

## MULTIFUNCTIONAL RESPONSE OF: FERRITE/EPOXY, MWCNT/EPOXY AND MWCNT/FERRITE/EPOXY NANODIELECTRICS

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### ABSTRACT

Multiwall Carbon nanotubes (MCNTs) constitute a popular reinforcing phase for the development of advanced nanocomposites, mainly because of their mechanical, thermal and electrical properties. Moreover, magnetic nanoparticles embedded in a polymer matrix influence both the dielectric and magnetic behaviour of the composite system.

In the present study, a series of composite nanodielectrics consisting of an epoxy matrix and iron oxide nanoparticles and/or MWCNTs have been developed and studied varying the filler type and content. The goal of the present study is to exploit in a single nanocomposite advanced mechanical, thermal, electrical and magnetic performance. The structure-properties relationships were investigated by means of Dynamic Mechanical Analysis (DMA), and Broadband Dielectric Spectroscopy (BDS).

Depending on the filler type and concentration, nanodielectrics exhibit either insulator to conductor transition or dielectric relaxation phenomena. Dielectric response includes three distinct relaxation modes attributed to interfacial polarization, glass to rubber transition ( $\alpha$ -relaxation) and motion of polar side groups ( $\beta$ -relaxation). The addition of small amount of  $\text{Fe}_3\text{O}_4$  nanoparticles seems to facilitate the transition from the insulating to the conductive performance, while nanocomposites with excessive ferrite content augment the insulating behaviour.

### INTRODUCTION

In recent years, polymer-based composites with high dielectric permittivity have drawn considerable attention, since they combine mechanical flexibility and excellent dielectric properties, which could be utilized in capacitors, actuators, generators, and electromagnetic interference shielding. According to the percolation theory, the dielectric permittivity of these composites increase significantly when the concentration of conductive filler is close to the critical concentration, defining the insulating to conductive behaviour transition. 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, conductive phase, 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 permittivity<sup>[1-6]</sup>.

Carbon nanomaterials, such as 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 novel 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, a series of composite nanodielectrics consisting of an epoxy matrix and iron oxide nanoparticles and/or MWCNTs have been developed and studied varying the filler type and content.

## 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<sub>3</sub>O<sub>4</sub> nanoparticles with diameter size less than 100 nm (obtained from Sigma-Aldrich) and MWCNTs (3-15 walls) with length 1-10 μm according to the provider (Plasmachem GMBH) were acting as filler.

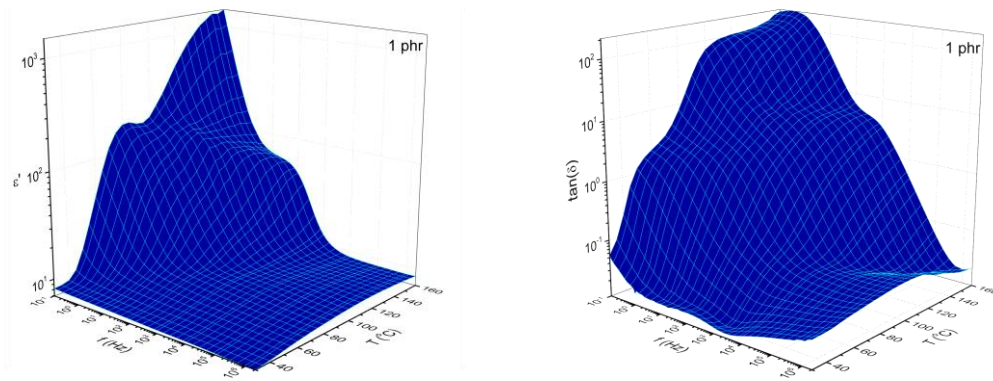
For the preparation of the nanocomposites, firstly, the filler (Fe<sub>3</sub>O<sub>4</sub> nanoparticles or MWCNTs) were dispersed into the prepolymer and stirred inside a sonicator. Then the curing agent was added at a 2:1w/w (prepolymer/hardener) mixing ratio and the mixture was stirred for 5 minutes. Subsequently, for the ternary systems, the MWCNTs were introduced into the mixture and the whole system was stirred 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 °C for 4 hours.

The thermomechanical investigation was carried out via Dynamic Mechanical Analysis (DMA) in the temperature range from room temperature to 100 °C with 5 °C/min heating rate, using TA Q800 device provided by TA Instruments in the three-point bending configuration, employing suitable rectangular shaped specimens, at f=1 Hz.

The dielectric response of the nanocomposites was studied by means of Broadband Dielectric Spectroscopy (BDS) using an Alpha-N Frequency Response Analyzer in the frequency range from 10<sup>1</sup>-10<sup>7</sup> Hz and temperature interval from 30 to 160 °C, with 5 °C temperature step. Temperature was controlled by Novotherm system. The sample was placed inside 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.

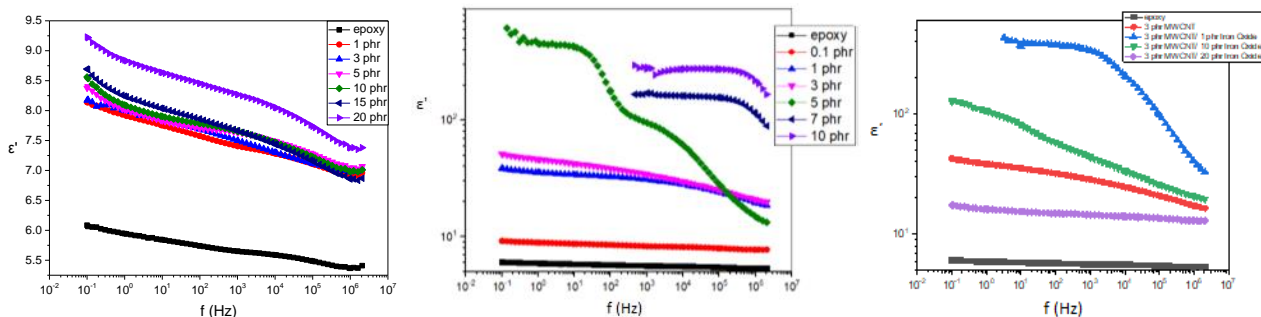
## RESULTS AND DISCUSSION

Figure 1 depicts the variation of the real part of dielectric permittivity (left) and the loss tangent (right) as a function of both frequency and temperature for the nanocomposite with 1 phr magnetite content. These spectra are representative of the recorded behaviour for all studied systems.



**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 in  $\text{Fe}_3\text{O}_4$  content.

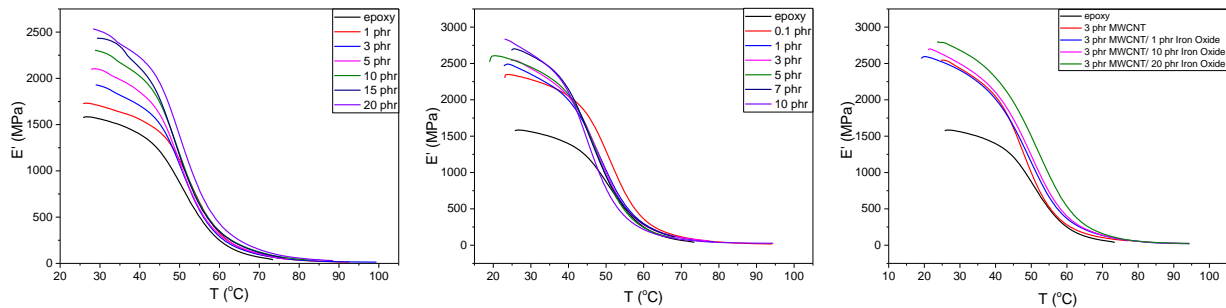
In all cases, the real part of dielectric permittivity increases with the temperature and diminishes rapidly with increasing frequency, because thermal agitation facilitates the alignment of induced and permanent dipoles with the applied field, while with the increase of the field's frequency, dipoles 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  $\alpha$ -relaxation mechanism. Relaxation mechanisms 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 are attributed to both the polymer matrix and the ceramic nano-inclusions. Interfacial polarization (IP) or Maxwell-Wagner-Sillars (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.  $\alpha$ -relaxation ascribed to glass to rubber transition of the polymer matrix, is recorded at intermediate frequencies, and  $\beta$ -relaxation due to the reorientation of small polar side groups of the main polymer chain at high frequencies.



**Figure 2.** Real part of dielectric permittivity as a function of frequency, for all the examined systems containing  $\text{Fe}_3\text{O}_4$  (left), MWCNT (middle), and 3 phr MWCNT/  $x$  phr  $\text{Fe}_3\text{O}_4$  (right) at 30 °C.

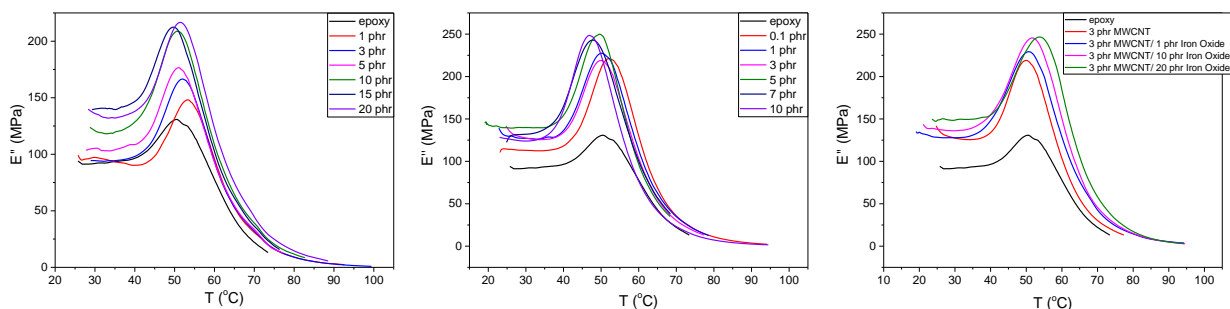
The real part of permittivity as depicted in Figure 2 for all systems increases with filler loading for all temperatures and across the whole frequency range, since permittivity values of both MWCNT and  $\text{Fe}_3\text{O}_4$  are remarkably higher compared to the respective of neat epoxy. The real part of permittivity is more sensitive to the presence of MWCNT, thus increasing by orders of magnitude since MWCNTs are highly conductive. The incorporation of low amount of magnetite nanoparticles in the nanocomposites seems to increase induced polarization. The significant enhancement of the dielectric permittivity is attributed to the interfacial polarization by the interaction between the filler and polymer matrix. The addition of  $\text{Fe}_3\text{O}_4$  could inhibit the aggregation of MWCNTs and make

them evenly dispersed in the three-phase composites. Further increase of iron oxide lowers the values of  $\epsilon'$  since its conductivity is more modest than MWCNTs'.



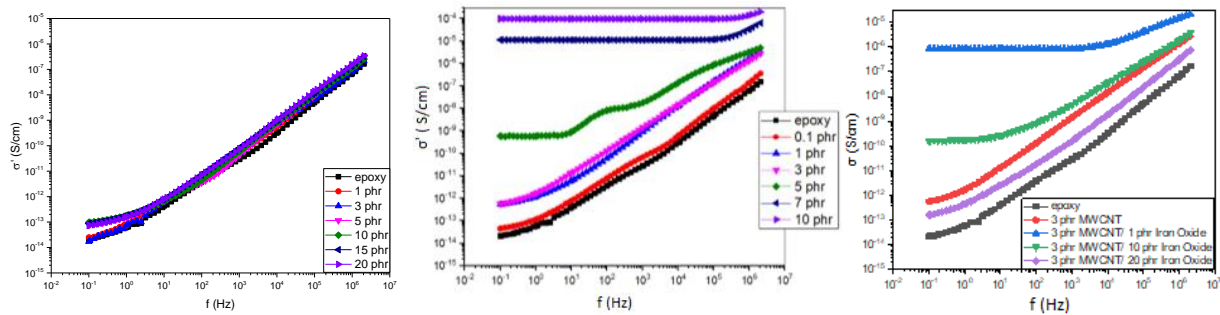
**Figure 3.** Storage modulus as a function of temperature, for all the examined systems containing  $\text{Fe}_3\text{O}_4$  (left), MWCNT (middle), and 3 phr MWCNT/  $x$  phr  $\text{Fe}_3\text{O}_4$  (right) at 30 °C.

Figure 3 shows the storage modulus ( $E'$ ) of the nanocomposites, as a function of temperature. The DMA tests were performed aiming to show the effect of elevated temperatures upon the stiffness of the materials. As shown in Figure 3, the storage modulus of the nanocomposites is higher than that of the neat epoxy, and gradually increases with filler loading. Since the high rigidness of the reinforcement's particles, and the adherence of filler to polymer in the nanocomposites, the nanoparticles form a network which is able to carry the applied stress. MWCNTs seem to have a greater impact on the thermomechanical properties of the nanocomposites. A step like decrease was recorded for all nanocomposites at 40 to 70 °C due to the  $\alpha$ -relaxation process, which is attributed to the glass to rubber transition of the polymer matrix. This mechanism was recorded with the formation of peak in the loss modulus diagram (Figure 4). The characteristic glass transition temperature for almost all nanocomposites with  $\text{Fe}_3\text{O}_4$  nanoparticles was higher than the neat epoxy, which implies strong interactions between macromolecules and the nano-inclusions.



**Figure 4.** Loss modulus as a function of temperature, for all the examined systems containing  $\text{Fe}_3\text{O}_4$  (left), MWCNT (middle), and 3 phr MWCNT/  $x$  phr  $\text{Fe}_3\text{O}_4$  (right) at 30 °C.

The addition of MWCNTs shifts the relaxation peaks towards lower frequencies due to the strong attractive interactions between the carbon nano-inclusions. Further addition of  $\text{Fe}_3\text{O}_4$  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 glass to rubber transition temperature ( $T_g$ ), of the nanocomposites.



**Figure 5.** AC conductivity as a function of frequency, for all the examined systems containing  $Fe_3O_4$  (left), MWCNT (middle), and 3 phr MWCNT/  $x$  phr  $Fe_3O_4$  (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. 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. Although, MWCNTs are the major contributor to the systems' conductivity, the addition of a small amount of magnetite nanoparticles seems to increase even further the recorded conductivity and more importantly to shift this critical concentration to lower values.

For the MWCNTs/epoxy nanocomposites, the conductive paths are difficult to be formed at such a low content. So, the increase of the MWCNTs content improves the probability of conductive inclusions to contact with each other and induces the formation of the conductive network. However, by embedding a small amount of  $Fe_3O_4$  into the nanocomposites, the interactions between the two kinds of filler can accelerate the percolative transition, resulting in a significant enhancement of the dielectric permittivity and conductivity of the nanocomposites. The optimization of dielectric properties can be attributed to the following aspects. Firstly, a small amount of  $Fe_3O_4$  can effectively promote the dispersion of MWCNTs in the polymer matrix and prevent the MWCNTs' agglomeration. Secondly, interfacial polarization increases remarkably due to the existence of extended interfaces between  $Fe_3O_4$ , MWCNTs, and the epoxy matrix. Interfacial polarization effect is consisted by a dipolar and a conductive process. The accumulation and trapping of charge carriers at the interface favours the dipolar part, while the migration of charges via interfacial paths the conductive one. The strength of interfacial polarization is related to the extend of the interface between the conductive MWCNTs,  $Fe_3O_4$  particles and the insulating matrix, the difference of conductivity between the polymer matrix and fillers, the shape and dimensions of the employed inclusions and the reinforcing phases' volume fraction. Therefore, the addition of  $Fe_3O_4$ , at a low content, appears to bridges adjacent MWCNTs, while at higher content increases the trapping positions for charges at the internal interfaces.

## CONCLUSIONS

In this study, sets of epoxy resin nanocomposites were developed varying the filler type and content (MWCNT's and Fe<sub>3</sub>O<sub>4</sub>). Their electrical response was investigated by means of Broadband Dielectric Spectroscopy (BDS). Depending on the filler type and concentration, the nanocomposites exhibited either transition from insulating to conductive behaviour 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 ( $\alpha$ -relaxation) and motion of polar side groups ( $\beta$  – relaxation). The addition of small amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles seems to enhance the induced polarization and facilitate the transition to the conductive performance, while nanocomposites with excessive ferrite content augment the insulating behaviour. The thermomechanical properties of the nanocomposites as studied by Dynamic Mechanical Analysis (DMA) revealed improved stiffness with the addition of both filler types, with MWCNT having a bigger impact on the nanocomposites' performance.

## ACKNOWLEDGEMENTS

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