DEVELOPMENT CHARACTERIZATION AND FUNCTIONALITY OF EPOXY RESIN/BARIUM OXIDE COMPOSITE MATERIALS

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Abstract

Epoxy resin/BaO composites were prepared and their dielectric properties were studied by means of Broadband Dielectric Spectroscopy (BDS) in the frequency range of 10^{-1}-10^{7} Hz and over the temperature range of 30° C-160° C varying the filler content. In the dielectric spectra three relaxation processes were detected, namely IP, α-relaxation and β-relaxation. Obtained results are analyzed via the dielectric permittivity and electric modulus formalisms. Nanofiller content affect the dielectric response of the composites via the particle-polymer and the particle-particle interactions. At low filler content, reduction of the macromolecular mobility causes a decrease of permittivity and an enhancement of glass transition temperature, while at high filler loading, permittivity increases in tandem with glass transition temperature because of the limited macromolecular mobility, and the high permittivity of the particles.

1. Introduction

The significance of ceramic-polymer nanocomposites is undeniable and the crystal nanoparticles which are homogeneously distributed in an amorphous host represent a novel class of engineering materials with numerous interesting properties such as excellent dielectric properties and simple methods of development [1-4]. Ceramics are the most commonly used dielectric materials because of their high values of dielectric permittivity and good thermal stability, on the other hand polymers exhibit high breakdown strength and better mechanical flexibility. It is essential to combine the high dielectric constant of ceramics with the high breakdown strength and processability of polymers in the development of polymer composite materials. The produced polymer composite system aims to combine the three desirable characteristics that is high dielectric constant, low dielectric loss and high breakdown field strength. The electrical response of polymer matrix particulate composites depends on various factors like the permittivity and conductivity of the constituent phases, the size, shape and volume fraction of the filler and the type of distribution of the inclusions. Another important factor is the interface between the polymer matrix and the ceramic filler as there are interactions between of them. It is notable to refer some basic characteristics of nanocomposites such as the small amount of filler, the nanometric filler's size and their large specific area [5-8]. Nanostructured multicomponent dielectric systems are defined as nanodielectrics. There are two basic categories of nanodielectrics: (i) polycrystalline semiconducting or insulating materials, with nanometric grain diameter and (ii) polymer composites reinforced with nanoinclusions which expected to have unique dielectric properties due to interfacial region between the polymer matrix and the nanofiller [9]. In the present work, composite systems of epoxy resin as the matrix reinforced with ceramic BaO particles have been prepared and studied at various filler contents. Dielectric properties were examined by means of Broadband Dielectric Spectroscopy (BDS) in a wide frequency and temperature range. Experimental data were analyzed by means of dielectric permittivity and electric modulus formalisms [8]. Three dielectric relaxations are recorded which are related to both the polymer matrix and the presence of the reinforcing phase.

2. Experimental

2.1 Materials and nanocomposites preparation

The nanocomposite samples were fabricated by commercially available materials. The polymer matrix was prepared by a low viscosity prepolymer epoxy resin (Epoxol 2004A, Neotex S.A., Athens, Greece) and a slow rate curing agent (Epoxol 2004B) supplied by the same company also. Barium oxide nanoparticles were purchased by Sigma Aldrich. Particle’s diameter was less than 500nm, according to the supplier’s datasheet. The preparation procedure is constituted by five steps:

(i) Epoxy prepolymer and curing agent were mixed in a 2:1 (w/w) ratio in order to prepare the epoxy resin matrix.
(ii) While the epoxy resin was in liquid state, the filler amount was added.
(iii) The filler/matrix mixture subjected to a slow rate stirring process and ultrasonication.
(iv) Homogenized mixtures were poured to moulds.
(v) The curing took place at ambient for seven days and followed by post-curing at 100°C for 4 h.

The main goal of the preparation procedure was to achieve fine dispersed nanoparticles with no extensive cluster and voids. The BaO content of the prepared specimens in parts per hundred resin (phr) per weight was the following: 0 (unreinforced epoxy), 0.1, 1, 3, 6, 10 and 15 phr.

2.2 Dielectric Measurements

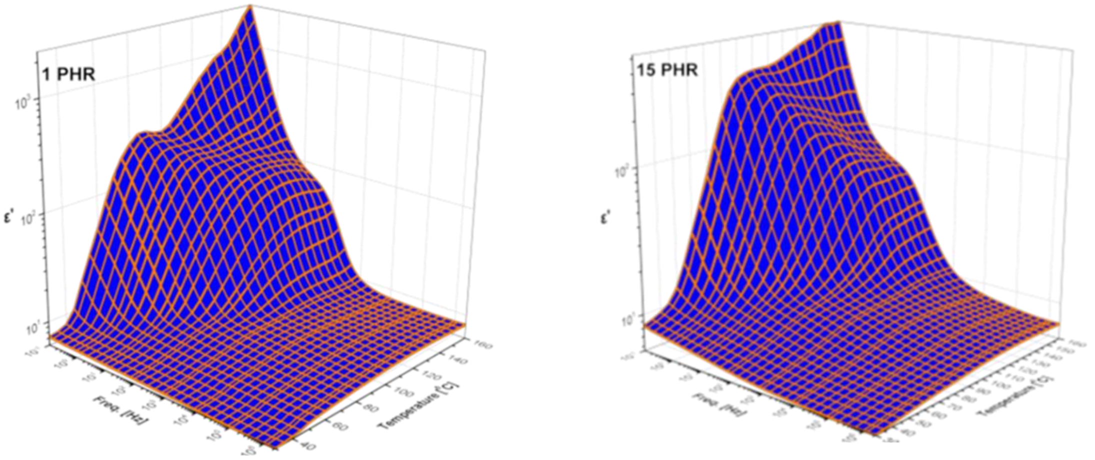
The dielectric characterization was held by means of BDS (in the frequency range of 0.1Hz to 10MHz) using an Alpha-N Frequency Response Analyzer and a BDS1200 dielectric cell. Temperature was controlled by a Novotherm system and data acquisition was conducted automatically via suitable software (Windeta). Dielectric devices and software were all provided by Novocontrol Technologies (Hundsagen, Germany). Furthermore, every examined specimen was isothermally (from ambient to 160°C with a temperature step of 10°C) frequency scanned. The amplitude of the applied voltage was 1000 mV. Specimens were placed between two gold-plated electrodes in a parallel-plate capacitor configuration.

3. Results and Discussion

Three dimensional (3-D) plots of the real part of dielectric permittivity (ε') and loss tangent ($\tan\delta$) are shown in Fig. 1 and Fig. 2 respectively, for the nanocomposites with 1 and 15 phr content, as a function of frequency and temperature. Similar spectra have been recorded for all studied nanocomposites. Permittivity attains high values in the low frequency and high temperature regions, conditions in which the maximum of polarization is achieved, since permittivity is proportional to polarization. As the frequency increases dipoles fail to follow the rapid alternation of the applied field, leading to low polarization level and permittivity values [10], due to the inactivity of the loads accumulated at the phases’ interface [11-12].

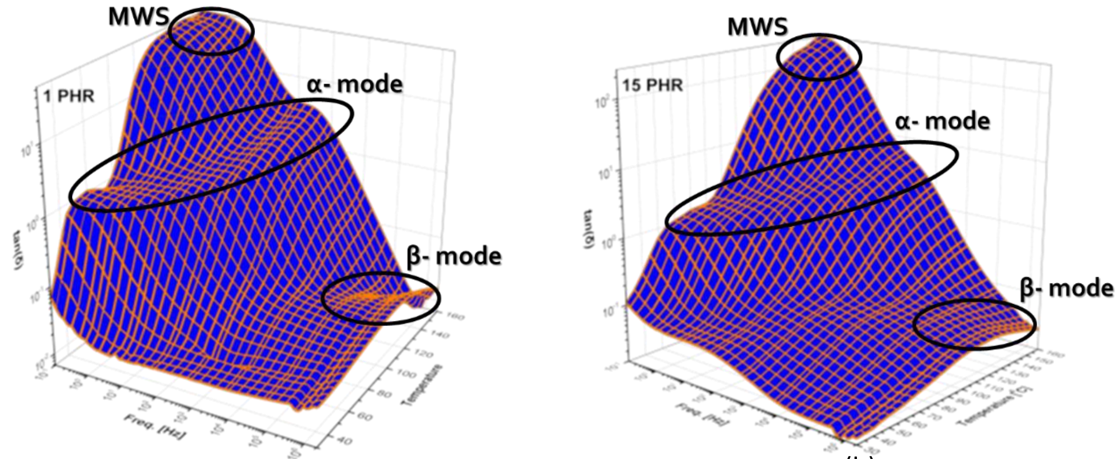
The very high values of the real part of dielectric permittivity at low frequencies indirectly indicate the possibility of the presence of the parasitic effect of electrode polarization.

Nevertheless, under isothermal conditions the real part of dielectric permittivity is decreasing rapidly at increment of the frequency. The very high values of ε′ raise obstructions in studying the dielectric behavior of composite materials due to the overlapping of processes. These processes are related to phenomena such as interfacial polarization or Maxwell-Wagner-Sillars effect (IP or MWS effect), electrode polarization or conductivity. Specifically the phenomenon of MWS is strongly related to the heterogeneity of the system and is more intense as the electrical characteristics of the sample's components diverge significantly [11-12]. Concerning the electrode polarization is an undesirable parasitic effect being the result of the charge concentration at the sample-electrode interfaces. To eliminate the effect of the phenomenon in data analysis the formalism of complex electric modulus (M*) is used (Fig.5, Fig.6) [13-14].



(a) (b)

Figure 1: Real part of permittivity (ε′) as a function of frequency and temperature for the samples (a) 1 phr and (b)15 phr in BaO content.



(a) (b)

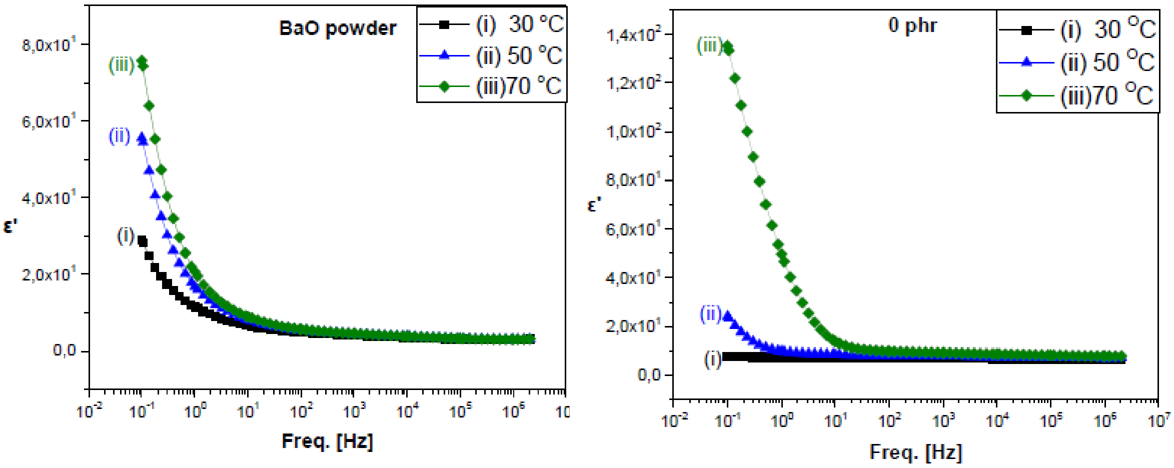
Figure 2: Tanδ as a function of frequency and temperature for the samples (a) 1 phr and (b)15 phr in BaO content.

In Fig. 2 three relaxations are recorded, the first one in the low frequency region, the second one in the intermediate and the third one corresponding at the high frequencies.

At high frequencies, the fastest process observed is attributed to lateral polar group motions of the main polymeric chain, and to be more specific in re-orientation of lateral polar portions of the polymeric chain (β-relaxation), this process is the weakest one [15].

At the intermediate frequencies, the recorded relaxation process is characterized as relatively slow (corresponding to a longer relaxation time) and is attributed to the transition from the glassy to the elastomeric phase of the amorphous polymeric matrix (α-relaxation) [15]. This transition is characterized by the glass transition temperature T_g, which is related to the location of the loss peak. The non-linear change in the position of the loss peaks with the temperature enhances the correlation of the particular process with the vitreous transition of the matrix [16]. The glass transition or α-relaxation are cooperative phenomena corresponding to micro-Brownian motions of the polymer chain [15]. These movements are related to changes in chain configuration, which lead to the rotation of the dipoles around the chain. These elemental motions are termed "local multimeric chain motions" can comprise large portions of the chains and are particularly complex. Thus, the local motions of the polymer chain take place in a high-density chain environment because of this high density intramolecular interactions contribute to α-relaxation process. Large parts of the macromolecular chains relax simultaneously because of the existence of cross links between the polymeric chains [16, 17].

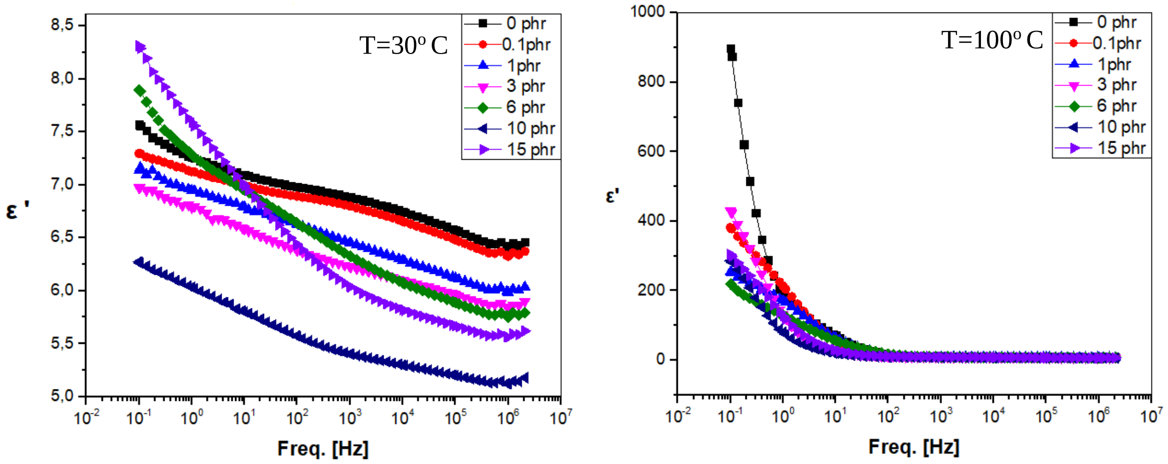
The slowest process is observed in the low frequency and high temperature range. This is attributed to the MWS phenomenon which is observed in heterogeneous materials with the accumulation of charges at the interface of the phases, where large dipoles are formed [1,8,18].



(a) (b)

Figure 3: Real part of permittivity (ε΄) as a function of frequency in 30° C, 50° C and 70° C for (a) BaO powder and (b) epoxy resin.

It is important to mention that the increase of BaO particles in composites causes a decrease of ε΄, as the BaO powder presents lower values of ε΄ than the neat epoxy (Fig. 3). Generally, the values of the real part of dielectric permittivity increase more at high temperatures and low frequencies. This phenomenon observed in all prepared samples (Fig. 4).



(a) (b)

Figure 4: Real part of permittivity (ε΄) as a function of frequency for all composites at (a) 30° C and (b) 100° C.

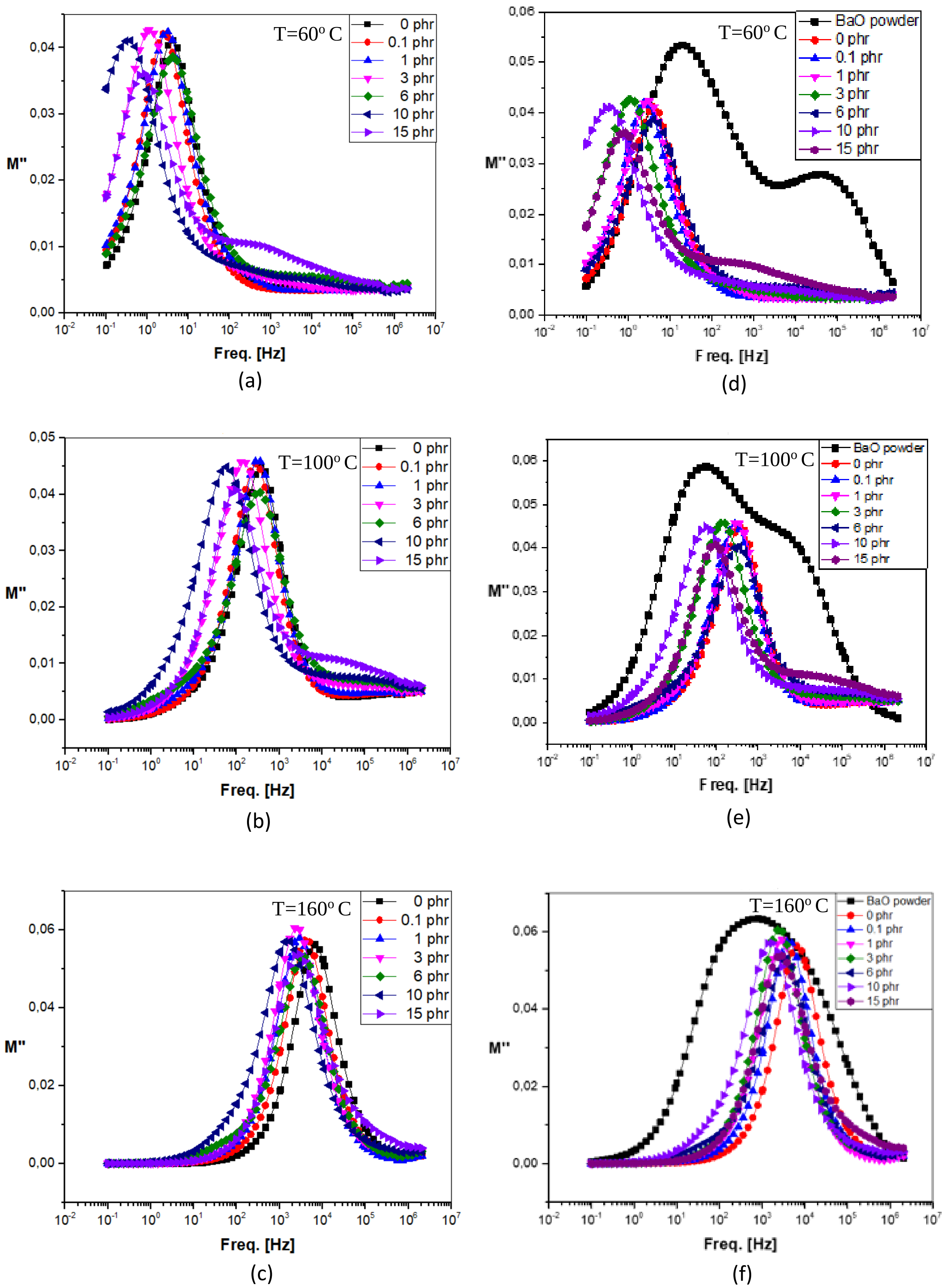
For a more insight study of the electrical relaxation phenomena in our composites, electric modulus is used which is defined as the inverse quantity of complex permittivity by the Eq. (1):

$$M^{*}=\frac{\mathbf{1}}{\varepsilon^{*}}=\frac{\mathbf{1}}{\varepsilon'-j\varepsilon''}=\frac{\varepsilon'}{\varepsilon'^{2}+\varepsilon''^{2}}+j\frac{\varepsilon''}{\varepsilon'^{2}+\varepsilon''^{2}}=M'+jM'' \qquad (1)$$

where ε′, M′ are the real and ε″, M″ the imaginary parts of dielectric permittivity and electric modulus respectively [1]. Electric modulus describes the same physical processes as ε΄ and tanδ that occur in the complex systems under the influence of an alternating field.

According to Fig. 5 at a, b, c, a relative reduction in the peak's intensity by increasing the content of inclusion it is noticed, in tandem with shifting the peaks to lower frequencies at a constant temperature. These peaks are attributed to the α-relaxation. Under isothermal conditions, the displacement of the peak of loss of α-relaxation to higher frequencies suggests facilitating the process, which translates into less energy consumption and essentially means a decrease in T_g. In our case, where there is a shift towards lower frequencies of the peak of loss of α-relaxation, strong interactions and good adhesion are indicated, while the glass transition temperature of the composite system is increased due to the anchoring of the polymer chains on the surface of the particles and the resulting difficulty [16, 19].

In Fig. 5 at d, e, f it seems that peaks rise with temperature and shifted to higher frequencies at a different rate. Thus, the difference in the dynamics of relaxation leads to the superposition of processes and ultimately to the formation of a broad peak at 160° C. At a first approximation, the low frequency process could be related to the growing interfacial polarization between BaO particles, while the process at relatively higher frequencies with the MWS effect due to accumulation of charges at the grain boundaries of the reinforcing phase.



(a) (d)

(b) (e)

(c) (f)

Figure 5: Imaginary part of electric modulus (M´´) as a function of frequency for all composites at (a) 60° C, (b) 100° C and (c) 160° C and imaginary part of electric modulus (M´´) as a function of frequency for all composites including BaO powder at (d) 30° C, (e) 100° C and (f) 160° C.

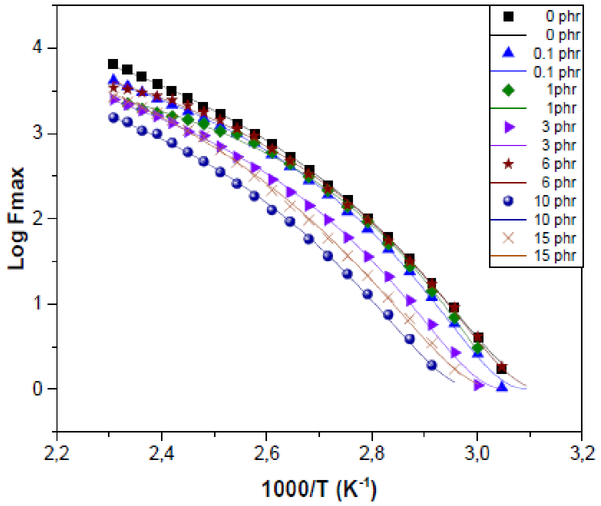


Figure 6: Loss peak position as a function of the inverse of reciprocal temperature for the α-relaxation. Each curve corresponds to different filler content.

In Fig. 6 the relaxation dynamics of α-mode is presented for all systems studied. The absence of a corresponding study on the processes of β-relaxation and IP is associated with the limited available points, which make any fitting procedure not reliable. The α-relaxation follows the temperature dependence according to the Eq. (2):

$$\boldsymbol{f_{max} = f_0 e^{-\frac{B}{T-T_0}}} \tag{2}$$

where $f_{\max}$ is the loss peak frequency at a given temperature, f_0 pre-exponential factor, B a constant associated with activation energy, and T_0 Vogel temperature, associated with the glass transition temperature (T_g) [20-22].

4. Conclusions

In the present study, the dielectric response of polymer matrix-ceramic BaO composites was investigated in a wide frequency and temperature range. The analysis of the results of dielectric spectroscopy was carried out in two formalisms: dielectric permittivity (ε) and electric modulus (M). On the curves of the electric permittivity as a function of the frequency, lower values of the real part of the electric permittivity of the composites are attributed to the lower permittivity values of barium oxide relative to the epoxy resin. In addition, an increase in the real part of the dielectric permittivity of the composites with increasing temperature was observed. It was considered appropriate to use the formalism of electric modulus (M), since it neglects the parasitic effect of the polarization of the electrodes. Three relaxation mechanisms were detected, which are attributed to the transition from glass to elastomeric phase (α-relaxation) of the matrix, re-orientation of polar side chains of the polymeric chain (β-relaxation) as well as to interfacial polarization (IP or MWS effect) between matrix and encapsulated phase. Finally, dynamics of α-relaxation was studied via VFT equation.

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