Impedance study of polymethyl methacrylate composites/multi-walled carbon nanotubes (PMMA/MWCNTs)

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A R T I C L E   I N F O

Article history:
Received 6 July 2011
Received in revised form
19 November 2011
Accepted 7 December 2011

Keywords:
Nanocomposites
Impedance
ac conductivity
Dielectric constant
Electrical percolation

A B S T R A C T

The dielectric behavior of polymethyl methacrylate/multi-walled carbon nanocomposites (PMMA/MWCNTs) was investigated using impedance spectroscopy technique. The composites were prepared using melt mixing with MWCNTs loading ranging from 0.01 to 10 wt%. The experimental results showed that the measured impedance reflects the insulating behavior of the host material (PMMA) with no appreciable effects of the filler less than 8.5 wt%. However, for the sample containing 10 wt%, the calculated value of dc conductivity increases with increasing temperature from $2.0 \times 10^{-6} \text{ (}\Omega \text{m})^{-1}$ to attain a value of $4.8 \times 10^{-5} \text{ (}\Omega \text{m})^{-1}$ at 110°C. The percolation threshold derived from the dielectric data was estimated to be higher than 8.5 wt% and lower than 10 wt%. A temperature dependent electrical relaxation phenomenon was only observed in the sample containing 10 wt% of MWCNTs. The frequency dependence of the ac conductivity data followed a power law.

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1. Introduction

The presence of metallic nanoparticles in controlled manner within an insulating matrix can greatly influence the electrical, mechanical and optical properties of the original material. In this context, carbon nanotubes (CNTs) have received enormous attention in order to produce new advanced composite materials with multifunctional properties. CNTs attracted attention as a conductive filler in insulating polymer matrices due to their excellent mechanical strength, high electrical and thermal conductivity. The preparation of carbon nanotube composite materials is now rapidly growing subject [1,2]. The CNT-based composites have been extensively studied using different matrix materials. In this regard, various polymers have been used to produce composites materials, such as, thermoplastics [3,4], thermosetting resins [5,6], liquid crystalline polymers [7,8], and water soluble polymers [9]. However, several methods have been developed to prepare MWCNTs/polymer composites, such as, melt processing [10,11], extrusion [12], mechanical stretching [13], spins coating [14], latex technology [15], a conjugated method [16], and in situ polymerization [17]. On other hand, carbon nanostructures differ with regard to their diameter, aspect ratio, crystallinity and crystalline orientation. These structural variations dramatically alter the intrinsic properties and behavior in composite systems. Carbon nanotubes have been used as conductive fillers in epoxy composites. It was shown that both the percolation threshold and the maximum conductivity appear to depend on the property of the conducting filler, dispersion of the conducting fillers in polymeric matrix, the alignment of CNTs in the matrix and the interaction between the fillers and the polymer [18–22].

In this paper the dielectric behavior of PMMA/MWCNT composites was reported using impedance spectroscopy technique in the frequency range 10 to $10^5$ Hz and in the temperature range 30–110°C at different content of MWCNTs.

2. Experimental

2.1. Materials

PMMA/MWCNT samples were prepared at Queen's University-Belfast. In order to achieve high state of dispersion of MWCNT in the PMMA matrix, the later was grounded from pellet size (mm) to a fine powder having an average particle size of 250 µm prior to melt mixing with an appropriate amount of MWCNTs. Samples prepared by the catalytic chemical vapor deposition method were chosen in our current investigation which marked as PMMA (powder) CNT-C in reference [23]. The details of the starting materials, the preparation method and structural properties were reported in [23].

2.2. Impedance Measurements

Ac impedance measurements were carried in the frequency range between 1 and $10^5$ Hz and in the temperature range 30–110°C, using a Solartron-1260 Impedance/Gain Phase

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Analyzer with a 1296 dielectric interface. Two software packages, Z-60 and Z-View were used to maximize the performance and data handling of the system. By measuring the amplitude and the phase shift of the resulting current, one can calculate the real and imaginary components of the complex impedance. From the calculated values of the real and imaginary components of complex impedance the real and imaginary components of dielectric constant, dielectric loss and ac conductivity were determined and plotted as a function of frequency at different temperatures.

3. Results and discussion

Generally, the electrical behavior of materials can be characterized in terms of four complex quantities, namely, impedance ($Z'$), admittance ($Y'$), modulus ($M'$) and permittivity ($\varepsilon'$). Employing impedance spectroscopy, the real and imaginary parts of $Y'$, $M'$ and $\varepsilon'$ can be determined from the real and imaginary components of $Z'$ [24,25].

In this paper we report our results in terms of the real and imaginary components of the complex $Z$ and $\varepsilon$ to study the effect of carbon nano-tubes weight ratio on the electrical behavior of PMMA/MWCNTs composites.

Fig. 1 shows the plot of real and imaginary components of the complex impedance of MWCNTs at different filler ratios, the general behavior for samples contain 0 up to 8.5 wt% shows the same features with no dispersion was observed in the impedance spectrum indicating that the material is highly capacitive. However, we conclude that introduction of MWCNTs into the PMMA matrix does not affect the electrical properties of the samples that contain less than 8.5 wt% of MWCNTs. Therefore, a comparison will be done for just the two samples contain 8.5 and 10 wt% since the behavior for the samples contain less than 8.5 wt% is similar.

The real component of the complex impedance is shown in Fig. 2a and b for the samples containing 10 and 8.5 wt% of MWCNTs respectively as a function of frequency at different temperatures. Impedance spectrum for 10%wt of MWCNTs shows high dependent on both frequency and temperature. The general feature of the graph is similar to the impedance of RC circuit in parallel where $Z$ varies with the inverse of frequency in the frequency range $10^2$ Hz to about $10^6$ Hz due to its predominant capacitive behavior, and then all the curves merge together at higher frequencies. This behavior clearly indicates the presence of charge polarization. However, at frequency less than 100 Hz the values of $Z'$ become frequency dependent and increase with decreasing temperature indicating an increase in its conductivity. For sample contains 8.5 wt% of MWCNTs, there is a dramatic increase in the values of $Z'$ (see Fig. 2b) with decreasing frequency and then the values of $Z'$ attain a constant value for frequencies above $10^6$ Hz. Similar to that observed for sample contains 10% of MWCNTs as a result of space charge polarization.

Fig. 1. Variation of the real and imaginary component of impedance ($Z$, $Z'$) with frequency. The figure shows different MWCNTs concentrations embedded into PMMA matrix for temperature $T=30\, ^\circ \text{C}$.

Fig. 2. Variation of the real component of impedance ($Z$) with frequency at different temperatures for the sample contains (a) 10 wt% and (b) 8.5 wt% of MWCNTs.
the distances between the fibers are too large with no possibility of hopping process.

To study this phenomenon closely, a complex impedance plot of $Z'$ versus $Z''$ (Nyquist plot) is plotted as shown in Fig. 4a for the sample containing 10 wt%. The plot yields a single semicircle centered at $(\frac{R_s + R_p}{2}, 0)$ with radius $R_p/2$ according to the relation $(Z' - \frac{R_s + R_p}{2})^2 + Z''^2 = \frac{R_p^2}{2}$, where the subscripts $p$ and $s$ refer to the equivalent parallel and series circuits respectively. The angular frequency $\omega_{\text{max}}$ of the peak maxima and the centers of the semicircles coincide, and are given by the reciprocal of the conductivity relaxation time ($\tau$) according to the relation $\omega_{\text{max}} = 2\pi f_{\text{max}} = \frac{1}{\tau} = \frac{\sigma_{\text{dc}}}{\varepsilon_0}$, where $\sigma$ corresponds to the dc conductivity, $\varepsilon_0$ is the permittivity of free space and $\varepsilon''$ is the dielectric loss. The diameter of the semicircle corresponding to the bulk resistance of the sample which decreases with increasing temperature [24]. This pronounced behavior can be attributed to an activated conduction mechanism. However, for fillers ratios ranging from 0 to 8.5 wt%, the plot of $Z'$ versus $Z''$ yields straight lines indicating that the material is highly capacitive (see Fig. 4b) [24,25].

Fig. 3. Variation of the imaginary component of impedance ($Z''$) with frequency at different temperatures for the sample contains (a) 10 wt% and (b) 8.5 wt% of MWCNTs.

Fig. 4. Complex impedance plot at different temperatures for the sample contains (a) 10 wt% and (b) 8.5 wt% of MWCNTs.

Fig. 5. The natural logarithm of dc conductivity versus $1/\text{absolute temperature}$ for the sample contains 10 wt% of MWCNTs.
Measuring the diameter of the semicircles allow us to determined the \( dc \)-conductivity of the material from the relation \( \sigma = 1/R_p(A/d) \), where \( A \) is the area of the sample and \( d \) is the thickness. The calculated value of \( dc \) conductivity increases with increasing temperature from \( 2.0 \times 10^{-6} (\Omega \text{m})^{-1} \) to attain a value of \( 4.8 \times 10^{-6} (\Omega \text{m})^{-1} \) at 110 °C. The \( dc \)-conductivity dependence on temperature was found to follow an Arrhenius equation in the form \( \sigma = \sigma_0 \exp(-\Delta E/kT) \) where \( \Delta E \) is the activation energy, \( k \) is the Boattman constant and \( T \) is the absolute temperature [25].

Fig. 5 shows the logarithmic plot of the \( dc \)-conductivity as a function of the reciprocal temperature. The nature of conductivity variation with rise in temperature together with a typical Arrhenius-type behavior suggests that the electrical conduction in the material is thermally activated. The activation energy, calculated from the slope of the graph was found to be \( 0.60 \pm 0.02 \text{ eV} \).

The above results indicate that the nano-tubes were specially separated from each other and the average distance between them is larger than that necessary for electron hopping or tunneling to take place (see [23] and the references therein). Additionally, the promoted interactions between polymer chains and functional groups on the surface of a nanotube may account for the overall reduction in electrical conductivity as a layer of insulating polymer may hinder electron flow by increasing the distance required for an electron to travel from tube to another one. Moreover, recent Monte Carlo studies have provided an estimate of the maximum tunneling distance is such composites to be about 1.8 nm [23]. In this case, the electrical properties are mainly governed by the electrical characteristics of the matrix. Therefore, the regions between the carbon nanotubes can be regarded as micro-capacitors network (insulating regions) leading to very high values of \( Z \). At 10 wt% ratio, the average distance becomes small enough where the electrons can tunnel through the polymer. As a result, the conductivity increases to attain a value \( 4.8 \times 10^{-6} (\Omega \text{m})^{-1} \).

The transition from an insulating to conducting composite as a function of filler loading is known as percolation [25]. This transition can only happen when the fillers were able to build a three dimensional network that facilitates electron hopping or tunneling. The reported percolation threshold for carbon/polymer
depends on the polymer matrix, the processing technology and the characteristics of carbon nanotubes. Sandler et al. [26] reported a percolation threshold of 11 wt% of multiwall carbon nanotubes/poly(3-octylthiophene) composites. On the other hand, Kymakis et al. [27] found that the percolation threshold of multi-walled carbon polymer/epoxy composites is in the order of 0.0025 wt%. For the samples of PMMA/MWCNTs used in this study the results reveal that the percolation threshold is between 8.5 wt% and 10 wt% [23].

Fig. 6 shows the frequency dependence of the dielectric constant at 30 °C for different volume fractions of MWCNTs. The figure clearly demonstrates that the dielectric constant is frequency independent when the concentration is 8.5 wt% or less. For the 10 wt% sample, the dielectric constant strongly depends on frequency and decreases all the way with increasing frequency. This behavior was ascribed to the way in which charges accumulated at the interface between the conducting MWCNTs and the insulating matrix [28]. Quantitatively, the dielectric constant at 30 °C decreases from ~22 to 10 in the frequency range 0.2–100 kHz. The dielectric constant at 1.0 kHz at different temperatures as a function of the volume fraction of MWCNT is shown in Fig. 7. The figure clearly shows a jump in the dielectric constant as the MWCNT content varies from 8.5 to 10 wt% confirming that the percolation limit lies in this region. This result supports our previous conclusion that below 10 wt%, the conductive particles are separated from each other and the electrical conductivity of the composite is dominated by an insulating matrix. Therefore, the value of the dielectric constant is close to that for pure PMMA. At the percolation threshold, these clusters form a connected three dimensional network through the bulk resulting in a jump in the dielectric constant.

The ac conductivity of all samples has been calculated from the dielectric loss according to the relation:

\[
\sigma' = \varepsilon_0 \varepsilon'' \Delta \epsilon'(\omega) = \varepsilon_0 \sigma'' = \varepsilon'' \Delta \sigma(\omega),
\]

where \( \varepsilon' \) and \( \varepsilon'' \) are the dielectric constant and the dielectric loss respectively. The total conductivity is given by:

\[
\sigma = \sigma_c + \sigma_m(\omega),
\]

where \( \sigma_c \) is the dc conductivity which can be obtained by extrapolating \( \sigma \) to \( \omega = 0 \), and \( \sigma_m(\omega) \) can be obtained by subtracting the dc conductivity from the measured total conductivity [24,25].

Fig. 8 shows the frequency dependence of the ac conductivity for sample contains 10 wt%. At low frequency, the conductivity has low values and nearly independent of frequency indicating a big share of capacitative elements in the sample. At high frequency, the values of the ac conductivity is close to that of semiconductor material and follow the universal Jonscher’s power law \( \sigma = \sigma_0 \omega^n \), where \( n \) is a fractional exponent used to describe the ac component contributing to the dispersive region [29].

Fig. 9 represents the ac conductivity determined by subtracting the dc conductivity from the measured conductivity. It can be seen from the figure that \( \sigma_m \) increases with increasing frequency. The variation of ac conductivity with frequency calculated for the exponent s is nearly temperature independent and its value in the order of 0.86 ± 0.02. This result is in a good agreement with the values reported in the literature for the inter cluster polarization mechanism [30]. A cartoon model illustrating the electrons hopping mechanism between the inter-cluster connecting networks is depicted in Fig. 10. The electrons hopping between the inter-cluster is not possible as the separating distance \( l \) between them exceeds a critical values \( l_c \) (i.e., below the percolation threshold). On the other hand, as the filling ratio exceeds the percolation limit, electrons hopping is possible and an increase in the electrical conduction in the PMMA matrix is observed.

4. Conclusions

The dielectric parameters of the PMMA matrix are greatly influenced by the addition of MWCNTs. The electrical properties of the PMMA matrix were not affected by the addition of low MWCNTs concentrations. The experimental data for the dielectric constant at filling ratio less than 8.5 wt% of CNT used in this study only show a monotonic increase of the dielectric constant with increasing concentration of nanotubes in the composite. However, at the optimum concentration of 10 wt% the material exhibits enhanced conductivity and shows values close to that of semicrystalline materials. This large increase in conductivity was explained by space charge polarization effect and percolation effect. The percolation threshold was estimated to be higher than 8.5 and lower than 10 wt%.

Acknowledgment

The financial support from the Hashemite University should be acknowledged.

References
