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To cite this article: S. Boukheir, Z. Samir, R. Belhimria, L. Kreit, M. E. Achour, N. Éber, L.C. Costa, A. Oueriagli & A. Outzourhit (2018): Electric Modulus Spectroscopic Studies of the Dielectric Properties of Carbon Nanotubes/Epoxy Polymer Composite Materials, Journal of Macromolecular Science, Part B, DOI: [10.1080/00222348.2018.1439243](https://doi.org/10.1080/00222348.2018.1439243)

To link to this article: <https://doi.org/10.1080/00222348.2018.1439243>



Accepted author version posted online: 09 Feb 2018.
Published online: 27 Feb 2018.



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Electric Modulus Spectroscopic Studies of the Dielectric Properties of Carbon Nanotubes/Epoxy Polymer Composite Materials

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ABSTRACT

The electrical properties of epoxy polymer/carbon nanotubes composites were characterized using impedance spectroscopy in the frequency range between 1 Hz and 10 MHz and temperature range between 25°C and 105°C. We report the analysis of the experimental data using the electric modulus formalisms to understand the dielectric relaxation mechanisms. The variation of the real and imaginary parts of the electric modulus versus frequency and temperature were suggestive of two relaxation processes, associated with dipolar relaxation and CNT-polymer interfaces. The Havriliak-Negami model of dielectric relaxation was used for modelling the relaxation processes, extracting the relaxation parameters.

ARTICLE HISTORY

Received 1 August 2017
Accepted 3 February 2018

KEYWORDS

Carbon nanotubes; dielectric relaxation; electric modulus; electrical properties; havriliak-negami model; impedance spectroscopy

Introduction

Carbon nanotubes (CNT) have recently emerged as the wonder materials of the new century and are being considered for a whole assortment of applications, ranging from large scale structures in automobiles to nanometer scale electronics.^[1] The electrical and electromagnetic properties of polymeric materials filled with multi-walled CNT have attracted enormous interest from both scientific and engineering standpoints.^[2-5] Based on the published results, it can be concluded that nanocomposites filled with high aspect ratio, conductive nanofillers exhibit more effective electromagnetic shielding and lower electrical percolation thresholds than the traditional composites based on microfillers such as carbon fiber. CNT are therefore highly attractive candidates for filler materials in composites.^[3]

In this work, the electrical properties of CNT/epoxy polymer composites were investigated to evaluate the change introduced by the CNT for various concentrations (up to 5.0%). From the electrical and dielectric results obtained from measurements in the frequency range of 1 Hz-10 MHz, we show that the addition of a small quantity of CNT

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significantly modified the electrical behaviour of a soft polymer matrix. Indeed, as the CNT concentration, ϕ , increased from 0.2% to 5.0%, the conductivity increased by five orders of magnitude. Electrical relaxation phenomena were present in these composites and their investigation was important to uncover the information related to molecular mobility polarization and conductivity mechanisms.^[6] Two dielectric relaxation processes were revealed in the frequency and temperature ranges of the measurements. One of these relaxations was associated with dipolar interactions at high frequencies for all CNT concentrations, whereas the other, appearing at lower frequencies, was consistent with the interfacial polarization effect and clearly appeared for all CNT concentrations at temperatures higher than 60°C, which was the glass transition temperature of the composite.^[7,8] These materials, consisting of an amorphous polymeric matrix and conductive CNT particles, are considered to be a heterogeneous, disordered system^[9] and the Havriliak–Negami equation is shown to describe their dielectric relaxations behavior.

Theoretical models

The effective complex permittivity $\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega)$ of a composite, in the frequency domain, characterizes the dielectric response of the system subjected to an external electric field, where ω , $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the angular frequency and the real and the imaginary parts of the complex permittivity, respectively. The imaginary part of $\varepsilon^*(\omega)$ can be written as the sum of two terms:

$$\varepsilon''(\omega) = \varepsilon''_{relax}(\omega) + \sigma_{DC}/\varepsilon_0\omega, \quad (1)$$

where σ_{DC} is the DC electrical conductivity and ε_0 is the vacuum permittivity. The term $\varepsilon''_{relax}(\omega)$ represents the contribution of the relaxation phenomena. Another way to analyze the raw experimental data is in terms of the electric modulus, $M^*(\omega)$, defined as the inverse of $\varepsilon^*(\omega)$, i.e.,

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = M'(\omega) + iM''(\omega), \quad (2)$$

where $M'(\omega)$ and $M''(\omega)$ are the real and the imaginary parts of the electric modulus, respectively, and can be expressed in terms of the complex dielectric constants via the following relations:

$$M'(\omega) = \frac{\varepsilon'(\omega)}{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)} \quad \text{and} \quad M''(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)}. \quad (3)$$

The use of the electric modulus offers some advantages in interpreting bulk relaxation processes, since it minimises variations in large values of permittivity and conductivity at low frequencies. Usually, in systems with a conductive component, an interfacial relaxation is obscured by conductivity and dielectric permittivity due to such common difficulties as electrode contact, space charge injection phenomena and

absorbed impurity conduction effects. By using the electric modulus formalism, such difficulties can be resolved.^[8]

To analyze the dielectric relaxations we used the Havriliak–Negami model to correctly fit the data.^[10,11] The real and imaginary parts of the modulus can be described by:

$$M' = M_{\infty} \frac{[M_s A^{\beta} + (M_{\infty} - M_s) \cos \beta \varphi] A^{\beta}}{M_s^2 A^{2\beta} (M_{\infty} - M_s) M_s \cos \beta \varphi + (M_{\infty} - M_s)^2}, \quad (4)$$

$$M'' = M_{\infty} M_s \frac{[(M_{\infty} - M_s) \sin \beta \varphi] A^{\beta}}{M_s^2 A^{2\beta} (M_{\infty} - M_s) M_s \cos \beta \varphi + (M_{\infty} - M_s)^2}. \quad (5)$$

Here

$$M_s = \frac{1}{\varepsilon_s}; M_{\infty} = \frac{1}{\varepsilon_{\infty}}; A = \left[1 + 2(\omega\tau)^{1-\alpha} \sin \frac{\alpha\pi}{2} + (\omega\tau)^{2(1-\alpha)} \right]^{1/2} \quad (6)$$

and

$$\varphi = \text{Arc tan} \left[\frac{(\omega\tau)^{1-\alpha} \cos \frac{\alpha\pi}{2}}{1 + (\omega\tau)^{1-\alpha} \sin \frac{\alpha\pi}{2}} \right]. \quad (7)$$

Here, M_{∞} is the modulus at high frequency, M_s is the static modulus, ε_s is the static relative permittivity at zero frequency, ε_{∞} is the relative permittivity at infinite frequency, τ is the relaxation time of the system, α is the shape parameter representing a symmetrical distribution of relaxation times and β is the shape parameter of an asymmetric relaxation curve.

Experimental

Materials

The multiwalled carbon nanotubes (MWCNT) were obtained from Cheap-Tubes Laboratories, USA. They had a diameter of about 50 nm, length in the range of 10–20 μm and purity higher than 95 wt%. They were dispersed in an insulating epoxy matrix DGEBA (diglycidyl ether of bisphenol A) produced by A. W. Chesterton Company, (USA), that had a density of 1.19 g cm^{-3} , DC conductivity of $1.4 \times 10^{-14} \text{ Sm}^{-1}$ and a glass transition temperature of about 60°C after polymerization. The CNT were mixed with the epoxy in various concentrations and stirred at room temperature, before adding 1% of hardener to make the mixture cohesive. Gelation took 5 minutes for each sample after pouring it into a mold at room temperature. The samples were unmolded after a few hours. Then they were left in rest for 24 h in order to reach a complete polymerization.

Differential scanning calorimetry measurements

Differential scanning calorimetry (DSC) was carried out using a DSC Q100 V9.9 Build 303 (TA Instruments Co.—USA) programmed between 0°C and 500°C , at a heating rate of $5^{\circ}\text{C}/\text{min}$. The results were used to determine the glass transition temperature of

the composite for four selected nanotubes concentrations besides the neat, undoped polymer.

Electrical measurements

For the electrical and dielectric measurements, we used samples with the shape of discs, having a thickness of 3 mm and diameter of 12 mm, cured as above. Before these measurements, the samples' surfaces were polished and covered with a thin layer of silver paint to ensure the electrical contact. DC conductivity measurements were carried out using a Model 617 electrometer (Keithley Instruments, LLC., USA). The experiment consisted of measuring the electrical resistance of each sample in order to determine the DC conductivity of the different composites, at a constant temperature of 25°C. The complex permittivity function, $\epsilon^*(\omega)$, was also measured, by using a dielectric analyzer Alpha-A combined with the impedance interface ZG4 (Novocontrol Technologies GmbH & Co. KG, Germany) in a 4-wire arrangement, in the frequency range from 1 Hz to 10 MHz under isothermal conditions at temperatures ranging between 25°C and 105°C. The samples were modeled by a lumped circuit consisting of a resistance and a capacitor in parallel. The experimental setup and the procedures for measuring $\epsilon^*(\omega)$ were similar to those in a previous study by several of us.^[12]

Results and discussion

Thermal results

The thermal properties of the CNT/Epoxy polymer composites were analyzed by the DSC technique. It was used to estimate the glass transition temperature, T_g , in these composite materials. The determination of T_g was carried out according to the method of the tangents.^[13] Figure 1 shows the DSC thermograms of the composites for five concentrations of CNT, in the temperature range from 30°C to 160°C, with T_g indicated. All measurements were carried out on samples of mass between 2.0 mg and 6.9 mg. It was observed that the

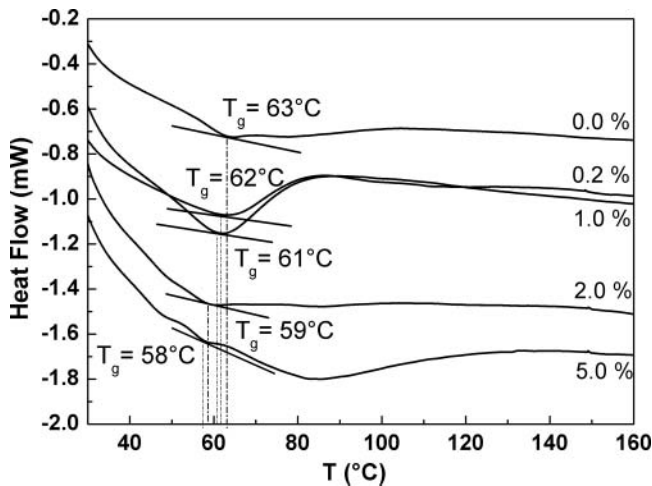


Figure 1. DSC thermograms of CNT/DGEBA polymer samples.

glass transition temperature decreased from 63°C for the neat polymer to 58°C for the sample with 5.0% CNT concentration. A decrease in T_g with increasing CNT content has also been reported in previous works and it can be attributed to the creation of a dense polymer package which is the result of this filler loading increase that affect the free volume of polymer.^[14-15] the phenomena of antiplasticization considered in terms of the free-volume formulation which leads to a decreased glass transition temperature were discussed also in other works.^[16-17]

DC electrical conductivity results

It is well known that the DC electrical conductivity of a polymer composite, as a function of the concentration of conducting particles, undergoes an insulator–conductor transition. This occurs at a critical concentration, ϕ_c , where the conductive particles contact each other and, as a consequence, a continuous electrical path is built throughout the polymer matrix.^[18] Figure 2 shows the CNT concentration dependence of the DC conductivity at constant temperature ($T = 300$ K). When the filler content was low, the mean distance between the conducting particles was large and the conductivity was restricted by the presence of the insulating matrix; however, by increasing the amount of fillers, the conducting particles became closer and, at the critical concentration, ϕ_c , the electrical properties were dominated by the particles,^[2] indicating an electrical percolation transition. We found $\phi_c = 2.7\%$ as the critical CNT concentration for our composite samples.

Dielectric and electric modulus results

At constant temperature

Figure 3 shows the imaginary and the real parts of the complex modulus for various concentrations of CNT, showing a decrease of the M'' maxima and the M' shoulders (in the inset of Fig. 3) with increasing concentration. The Nyquist plot of M'' as a function of M' is exhibited

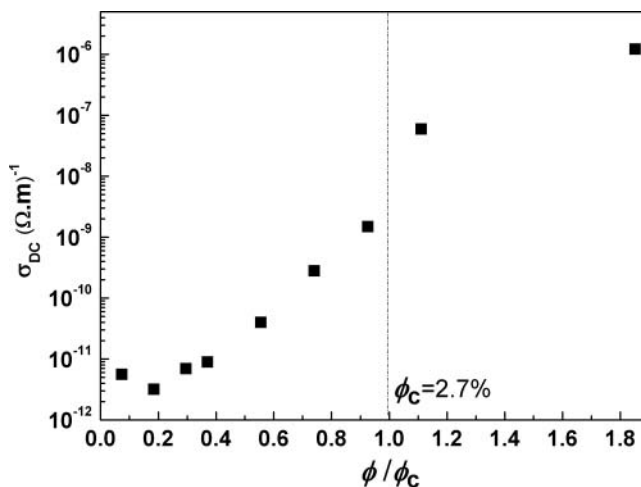


Figure 2. Variation of the DC conductivity, σ_{DC} , as the function of the CNT concentration ϕ at room temperature.

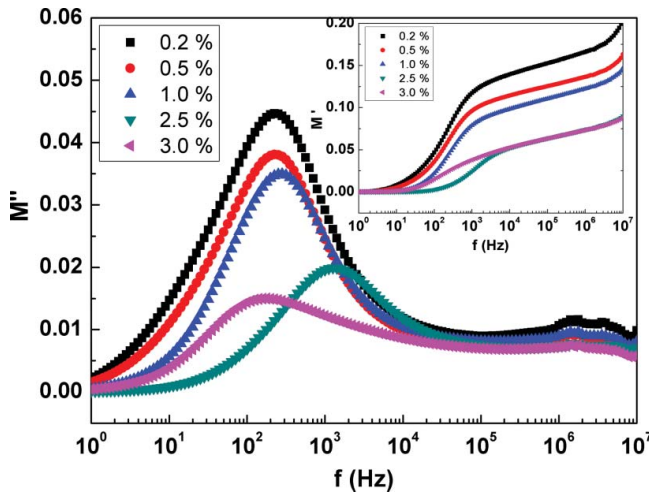


Figure 3. Imaginary part of the electric modulus, M'' , as a function of frequency for various CNT concentrations at a constant temperature of 85°C . The inset is a similar plot for the real part, M' .

in Fig. 4a for various CNT concentrations at 25°C . Two different relaxations are depicted for the $\phi = 3.0\%$ CNT concentration, while for ϕ equal 0.2%, 0.5%, 1.0% and 2.5%, only the beginning of the second relaxation is seen at low M' . Increasing the temperature to 85°C , both relaxations appeared more clearly for all concentrations (Fig. 4b). The observed relaxation behavior is the result of the combination of two polarization mechanisms that depend on the physical movement of the charges responsible for the dipoles and on the length of time required for their displacement.^[6] One mechanism originates from the dielectric properties of the polymer, which is generally attributed to the reorientation of dipoles, in particular of the polar OH groups. The other mechanism is related to the presence of the carbon

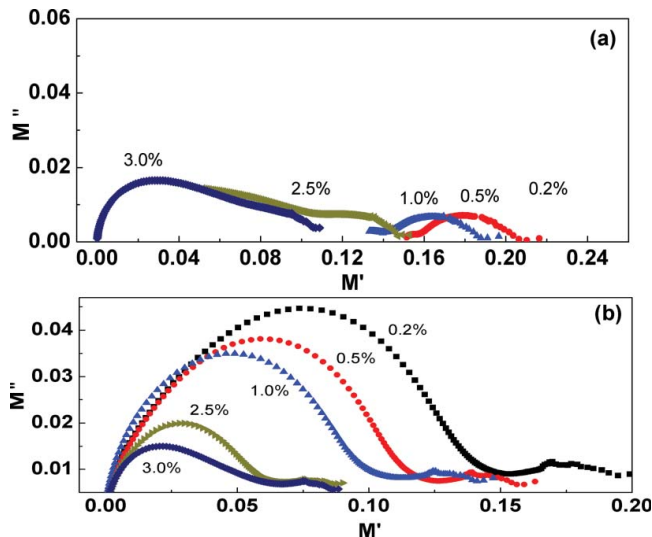


Figure 4. Imaginary part, M'' , of the complex modulus versus the real part, M' , for the various concentrations of CNT; (a) $T = 25^{\circ}\text{C}$. (b) $T = 85^{\circ}\text{C}$.

particles.^[19] This polarization mechanism causes an electric charge concentration at the carbon-epoxy interface,^[7] giving rise to Maxwell–Wagner–Sillars (MWS) polarization.^[8,19] In polymers and polymeric composite materials, interfacial polarization is almost always present because of the additives, fillers or even impurities which make these systems heterogeneous.^[8] The peaks of M'' formed at low frequencies in Fig. 3 (corresponding to those at low M' in Fig. 4) have been reported for the epoxy resin as being the consequence of interfacial relaxation processes.^[8]

At variable temperature

The temperature variations of the effective electric modulus spectra of a specific sample of the composite with $\phi = 1.0\%$ are shown in Fig. 5, which depicts the imaginary part and, in the inset, the real part of the electric modulus as a function of the frequency. For the temperatures of 25°C and 45°C, only one relaxation was noticed, at high frequencies. For temperatures at and above 65°C, a second relaxation, at low frequencies, also became detectable. Actually, some evidence of this second relaxation, though occurring below the tested frequency range, can be noticed already in the spectrum for 45°C. The relaxations may be characterized by two quantities: the location, f_{\max} , and the amplitude, M''_{\max} , of the maximum of the dielectric loss peak. Examination of Fig. 5 implies that for the low frequency relaxation f_{\max} depended strongly on the temperature; this dependence was weaker for the high f relaxation. Interestingly, for the latter relaxation, the amplitude M''_{\max} was nearly the same for all measurement temperatures. These conclusions were confirmed by the $M''(M')$ Nyquist plots belonging to various temperatures for the same sample, shown in Fig. 6. As already mentioned above, the relaxation peaks which appear at high f for all the concentrations below the percolation threshold and for the whole temperature range, have been attributed to the reorientation of dipolar groups. The relaxation at low frequency, which becomes detectable near the glass transition temperature, is related to the interfacial MWS polarization at the CNT–polymer interfaces.

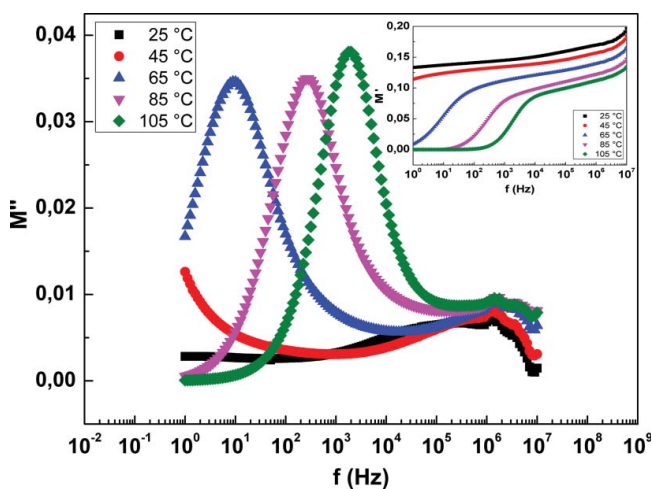


Figure 5. Imaginary part of the electric modulus, M'' , as a function of frequency for various temperatures at the concentration of $\phi = 1.0\%$. The inset is a similar plot for the real part M' .

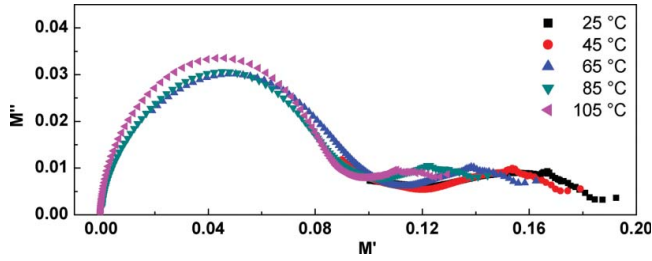


Figure 6. Imaginary part, M'' , of the complex modulus vs its real part, M' , for various temperatures, at the concentration of $\phi = 1.0\%$.

The experimental results can be theoretically interpreted in the framework of the Havriliak–Negami (H-N) model. In order to calculate its characteristic parameters, (α , β , M_s , M_∞), the experimental M' and M'' data were fitted by theoretical values (M'_{th} and M''_{th}) of the H-N model through a numerical simulation in the complex plane. The best fit parameter values of α , β , M_s , and M_∞ were obtained by a successive approximation method, minimizing the expressions^[20]:

$$x_{M'}^2 = \sum_i (M'_{th} - M')^2, \quad (8)$$

$$x_{M''}^2 = \sum_i (M''_{th} - M'')^2 \quad (9)$$

The Nyquist plots of the complex electric modulus of the sample with $\phi = 1.0\%$ CNT concentration for the various temperatures are depicted separately in Fig. 7 for the dipolar

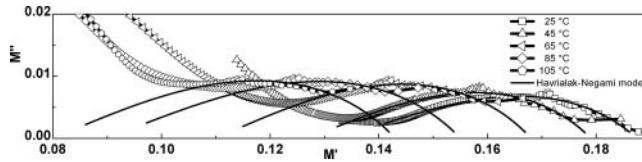


Figure 7. Nyquist plot of the complex electric modulus of the sample with $\phi = 1.0\%$ CNT concentration at various temperatures for dipolar relaxation peaks. Solid lines are fits to the Havriliak-Negami equations.

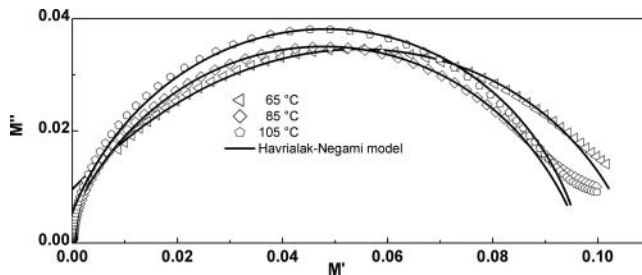


Figure 8. Nyquist plot of the complex electric modulus of the sample with $\phi = 1.0\%$ CNT concentration for MWS relaxation peaks. Solid lines are fits to the Havriliak-Negami equations.

Table 1. Parameters evaluated by fitting data according to the Havriliak-Negami equations for composite samples of $\phi = 0.2\%$, 1.0% and 3.0% ; dipolar relaxation peaks.

ϕ (%)	T (°C)	α	β	$\Delta M = M_{\infty} - M_s$	τ (10^{-7} s)
0.2%	25	0.42	0.53	0.066	5.640
	65	0.485	0.53	0.069	0.790
	105	0.49	0.55	0.082	0.450
1.0%	25	0.44	0.45	0.052	6.330
	65	0.49	0.48	0.058	0.710
	105	0.49	0.50	0.063	0.564
3.0%	25	0.48	0.54	0.040	2.000
	65	0.51	0.60	0.042	1.004
	105	0.50	0.625	0.046	0.709

relaxation and in Fig. 8 for the MWS relaxation. In the figures the solid lines represent the best fits to the Havriliak-Negami equations (4)–(7). They show that at the concentration used ($\phi = 1.0\%$), below the percolation critical concentration $\phi_c = 2.7\%$, the relaxation processes can be well interpreted using the H-N model. The parameters (α , β and $\Delta M = M_{\infty} - M_s$), evaluated by fitting the experimental data in Fig. 7 and Fig. 8, are listed in Table 1 and Table 3, respectively, for the three temperatures, and for the three CNT concentrations, including samples below ($\phi = 0.2\%$, 1.0%) and above ($\phi = 3.0\%$) the percolation threshold. In the case of the dipolar relaxation, the fitting to the H-N model provided α and β values close to each other, for all concentrations and even for increasing temperatures (Table 1). For these dipolar relaxation peaks, the modulus strength, ΔM , increased with the increase of the temperature for each CNT concentration, while at a constant temperature, ΔM decreased with the increase of filler concentration. In this case, α increased with both the increase of temperature and the increase of the CNT concentration, indicating fewer dipoles interactions. For the MWS relaxation, the same parameters in Table 3 exhibited higher values compared with those reported in Table 1. Nevertheless, the same remarks hold

Table 2. Activation energy for various volume concentrations of CNT obtained from the electric modulus.

ϕ (%)	E (meV)
0.2	2.70
0.5	2.70
1.0	2.60
3.0	2.50

Table 3. Parameters evaluated by fitting data according to the Havriliak-Negami model for composite samples of $\phi = 0.2\%$, 1.0% and 3.0% ; MWS relaxation peaks.

ϕ (%)	T (°C)	α	β	$\Delta M = M_{\infty} - M_s$	τ (10^{-2} s)
0.2%	65	0.75	0.73	0.143	1.700
	85	0.78	0.75	0.140	1.590
	105	0.83	0.76	0.136	0.071
1.0%	65	0.74	0.74	0.107	5.920
	85	0.77	0.76	0.099	1.790
	105	0.81	0.78	0.097	0.056
3.0%	25	0.62	0.68	0.055	9.100
	65	0.67	0.71	0.056	0.200
	85	0.70	0.72	0.054	0.089
	105	0.76	0.73	0.049	0.025

Table 4. Activation energy for various volume concentrations of CNT obtained from the electrical modulus.

ϕ (%)	E (meV)
0.2	5.9
0.5	5.1
1.0	2.6
3.0	2.2

in this case too; the values of α and β do not show a large gap. An increase of α with the increase of temperature was noticed for each sample, while α had a decreasing tendency upon increasing the CNT concentration indicating an increase of the heterogeneity. For this kind of relaxation, the modulus strength (ΔM) in Table 3 diminished with both increasing temperature and CNT concentration. Similar results were obtained by Tsangaris et al.^[8] for the binary composites of epoxy resin with Kevlar (poly-paraphenylene terephthalamide) fibres, and in hybrid composites of epoxy resin with Kevlar fibres and aluminum particles as fillers. These authors showed that the increase in heterogeneity shifts the relaxation process to lower frequencies indicating the MWS nature of the effect.

In order to further characterize the dielectric relaxation in the CNT/DGEBA composites, it is important to estimate the activation energy associated with the relaxation process; it can be obtained from the temperature dependence of the apparent relaxation time, according to the relation^[20,21]:

$$\tau = \tau_0 * \exp\left(\frac{E}{K_b T}\right). \quad (10)$$

Here E is the activation energy associated with relaxation process, τ is the relaxation time, K_b is the Boltzmann's constant, and T is the absolute temperature. Plotting the relaxation times that best fit the experimental M spectra versus the inverse of temperature yielded the activation energies that are listed in Tables 2 and 4; they show a decrease in E with the increase of CNT concentration, both for the dipolar and the MWS relaxations. It is noteworthy that the E values were significantly sensitive to the concentration, ϕ , of the CNT. These results indicate the existence of an interaction between the filler and the polymer for CNT loadings below the percolation threshold.

Conclusions

The electrical modulus formalism was used to interpret the dielectric relaxation processes of CNT/epoxy composite and is shown to be suitable for the investigation of their dielectric behavior. According to the analysis of the behavior of the composites studied in this work, the complex permittivity and the complex electric modulus contained the same information. However, the electric modulus formalism was capable of revealing the interfacial relaxation which, in most cases, is covered by the conductivity of the material when represented in the dielectric permittivity mode. Thus, this effective representation of the information offers a significant advantage and makes possible the determination of the relaxation parameters and the activation energies using the

relaxation times. The dipolar and MWS relaxations led to different behaviors of the parameters with changes in the CNT concentration and temperature. The calculated relaxation parameters and the broader distribution of relaxation times showed that when the filler concentration increased, the system became more heterogeneous.

Acknowledgment

Financial support by the Moroccan (CNRST) – Hungarian (NKFIH) bilateral project TÉT_12_MA-1-2013-0010 and the Budapest Neutron Centre (www.bnc.hu) are gratefully acknowledged. We also acknowledge FEDER funds through the COMPETE 2020 Programme and National Funds through the FCT – Portuguese Foundation for Science and Technology under the project UID/CTM/50025/2013.

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