Effect of temperature and filler concentration on the electrical parameters of a dispersion of carbon nanotubes in an epoxy matrix

S.BOUKHEIR[1,2,*], M.E. ACHOUR[2], OUERIAGLI[1], A. OUTZOURHIT[1], N.ÉBER[3], L.C. COSTA[4]

[1]LN2E Laboratory , Faculty of Sciences, Sémlalia, Cadi Ayyad University, Marrakech, Morocco

[2]LASTID Laboratory , Faculty of Sciences, Ibn Tofail University, Kenitra, Morocco

[3]Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences Budapest, Hungary

[4]I3N and Physics Department, University of Aveiro, Aveiro, Portugal

Corresponding author : E-mail: boukheirsofia@gmail.com

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Abstract. We have investigated the electrical properties of carbon-nanotubes-loaded DGEBA polymer composites in the frequency range between 1Hz and 10 MHz and temperature range between 25°C and 105°C. The frequency dependence of electrical data have been analyzed in two frameworks: the electrical modulus formalism with the Kohlrausch-Williams-Watts stretched exponential function (KWW) and the electrical conductivity by using the Jonscher's power law. The stretching exponent β_{KWW} and the Jonscher exponent n are found to be temperature dependent for all carbon nanotubes concentrations and show a very slight variation with increasing the amount of filler percentage at room temperature.

Introduction

Multiwall carbon nanotubes (MWCNTs) have several characteristics (such as flexibility, low mass density, and large aspect ratio) that make them excellent for improving the electrical properties of polymers [1]. Due to their reduced size and dimensionality, carbon nanotubes form complex networks of aggregates within the composite materials [2]. Samples containing different volume concentrations (0.2% to 5%) of MWCNT were studied by impedance spectroscopy. Complex impedance spectroscopy is a nondestructive method that allows us to study the electrical properties of multiwall-carbon-nanotubes-based polymer composite samples. This technique can correlate the structural and electrical characteristics of composites in a wide range of frequencies and temperatures, as we already reported in previous works [3]. It is by now well demonstrated that carbon nanotubes and carbon-nanotube-based polymer composites have the potential to be applied as effective sensing devices in various applications [4]. In the present paper we report the electrical conductivity and modulus properties of epoxy polymer composites loaded with multiwall carbon nanotubes, investigated in the frequency range of 1 Hz to 10 MHz and temperature range between 25°C and 105°C. The obtained spectra were analyzed by appropriate theoretical models, as discussed below.

Methodology

The composite samples investigated were MWCNTs (Cheap-Tubes, USA Laboratories) with the diameter of the primary CNT about 50 nm, the length in the range of 10 – 20 μm and the purity higher than 95wt%, dispersed in an insulating epoxy matrix DGEBA (diglycidylic ether of bisphenol A) with a density of 1.19 (g/cm^3), a conductivity of the order of $\sigma_{\mathrm{DC}} = 1.4*10^{-14}$ $(\Omega\mathrm{m})^{-1}$ and a glass transition temperature about $T_{\mathrm{g}} = 60$ °C. We added the MWCNTs to the epoxy resin in different concentrations, before adding 1% of hardener to make each mixture cohesive. The mixture was stirred at room temperature. Each sample of the MWCNTs /DGEBA took 5 min to gelate after pouring it into the mold. After a few hours we unmolded our samples, which took several weeks for reaching a complete polymerization. The percolation threshold for this series of samples is about ϕ_C =2.7%. The temperature dependent AC impedance spectra were measured with a Novocontrol Alpha-A Analyzer combined with the impedance interface ZG4 in a 4 wire arrangement, in the frequency range of 1 Hz to 10 MHz. Measurements and data recording were performed with the WinDeta software [5].

The bulk AC conductivity was determined by nonlinear mean-square-deviation curve fitting of the impedance spectrum using the WinFit program provided by Novocontrol, Hundsagen, Germany [5].

Theoretical models

The electrical modulus, M*, is defined as:

$$M^*(\omega) = M^{'}(\omega) + iM^{''}(\omega) \qquad (1)$$

where M'(ω) and M"(ω) are the real and imaginary parts of the electrical modulus. The non-exponential conductivity relaxation could be described by using the Kohlrausch-Williams-Watts (KWW) function [6], which represents the distribution of the relaxation times in charges conducting materials [7]. The frequency dependent complex modulus can be given as:

$$M^*(\omega) = M_\infty \left[1 - \int_0^\infty \exp(i\omega t)\,(-d\emptyset/dt)dt\right] \qquad (2)$$

$$with \quad \emptyset(t) = \emptyset_0 \exp\left(-\frac{t}{\tau_\sigma}\right)^{\beta_{KWW}} \qquad (3)$$

where M_∞ represents the asymptotic value of $M'(\omega)$ when $\omega \to \infty$, τ_σ is the conductivity relaxation time and β_{KWW} is the Kohlrausch exponent; its value is located in the range $0 < \beta_{\mathrm{KWW}} \leq 1$. Furthermore, the total conductivity at a given temperature over a wide range of frequencies can be written as [8]:

$$\sigma_{tot}(\omega, T) = \sigma_{DC}(T) + \sigma_{AC}(\omega, T) \qquad (4)$$

Here σ_{DC} is the DC conductivity and

$$\sigma_{AC}(\omega, T) \propto \omega^{n(T)} \qquad (5)$$

is the AC electrical conductivity following Jonscher's power law [9]; $n(T)$ is the power exponent depending on the temperature, which fulfils $0 \leq n(\mathrm{T}) \leq 1$.

Results

Figure 1 shows the variation of the conductivity as a function of the frequency at room temperature, for three different volume concentrations of MWCNT. At low frequencies, for the concentrations above ϕ_C, the AC conductivity is almost independent of frequency, approaching the DC conductivity in the plateau region, while at high frequency the conductivity has a dispersion that shifts to higher frequencies with increasing MWCNT. Several studies show that the dielectric response of the composites conductor/insulator obeys the Jonscher power laws [9]:

$$\sigma_{\mathrm{AC}}(\omega) = A\,\omega^{n(T)}.$$

The relaxation behavior is analyzed using the complex electric modulus, which reflects only the dynamic properties of the sample without the polarization effects at the interface, with a Kohlrausch-Williams-Watts (KWW) distribution of relaxation times. The variation of imaginary M" (ω) part of the electrical modulus as a function of frequency at room temperature is shown in Figure 2. the asymmetric M"(ω) is immediately suggestive of stretched exponential relaxation behaviour.

The parameters n and β_{KWW}, which were obtained from the analysis by fitting to the Jonscher's power law and the Kohlrausch-Williams-Watts (KWW) function, respectively, are depicted in Figure 3 as the function of the concentration of the carbon nanotubes at room temperature. The parameter β_{KWW} is calculated by using the relation $\beta_{\mathrm{KWW}} = 1.14/FWHM$, where $FWHM$ is the full width at half height of the frequency dependent modulus spectrum. The exponent n was measured as the slope of the frequency dependent AC conductivity spectrum in the high frequency region. We found n values ranging between 0.84 and 0.94, and β_{KWW} values ranging between 0.40 and 0.50. Below a concentration of 2.0% of MWCNT, the two parameters do not show any significant change with increasing the concentration, but we can observe that they slightly decrease above this MWCNT concentration of 2.0%.

The temperature dependence of the stretched exponent β_{KWW} and the Jonscher exponent n is depicted in figure 4; $n(T)$ decreases slightly with the temperature increasing from 25°C to 105°C, whereas β_{KWW} increases significantly with temperature. The variation of n with temperature can be related to the existence of a distribution of the relaxation parameters [10].

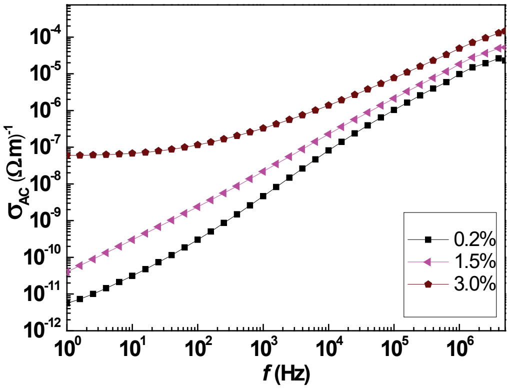

Fig 1. σ_{AC} versus frequency at room temperature for three selected carbon nanotube concentrations.

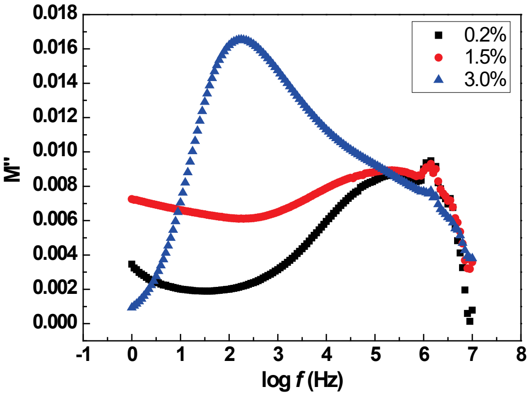

Fig 2. Imaginary part of the complex modulus at room temperature for three selected carbon nanotube concentrations.

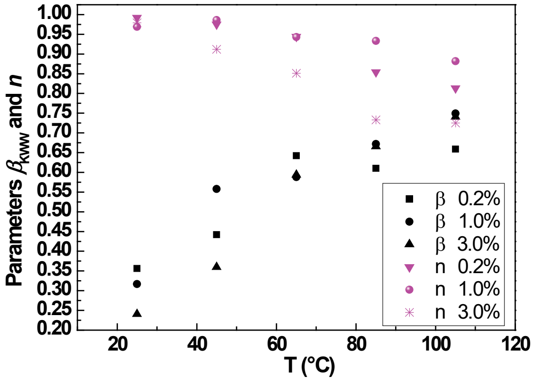

Fig. 3. Electrical parameters, β_{KWW} (obtained from fitting by KWW function) and n (from the conductivity power law), as a function of volume concentrations of carbon nanotubes, at room temperature.

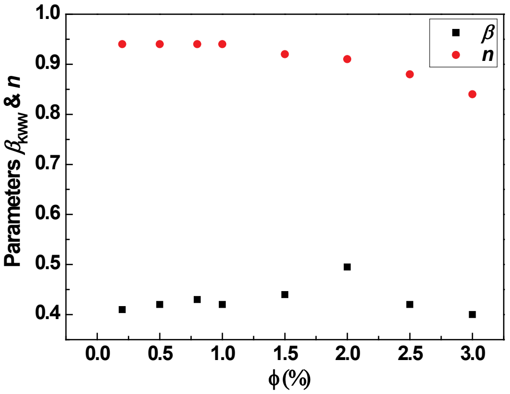

Fig. 4. The temperature dependence of the stretched exponent β_{KWW} and the Jonscher exponent n.

Conclusion

The complex electric modulus model and the Jonscher's power law have been used to investigate the electrical properties of carbon-nanotubes-loaded polymer composites. The stretching exponent β_{KWW} representing the degree of interaction and the exponent n obtained by Jonscher's power law are found to be temperature-dependent. This result confirms the fact that the dielectric response show significant change with temperature.

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