increase of the sample conductivity.

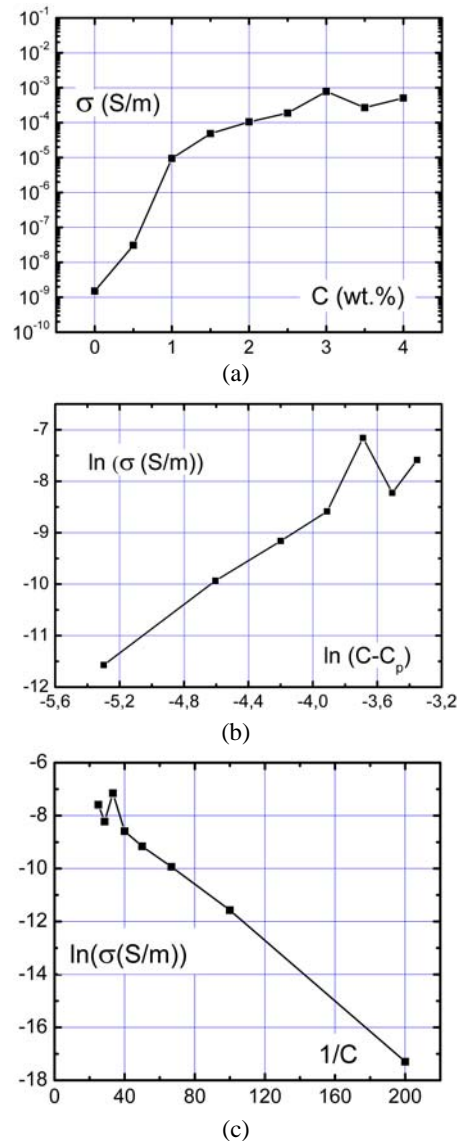


Fig. 6 Conductivity of fMWCNT-epoxy composites as a function of the fMWCNT mass concentration at RT.

Percolation-like conduction mechanisms occur in resins containing clusters of conductive fillers in close contacts. When the conducting fillers are not touching, tunneling between them is possible and the conductivity depends on the concentration of fillers as [20, 21]:

$$\sigma = \sigma_2 \exp(-K/C) \quad (2)$$

where  $\sigma_2$  and  $K$  are constants.

The tunneling mechanism is more probable in resins with a homogeneous distribution of fillers. In our samples, fMWCNTs are expected to distribute rather homogeneously, due to functionalization and sonication. As shown in Fig. 6(c), a tunneling mechanism is also compatible with experimental conductivity values, as long as the tunneling barrier does not vary with the applied

voltage. The last assumption is consistent with the observed linear current-voltage dependence. The percolation and tunneling mechanisms can coexist since the fMWCNT-epoxy resin can contain simultaneously regions with and without fMWCNT aggregates.

The temperature dependence of conductivity of several fMWCNT-epoxy composites was determined by applying a constant voltage of 5 V, heating the samples from RT up to 155 °C and subsequently cooling down to 55 °C. In Figs. 7(a) and 7(b) typical temperature dependences of conductivity are displayed for the samples with fMWCNT concentrations of 0.5 wt. % and 1 wt. %, respectively. Below 100 °C, the conductivity depends weakly on temperature for both samples, consistent with the suggested temperature-independent conduction mechanisms: percolation and direct tunneling. As in the case of dielectric constant, the conductivity is not reproducible at heating/cooling cycles, behavior that can be explained by the fact that heating occurs beyond 50 °C, threshold associated to the spatial rearrangements in composites. For all samples, we have observed an increase in conductivity at heating followed by a decrease in  $\sigma$  at cooling. Moreover, the conductivity values at heating and cooling differ significantly. For example, at 75 °C the ratio between these  $\sigma$  values is 2.25 for the 0.5 wt. % fMWCNT-epoxy compound and 1.56 for the 1 wt. % fMWCNT-epoxy compound. Such large differences between the conductivity at heating and cooling could be caused by the post-curing effect.

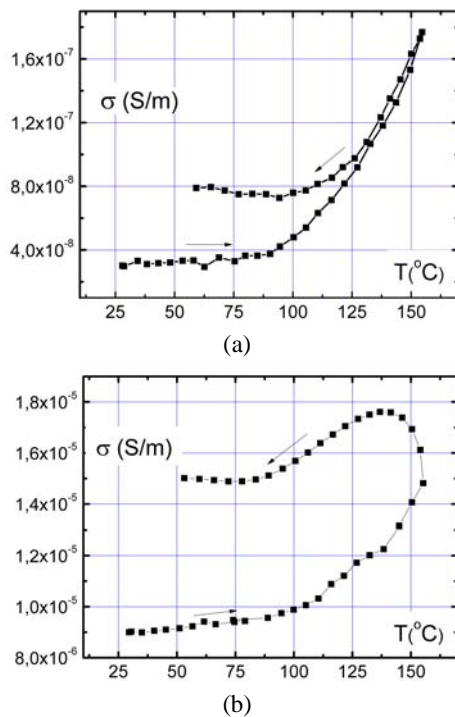


Fig. 7 Temperature dependence of the conductivity of epoxy composites with fMWCNT concentrations of (a) 0.5 wt. % and (b) 1% wt.

Indeed, similar large thermal hysteresis curves as in Fig. 7(b) are observed for many parameters (for example, density [10] and refractive index [22]) during curing, when the curing temperature of a thermosetting resin, such as DGEBA, differs from the  $T_g$  of the fully cured resin. The change in these parameters occurs because the epoxy network formation increasingly restricts the chain packing as the curing degree increases [10].

On the other hand, close to the percolation threshold, where conductive networks are just formed, the thermal hysteresis of conductivity associated to post-curing can be accompanied by other non-hysteretic and thermally-activated mechanisms at high temperatures. This is the case in Fig. 7(a), where the much lower conductivity value for the 0.5 wt. % fMWCNT-epoxy compound compared to that of the 1 wt. % fMWCNT-epoxy compound in Fig. 7(b) shows a peak almost reversible with the temperature above 125 °C.

The temperature dependence of  $\sigma$  in Fig. 7(a) can be used to identify the conduction mechanism associated with the high temperature region. In epoxy composites several conduction mechanisms are known to occur: variable range hopping of the Efros or Mott type at temperatures generally below RT [23], thermal fluctuation or electric field induced tunneling and simple activation-type conduction mechanisms [24], as well as several thermally activated conduction mechanisms described by generalized Arrhenius dependences [25]. Different transport mechanisms can dominate in different temperature ranges [23].

Taking into account the high temperature range in which the rapid increase of conductivity occurs, the most probable mechanism is a simple thermally activated conduction. Indeed, from Fig. 8 it follows that the conductivity at high temperatures satisfies the relation:

$$\sigma = \sigma_3 \exp(-E_a / k_B T) \quad (3)$$

where  $\sigma_3$  is constant and  $E_a$  is the activation energy of the process. The value obtained by fitting the experimental data in Fig. 8 is  $E_a \cong 0.32$  eV.

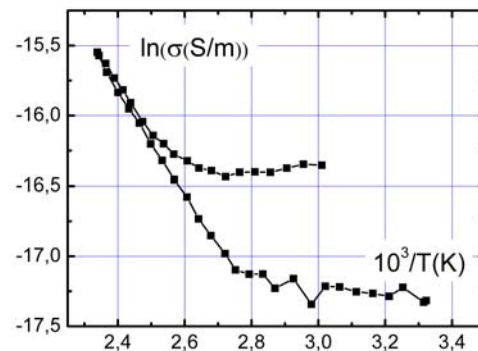


Fig. 8 Temperature dependence of the conductivity of the 0.5 wt. % fMWCNT-epoxy composite.

## 5. Conclusions

Functionalized MWCNT-epoxy composites with different fMWCNT mass concentrations were prepared and their structural, dielectric and electric characteristics, as well as their temperature dependence were investigated. It was found that low concentrations of fMWCNT significantly influence the bonds within composites as evidenced by FTIR measurements. DSC investigation showed a non-significant influence on  $T_g$  values with increasing concentration of fMWCNTs.

Dielectric measurements in a wide range of frequencies and temperatures were performed and non-reproducible values at heating and cooling were evidenced for the epoxy resin and the fMWCNT-epoxy composites when the temperature increased beyond 50 °C.

Percolation thresholds were observed for epoxy composites with only 0.5% wt. fMWCNT. Such low percolation thresholds are possible due to the high aspect ratio of the fMWCNT and to their functionalization, which assures a good dissipation into the epoxy matrix. The percolation conduction mechanism can coexist with tunneling at RT, while a thermally activated mechanism dominates electrical conduction at high temperatures. Electrical measurements also showed non-reproducible values at heating and cooling if temperatures beyond 55 °C were reached.

It was shown that the post curing process heavily affects the electrical properties of the resin and fMWCNT-epoxy composites. The non-reproducibility of dielectric and electric measurements were associated to post-curing effects that take place in the RT-cured samples. For temperatures lower than  $T_g$ , both permittivity and losses show reproducible values. Our results demonstrate that dielectric and/or electric measurements can provide a very sensitive method to monitor the behavior of fMWCNT-epoxy composites in various curing stages.

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\*Corresponding author: berbecaru2ciceron@yahoo.com