INFLUENCE OF TEMPERATURE ON DIELECTRIC PERFORMANCE OF EPOXY NANOCOMPOSITES WITH INORGANIC NANOFILLERS

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In this paper, the influence of the temperature, between 27 and 80 °C, on the dielectric performances of some epoxy based nanodielectrics is analyzed by dielectric spectroscopy over a frequency range of $10^{-4} – 10^{6}$ Hz. Differences in dielectric behaviour of the tested samples were observed depending on the presence and the concentration of the inorganic nanofillers, as well as on the temperature at which the measurements were performed.

The results obtained at higher temperatures (60 - 80 °C) show an important increase of the permittivity at low frequencies with respect to the results at 27 °C.

Keywords: epoxy, nanodielectrics, dielectric spectroscopy, energy storage.

1. Introduction

Dielectric nanocomposites are among the most studied dielectrics in the last years and the promising results reported in literature recommend these new materials for applications ranging from dielectrics for high energy storage capacitors up to electrical insulations with low losses and high breakdown resistance. Nanodielectrics, as these materials are often referred to, are made of polymers mixed with nano-fillers having at least one dimension up to 100 nm and a concentration usually lower than 10 wt% in content [1-15]. Recently, epoxy based nanodielectrics have been increasingly investigated for their electrical properties, due to several advantages remarked when compared with epoxy composites with micrometer sized fillers [2]. *Fothergill et al* analyzed by dielectric spectroscopy and space charge measurements epoxy based composites filled with micro- and nano-sized particles, like titania (TiO_2), alumina (Al_2O_3) and zinc oxide (ZnO) [16]. Their conclusions were that the dielectric properties of this type of nanocomposites would be mainly controlled by Stern-Gouy-Chapman layers around the particles. *Smith et al* reported that polymer nanocomposites with

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nano-fillers can exhibit improved dielectric breakdown strength and voltage endurance when compared to their neat resin or micrometer particle-filled counterparts [17]. *Zou et al* studied the influence of humidity on the dielectric properties of epoxy nanocomposites filled with silica [18, 19]. The importance of interfacial regions in determining the better properties of nanodielectrics with respect to microcomposites was emphasized in a study of *Nelson et al*, where they analyzed the dielectric behaviour of epoxy composites filled with nano- and micro-sized TiO_2 in the frequency domain of 10^{-4}-10^6 Hz [20]. *Maity et al* have remarked the presence of low frequency dispersion below 100 Hz for both neat epoxy and Al_2O_3 filled epoxy nanocomposites, and lower permittivity values for the nanocomposites than in unfilled epoxy [21]. Therefore, encouraging steps have been made towards the understanding and controlling the phenomena in the field of epoxy nanocomposites, but we are still far from finding all the secrets of these promising materials.

In our previous research on epoxy nanocomposites we added inorganic nanofillers (SiO_2, TiO_2 and Al_2O_3) in an epoxy matrix in an attempt to obtain better electrical insulating materials, i.e. with higher resistivity, smaller permittivity, lower dielectric losses and/or higher breakdown strength than the neat polymer. The results obtained by dielectric spectroscopy [29] over a frequency range of 1 mHz – 1 MHz and at temperatures of 27 °C and 60 °C have showed that the dielectric behaviour was very little influenced by the type of the filler at low filler concentration (0.5-1 wt%), all the nanocomposites having permittivity values higher than in neat polymer, this showing that the dominant effect on the dielectric behaviour is not the filler permittivity but the filler-polymer interface. However, the increase of the TiO_2 filler concentration up to 5 wt.% lead to lower permittivity values with respect to the unfilled epoxy, a reduced chain movement due to the presence of the nanoparticles being thought to be responsible for this result. Therefore, our first results indicated that the presence of nanofillers can lead to higher or lower relative permittivity (ε_r') values than in the neat epoxy depending on the type and concentration of nanoparticles.

Our more recent results [30] have showed that, at low filler concentrations (0.5-1 wt%), the resistivity of the above epoxy nanocomposites is smaller than in the neat polymer with one-two orders of magnitude, while an increase of resistivity is noticed at higher filler concentration (5 wt%) up to a level close to that of the neat resin. This behaviour was found to be well correlated to that of the dielectric breakdown strength (E_{bd}), which was found also to be reduced (between 5 and 15 %) than for the neat epoxy for smaller nanoparticle concentrations but with an increase with the filler level up to values higher with 20 %, as it was obtained for SiO_2 filler at 5 wt%.

Therefore, our previous results have shown that the epoxy nanocomposites could have an improved behaviour as electrical insulation than the neat resin,

depending on the conditions of fabrication and/or testing. Besides the use of nanocomposites as electrical insulations, another industrial application potential of these materials could be as dielectrics for electrical energy storage [31]. In this case, as the electrical energy density is given by $w_e = \frac{1}{2}\varepsilon_0\varepsilon_r E_{bd}^2$, where ε_0 is the permittivity of vacuum, the objectives for nanocomposites to have high dielectric breakdown strength and resistivity, and low dielectric loss remains as in the case of electrical insulations, but the particular focus is on the increase of the permittivity, which must be achieved without compromising the breakdown strength of the polymer.

Starting from these considerations, in the present work a special attention is given to the analysis of the inorganic nanofillers potential in increasing the permittivity of epoxy resin and to a better understanding of the dielectric behaviour of epoxy-inorganic nanocomposites.

2. Experimental

The materials tested in this study were epoxy resin-Al_2O_3, epoxy resin-TiO_2 and epoxy resin-SiO_2 nanocomposites, as well as neat epoxy polymer. The polymer matrix was a Bisphenol-A based epoxy resin of type Araldite LY554, and a Triethylenetetramine (TETA) of type HY 951 was used as hardener. The content of nanofillers of the tested formulations was 0.5 and 1 wt%. The average diameter of the SiO_2 and of the TiO_2 nano-particles was 15 nm while the average diameter of the Al_2O_3 nano-particles was 40 nm. The nanocomposite samples for electrical tests performed in this study were plaques of square shape (10 x 10 cm^2) having the thickness of 1 mm.

The real part of the permittivity (ε_r') and the loss tangent (tan δ) were determined by dielectric spectroscopy (DS) using a Novocontrol ALPHA-A Analyzer in combination with an Active Sample Cell ZGS, over the frequency range $10^{-4} – 10^6$ Hz and for temperatures from 27 to 80 °C. Four disks of 40 mm diameter were cut from one plaque of each formulation and tested by dielectric spectroscopy.

3. Results and discussion

The results from dielectric spectroscopy measurements at 27 °C on samples of neat epoxy resin and of nanocomposites with 0.5 wt% alumina (Al_2O_3), silica (SiO_2) and titania (TiO_2) nanoparticles are shown in Figure 1, while the results for the nanofiller level of 1 wt% are shown in Figure 2. An increase of the real part of the permittivity and of the dielectric loss values in nanocomposites

with respect to the neat epoxy can be noticed in the entire frequency range, for all three filler types and for both filler concentrations.
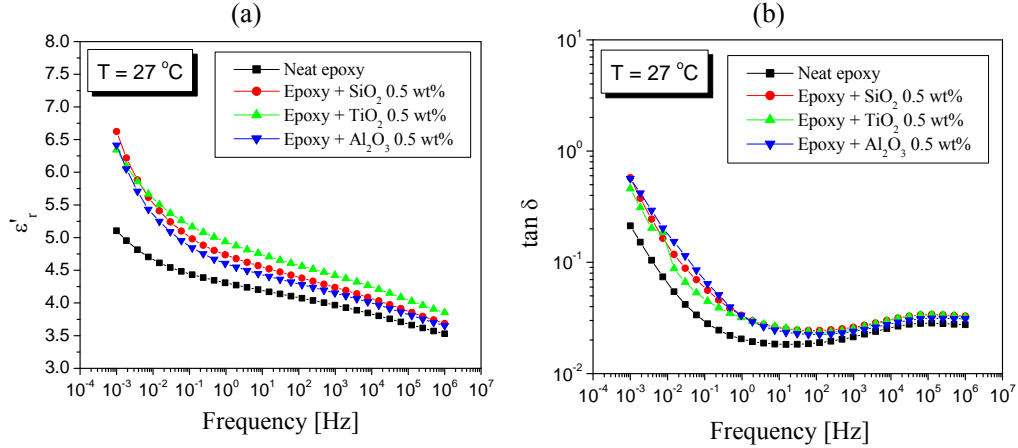

Fig. 1. Frequency variation of ε_r' (a) and of tan δ (b), for epoxy-SiO$_2$, epoxy-TiO$_2$ and epoxy-Al$_2$O$_3$ nanocomposites with 0.5 wt.% filler concentration, at 27 °C.

Fig. 2. Frequency variation of ε_r' (a) and of tan δ (b), for epoxy-SiO$_2$, epoxy-TiO$_2$ and epoxy-Al$_2$O$_3$ nanocomposites with 1 wt.% filler concentration, at 27 °C [29].
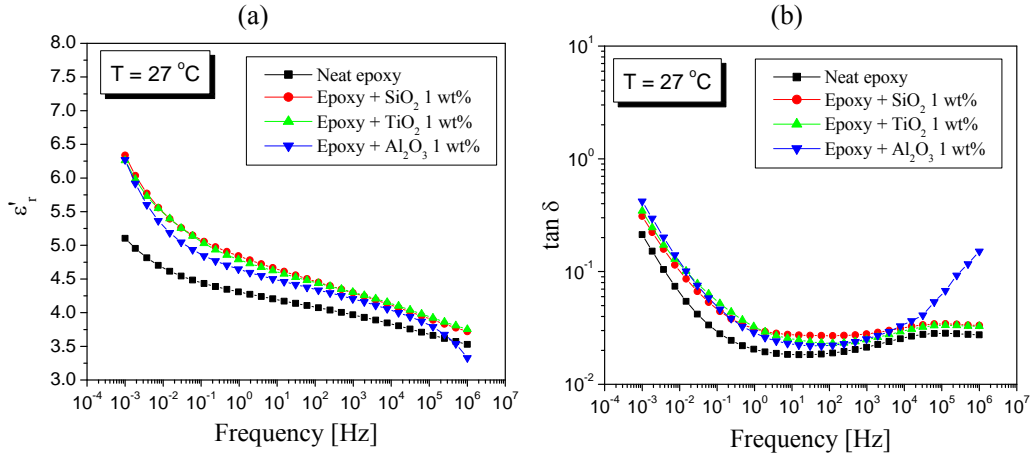
No significant differences in dielectric behaviour depending on the filler type were observed from the measurements at 27 °C. It can be remarked that both the real part of the permittivity (ε_r') and the dielectric loss (tan δ) sharply increase with the decrease of frequency, this suggesting a "low frequency dispersion" (LFD) behaviour, already reported on other epoxy nanocomposites [21, 16]. Dissado and Hill model to explain LFD is based on the concept of cluster, which is a region with partial structural regularity where quasi-mobile charges (especially ions) moves by hopping to unoccupied sites. When the access to sites

is restricted the conduction may be due to a combination of intracluster and intercluster motions [21, 27]. The cluster approach was extended by Schonhals and Schlosser for amorphous polymers, by considering intramolecular motions (some chain units) for short times (high frequency), and intermolecular and large scale molecular motions of many chain units for long times (low frequency) [32].

The above results and the ones presented in [29] showing that the increase of TiO_2 filler concentration up to 5 wt.% has lead to a decrease of permittivity up to values lower than in the neat epoxy, have determined us to continue the investigations on the possibility to increase the permittivity in epoxy nanocomposites only on those having as filler Al_2O_3 and SiO_2, at low concentrations, which have more promising dielectric performances in this sense. The fact that the increase in permittivity is comparable or even higher in the case of Al_2O_3 and SiO_2 fillers (having dielectric constants lower than 10) than for TiO_2 filler (with a much higher dielectric constant of 50-100) suggests that adding high dielectric permittivity fillers into polymers is maybe not the best idea for increasing the effective dielectric permittivity of the nanocomposite. An explanation for this comes from the fact that when the filler has a much greater permittivity than the polymer matrix, the increase of the nanocomposite effective permittivity comes mainly from the increase of the average electric field in polymer matrix, while very low fields act on the high permittivity nanoparticle and on its nearest interface region. The presence of much lower contrast in permittivity between filler and matrix, as for Al_2O_3 and SiO_2, generates a much lower inhomogeneous electric filed in nanocomposites and hence, the increase in nanocomposite effective permittivity is mainly due to the increase of the number of quasi-mobile charges and of dipolar movements in the filler-matrix interface.

Thus, the following tests in the present study were performed at different higher temperatures up to 80 °C, and in an extended frequency range up to 10^{-4} Hz at the lower bound.

The results obtained at 60 °C, for Al_2O_3 and SiO_2 epoxy nanocomposites, as for the neat epoxy, are shown in Fig. 3.

The dielectric behaviour of the tested samples at 60 °C emphasizes a thermally activated relaxation at low frequencies ($\approx 10^{-1}$ Hz) for the neat epoxy and for the tested nanocomposites, as well. The relaxations arising at low frequencies show that large scale molecular motions and intercluster movements are activated at 60 °C. The amplitude of relaxation, i.e. the difference in ε_r' values before and after relaxation, are much higher for nanocomposites than for the neat resin, reaching ≈ 300 at very low frequencies in the case of 1 wt% Al_2O_3 filler. The fact that the relaxation characteristic frequency does not change by nanostructuration (by adding inorganic fillers in epoxy matrix) indicate that the quasi-mobile charges introduced in polymer with the filler during the

nanocomposite fabrication have the same restrictions of movement as those existing in the neat resin.
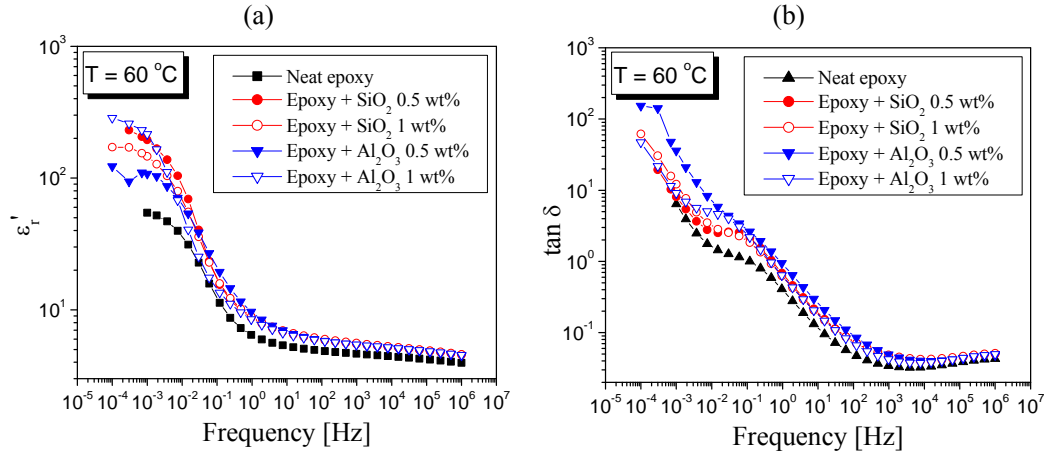

Fig. 3. Frequency variation of ε_r' (a) and of tan δ (b), for neat epoxy and for epoxy-SiO$_2$ and epoxy-Al$_2$O$_3$ nanocomposites with 0.5 and 1 wt.% filler concentration, at 60 °C.

It is already well known that the filler-polymer interface plays a critical role in defining the properties of nanocomposites. One of the models proposed for the interface structure is the Tanaka's multi-core model describing the interface as consisting in three layers (Figure 4) [33]. First (bonded) layer is thought to be a very thin region where the polymer is tightly bond to particle, the second (bound) layer corresponds to strong bonds between the first layer and the polymer chains, while the third (loose) layer is a region with different chain conformation, chain mobility, free volume and crystallinity from the polymer matrix, loosely coupled and interacting with the second layer. The thicknesses of the above layers are considered to be 1 nm, several nm and several tens of nm for the first, second and third layer, respectively.

In addition, the Tanaka's model considers also a coulombic interaction determining an electric double layer overlapping the above three layers. This electric layer is a diffuse layer consisting of mobile charge carriers of opposite polarity with respect to the nanoparticle charge, which decay exponentially with the distance from the nanoparticle.
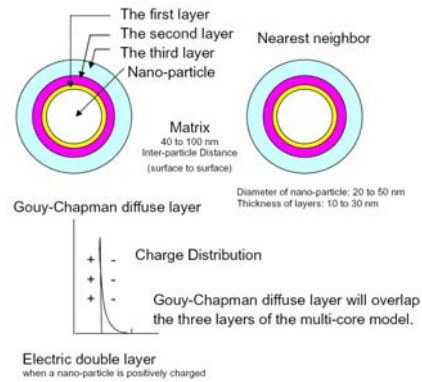
Fig. 4.Tanaka's multi-core model for nanoparticle-polymer interfaces [33].

The quasi-mobile charges introduced in the tested epoxy nanocomposite with the filler, and responsible for the enhanced relaxation but having the same characteristic frequency observed in Figure 3, could be connected to the chain units from the loose layer, where the the chain mobility and the presence of shallow traps and free volume are higher than in other regions.

The influence of temperature between 27 and 80 °C on the dielectric behaviour of Al_2O_3 epoxy nanocomposites with 1 wt% filler content is shown in Figure 5. It can be noticed that the low frequency relaxation arise at higher frequencies with the increase of temperature, which is expected for a thermally activated polarization process as the one present in this case. Another observation is that the tan δ peak corresponding to the relaxation does not modify significantly with the temperature, this indicating that temperature increase does not affect considerably the relaxation activation energy.
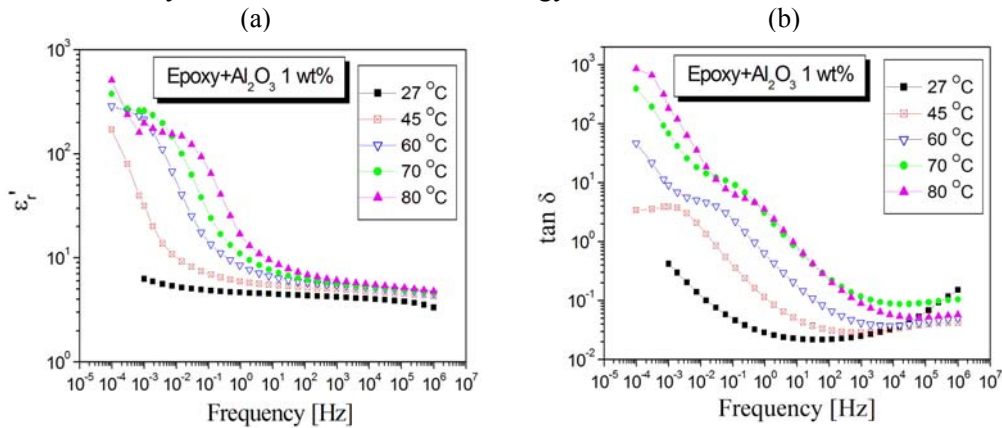

Fig. 5. Frequency variation of $ε_r'$ (a) and of tan δ (b), for epoxy-Al_2O_3 nanocomposites with 1 wt.% filler concentration, at different temperatures between 27 and 80 °C.

6. Conclusions

The studied epoxy nanocomposites with low concentrations of Al_2O_3 and SiO_2 nanoparticles exhibit an increase of dielectric permittivity at low frequencies of the electric field compared to the neat polymer. The thermally activated relaxation observed in neat epoxy is amplified by the nanofiller presence without changes of characteristic frequency.

The relaxations are shifted to higher frequencies with the increase of temperature, but without a significant modification of the dielectric loss peak.

The addition of inorganic nanofillers in epoxy resin could be a solution for improving the dielectric performances needed for better electrical energy storage dielectrics, but further studies have to improve the understanding and the controlling of the filler-polymer interfaces.

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