PROBING THE ELECTRIC RESPONSE AND FUNCTIONALITY OF MWCNT/ Fe_3O_4/ EPOXY HYBRID NANOCOMPOSITES

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Abstract

In this study, a set of hybrid systems was developed varying the filler type and content (MWCNT's and Fe_3O_4), and their electrical response was investigated by means of Broadband Dielectric Spectroscopy (BDS), which has been proved to be a powerful tool for the investigation of molecular mobility, phase changes, conductivity mechanisms and interfacial effects in polymers and complex systems , in the frequency range 10^{-1}-10^{7} Hz and temperature interval from 30°C to 160°C.

Depending on the filler type and concentration, the nanocomposites exhibited either insulator to conductor transitions or dielectric relaxation phenomena arising from both the filler and the polymeric matrix. Three distinct relaxation modes were recorded and were attributed to interfacial polarization, glass transition (α-relaxation) and motion of polar side groups (β – relaxation). The addition of small amount of Fe_3O_4 nanoparticles seems to facilitate the transition to the conductive phase, while nanocomposites with excessive ferrite content augments the insulating behavior.

1. Introduction

In recent years, polymer-based composites with high dielectric permittivity have drawn considerable attention because their combination of mechanical flexibility and excellent dielectric properties could be utilized in capacitors, actuators, generators, and electromagnetic interference shielding [1-3]. According to the percolation theory, the dielectric constants of these composites increase significantly when the concentration of conductive fillers is close to a critical concentration. It was found that the percolation threshold can be greatly reduced by a high-aspect-ratio conductive filler, because the conductive network can be formed effectively at low fraction. Meanwhile, the high surface area and high conductivity of low-dimensional particles can greatly enhance the polarization of the composite material and result in the improvement of the dielectric constant [1-6].

Since their discovery in 1991, carbon nanotubes (CNTs) have been widely used as filler in the fabrication of advanced nanocomposites due to their unique physical properties, especially mechanical, thermal, and electrical. Hybrid nanocomposites have been prepared by employing metal oxide particles in addition to CNTs to provide new functionality such as magnetic and optoelectronic properties. Among transition metal oxides, iron oxide has got much attention due to its abundance, low cost, corrosion resistance, high chemical stability and ecofriendly nature. A better understanding of the relationships between processing, interfacial optimization, and composite properties is a major goal of this area of research, which may lead to new multifunctional polymer nanocomposites [7-9]. In the present study, Fe_3O_4/MWCNT/epoxy ternary nanocomposites were prepared to integrate the advantages of the two kinds of fillers and their electrical properties have been investigated.

2. Experimental

A set of hybrid polymer nanocomposites was prepared by employing a two component commercially available epoxy resin (Epoxol 2004 provided by Neotex S.A., Athens, Greece) acting as matrix , while Fe_3O_4 nanoparticles with diameter size less than 100 nm (obtained from Sigma-Aldrich) and MWCNTs (3-15walls) with length 1-10μm according to the provider (Plasmachem GMBH) were acting as filler.

For the preparation of the nanocomposites, firstly, the MWCNTs were dispersed into the prepolymer and stirred inside a sonicator. Then the curing agent was added at a 2:1 (prepolymer/hardener) mixing ratio and the mixture was stirred for 5 minutes. Subsequently, the magnetite nanoparticles were introduced into the mixture and the whole system was stirred by hand in a sonicator for 10 minutes and then was poured into suitable silicon moulds to be cured for seven days at room temperature. After polymerization the samples underwent a post curing treatment at 100 oC for 4 hours.

The dielectric response of the nanocomposites was studied by means of Broadband Dielectric Spectroscopy using an Alpha-N Frequency Response Analyzer in the frequency range from 10^{-1}-10^{7} Hz and temperature interval 30 to 160 ^{o}C, with 5 ^{o}C temperature step controlled by Novotherm system. The sample was placed inside the the dielectric cell BDS 1200 and the experimental data were obtained automatically via suitable software (Windeta), by performing isothermal frequency scans. The amplitude of the time varying voltage was equal to 1V in all cases. Both devices as well as the dielectric cell and software were supplied by Novocontrol Technologies.

3. Results and Discussion

A representative for all examined systems diagram of the variation of the real part of dielectric permittivity and loss tangent as a function of temperature and frequency is displayed in Fig. 1.

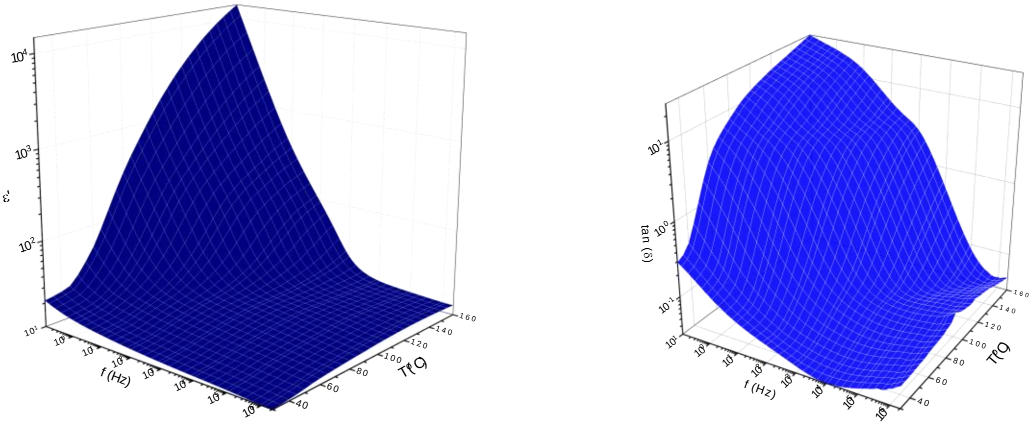

Figure 1. (Left) Real part of dielectric permittivity and (right) loss tangent as a function of temperature and frequency for the nanocomposite with 1 phr MWCNT and 10 phr in Fe_3O_4 content.

In all cases, the real part of dielectric permittivity increases with the temperature and diminishes rapidly with increasing frequency, because thermal agitation facilitates the alignment of induced and permanent dipoles with the applied field, while with the increase of frequency dipoles don’t have the necessary time to be aligned with the externally applied field. The formation of a shoulder at intermediate temperatures and frequency is attributed to a relaxation mechanism. These relaxations mechanism become more evident by the formation of peaks in the plot of loss tangent versus temperature and frequency (Fig. 1 right). Three different relaxation mechanisms were recorded and were attributed to both the polymer matrix and the ceramic nanoinclusions. Interfacial polarization (IP) or MWS effect is observed at low frequencies and high temperatures due to the heterogeneity of the systems, which favors the accumulation of unbound charges at the systems’ interface. α-relaxation ascribed to glass to rubber transition of the polymer matrix, is recorded at intermediate frequencies, and β-relaxation due to the re-orientation of small polar side groups of the main polymer chain at high frequencies. In nanocomposites with filler content higher than the critical concentration IP is not present, since conductive paths have been formed inside the nanocomposite and charges no longer remain at the interface, migrate through the whole system participating thus to electrical conduction, cancelling at the same time the occurrence of IP.

The variation of the real part of dielectric permittivity as a function of frequency is depicted in Fig. 2, for all the examined system, at 30 °C.

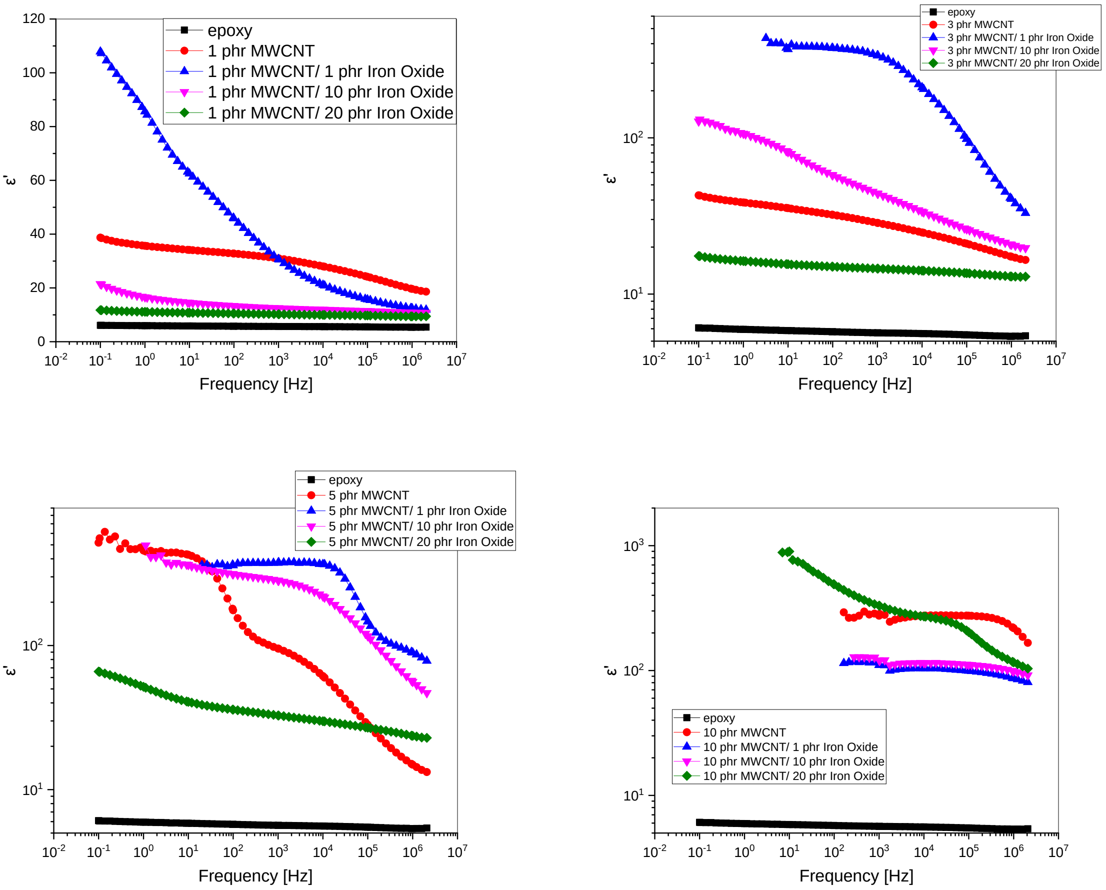

Figure 2. Real part of dielectric permittivity as a function of frequency, for all the examined systems containing 1 phr MWCNT (upper left), 3 phr MWCNT (upper right), 5 phr MWCNT (lower left) and 10 phr MWCNT (lower right) at 30 °C .

The real part of permittivity increases with filler loading for all temperatures and across the whole frequency range, since permittivity values of both MWCNT and Fe_3O_4 are remarkably higher compared to the respective of neat epoxy. The real part of permittivity is more sensitive to the presence of MWCNT increasing by orders of magnitude since MWCNTs are highly conductive. The incorporation of low amount of magnetite nanoparticles in the nanocomposites seem to increase induced polarization. The significant enhancement of the dielectric constant is attributed to the interfacial polarization by the interaction between the filler and polymer matrix. The addition of Fe_3O_4 can inhibit the aggregation of MWCNTs and make them evenly dispersed in the three-phase composites. Further increase of iron oxide lowers the values of ε′ since its conductivity is more modest than MWCNTs’.

The variation of the real and imaginary part of the electric modulus as a function of frequency at 160°C, for the examined systems is depicted in Fig. 3. The recorded loss peaks in (M″) are associated with α-relaxation process. The addition of MWCNTs diminishes the maximum values of M″ and shifts the relaxation peaks towards higher frequencies due to the strong attractive interactions of the carbon nanoinclusions. The addition of the Fe_3O_4 nanoparticles shifts the transition to higher temperatures signifying stronger adhesion between the matrix and the nanofiller, as the macromolecules anchor on the ceramic nanoparticles. The latter results in an increase of Tg , for the nanocomposites that are not in the conductive phase.

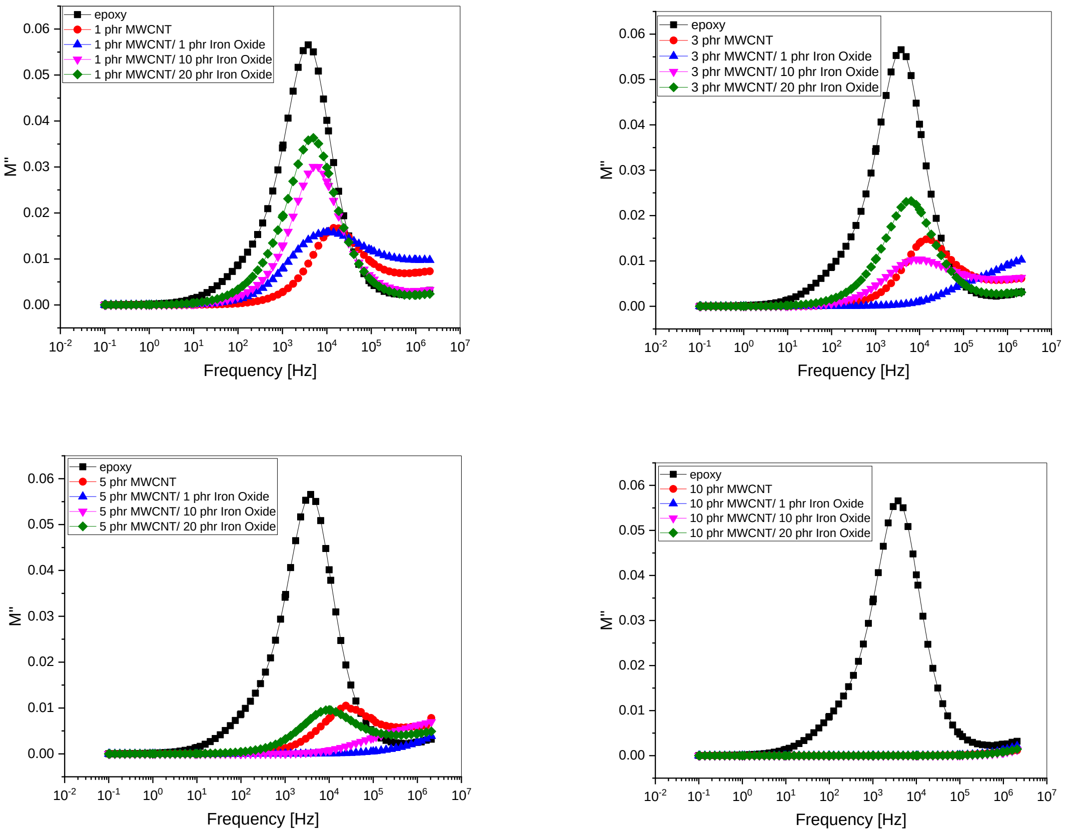

Fig. 3. Imaginary part of electric modulus as a function of frequency, for all the examined systems containing 1 phr MWCNT (upper left), 3 phr MWCNT (upper right), 5 phr MWCNT (lower left) and 10 phr MWCNT (lower right) at 160 °C.

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The variation of the ac conductivity as a function of frequency is depicted in Fig. 4, for all the examined system, at 30 °C.

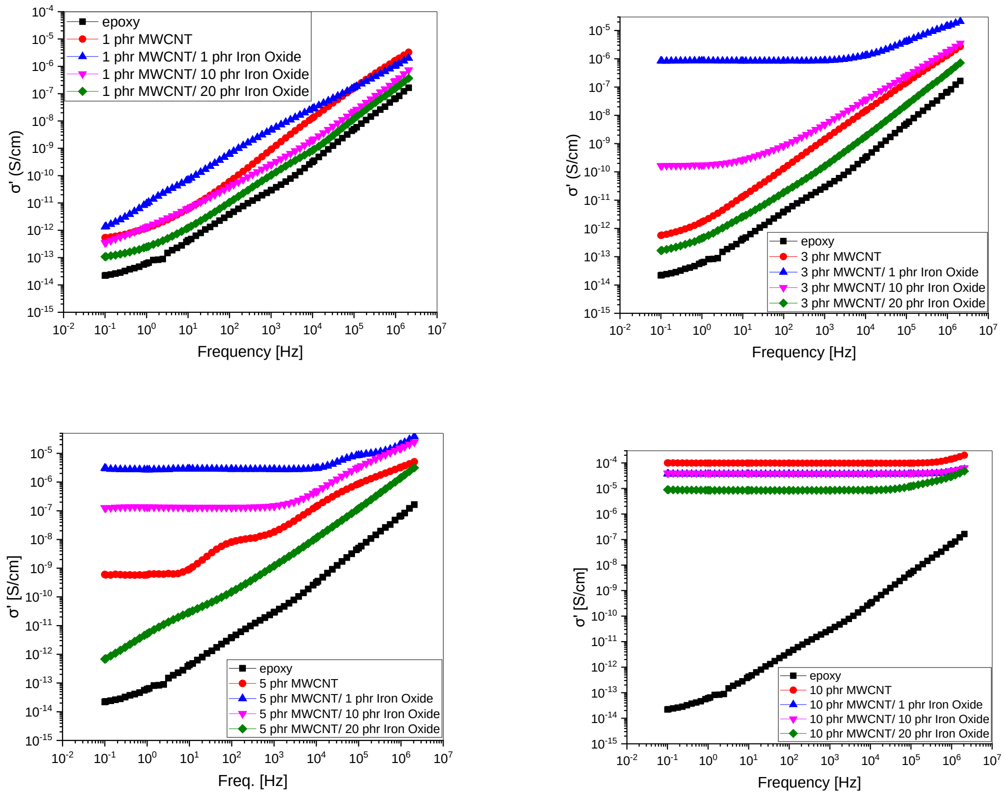

Fig. 4. AC conductivity as a function of frequency, for all the examined systems containing 1 phr MWCNT (upper left), 3 phr MWCNT (upper right), 5 phr MWCNT (lower left) and 10 phr MWCNT (lower right) at 30 °C .

In the low frequency edge conductivity tends to acquire constant values, at about the DC level, while after a critical frequency varies as a power of frequency. The content of the conductive phase (MWCNTs) is the primary responsible for the overall conductivity of the polymer nanocomposites. A substantial increase of conductivity in a small range of MWCNTs content is observed.The alteration of conductivity values by several orders of magnitude, shows the transition from the insulating to the conductive behaviour. Critical concentration or percolation threshold is a parameter governing the transition from insulating to conductive behaviour. Increasing the concentration of the conductive phase decreases the mutual distance of inclusions. At a critical content a conductive path is formed within the matrix, through which charge carriers can migrate, resulting in the increase of conductivity. At even higher content of the filler, a three-dimensional network of conductive paths is formed and system’s conductivity remains practically constant being independent from variations in conductive phase content.While MWCNTs are the major contributor to the systems‘ conductivity , the addition of small amount of magnetite nanoparticles seems to increase even further the recorded conductivity and more importantly to shift this critical concentration to lower values.

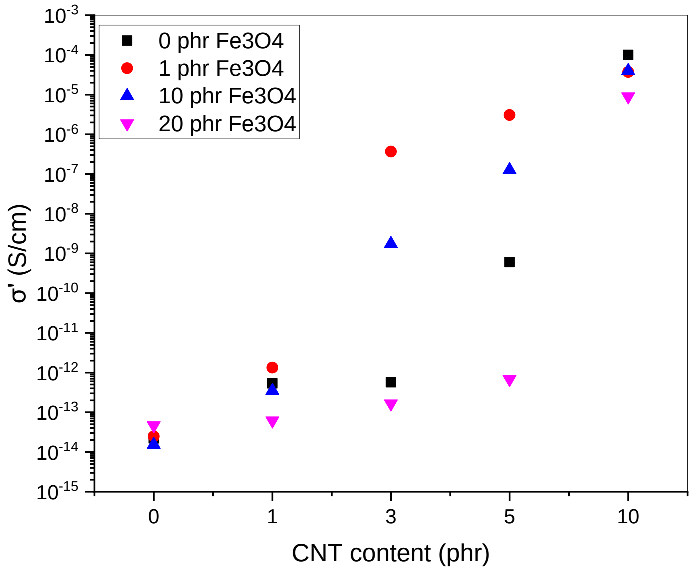

Figure 5. AC conductivity as a function of the MWCNT content at 30 °C and 0.1 Hz, for all examined systems.

For the MWCNTs/epoxy nanocomposites, the conductive paths are difficult to be formed at a low content. So, the increase in the MWCNTs content improves the probability of MWCNTs to contact with each other and induces the formation of the conductive network. However, by filling a small amount of Fe_3O_4 into the nanocomposites, the interaction between the two kinds of the filler can accelerate the percolation transition, resulting in a great increase in the dielectric constant and conductivity of the composites. The excellent dielectric properties can be attributed to the following aspects. First, a small amount of Fe_3O_4 can effectively promote the dispersion of MWCNTs in the polymer matrix and prevent the MWCNTs' agglomeration. Second, interfacial polarization can increase greatly due to the existence of a large number of interfaces between Fe_3O_4, MWCNTs, and the epoxy matrix. The interfacial polarization can arise from the significant accumulation of charge carriers at the interface between the conductive MWCNTs and Fe_3O_4 particles and the insulating polymer due to the difference of conductivity between the polymer matrix and fillers. Therefore, the addition of Fe_3O_4 brings more positions for charge accumulation on the internal interfaces.

4. Conclusions

In this study, a set of hybrid systems was developed varying the filler type and content (MWCNT's and Fe_3O_4), and their electrical response was investigated by means of Broadband Dielectric Spectroscopy (BDS). Depending on the filler type and concentration, the nanocomposites exhibited either insulator to conductor transitions or dielectric relaxation phenomena arising from both the filler and the polymeric matrix. Three distinct relaxation modes were recorded and were attributed to interfacial polarization, glass transition (α-relaxation) and motion of polar side groups (β – relaxation). The addition of small amount of Fe_3O_4 nanoparticles seems to enhance the induced polarization and facilitate the transition to the conductive phase, while nanocomposites with excessive ferrite content augments the insulating behavior.

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