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Dielectric response and relaxation phenomena in composites of epoxy resin with $BaTiO_3$ particles

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Abstract

Dielectric properties and relaxation phenomena of composite materials (epoxy resin—barium titanate) were studied as a function of ceramic content. The composites were prepared mixing both components and pouring them into suitable moulds. Some composites were made using tetrahydrofuran (THF) because it helped to reduce matrix viscosity, facilitating the system mixture. Dielectric measurements showed that dielectric constant of composites depended on the filler amount, the temperature and the frequency. Dielectric losses also were influenced by the temperature and by the frequency through relaxation process, even though volume fractions did not have influence on losses.

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1. Introduction

New generation of passive electronic devices will require high performance with lower cost, size and weight, besides a very high reliability. These requirements demand significant efforts in research and development; nevertheless it is possible to combine different materials in order to obtain optimum properties [1]. One of the most advantageous solutions involves using integral passive technology, in which resistors, inductors, and capacitors are embedded directly into printed wiring boards substrate.

Current researches have studied composite materials made of ceramics and polymers, such as dielectric material in capacitors [2], because ceramics have high dielectric performance and polymers have low cost and are easily processed. Therefore, polymer–ceramic materials have aroused much attention for uses in microelectronics packaging [3].

As the dielectric properties are strongly influenced by the ceramic phase (content, particle size and distribution), processing techniques are very important, because dielectric performance of the final composite can be affected by porosity grade or filler distribution. In the same way, the necessary amount of filler has to be enough (more than 30% in volume), to change the permittivity of the composite, but these high levels may make processing the materials more difficult. Therefore it is necessary to use polymers with low viscosity or to introduce solvents, increasing the relaxation phenomena and dielectric losses. Furthermore, the matrix must have very low dielectric losses in order to optimise the device working.

To explain and predict the effect of each phase on the composite dielectric properties, various dielectric mixing models have been proposed and investigated during the past decade [3]. However, all these models are only based on the conventional data interpretation, such series, parallel, Hashing–Shtrikman and Lichtenecker models [4]. The first ones are based on the rule of mixture, while Lichtenecker is a formula which considers the composite as a random mixture of nearly spherical inclusions [3].

In this work, the electrical relaxation phenomena in composites made of barium titanate particles in an epoxy polymer were studied. Composites were made using pure epoxy and epoxy diluted in a solvent (tetrahydrofuran, THF) for reducing the polymer viscosity. Dielectric measurements

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were analysed to study relaxation phenomena as a function of frequency, temperature and filler volume fraction.

2. Experimental

Epoxy DER 325 (Dow Chemical) was chosen because of its good dielectric properties ($\varepsilon = 4.18$, tan $\delta = 0.0082$). DEH 324 (Dow Chemical) was the curing agent (12.5 phr). Pure resin and resin with 9% wt of THF (Dorwil Chemical), was characterised by differential scanning calorimeter analysis (DSC). ASTM D3418-82 was followed and the tests were performed using a Shimadzu DSC-50 in nitrogen atmosphere and a heating rate of 10 °C/min from ambient temperature to 200 °C. The glass transition temperature was taken as the midpoint value between the onset and the completion of the transition. Commercial barium titanate, $BaTiO_3$ (TAM Ceramics, Inc.) was used as a filler. It was doped with 0.6% wt of Nb_2O_5 to modify its dielectrical properties. Powders were mixed in isopropilic alcohol by agitation at 6000 rpm for 5 min. Afterwards, the alcohol was eliminated by heating at 65 °C until constant weight. One fraction of powder was thermally treated at 1350 °C for 180 min. using heating and cooling rates of 3 °C/min. Another part was pressed into disks of 1 cm diameter and 0.2 cm thick at 20 MPa, and then sintered at the same conditions as the powder.

The powder was milled using a planetary mill with ZrO_2 balls (Fritsch, Pulverisette 7) for 90 min, in isopropilic medium. Particle size distribution was measured by Micromeritics equipment. X-ray diffraction (XRD) study of the $BaTiO_3$ samples was carried out on sintered samples, using Philips PW 1050/25 equipment with Co Kα radiation and a Fe filter, at 40 KV and 30 mA. From the (002) and (200) diffraction profiles, a semi-quantitative study of the cell distortion was performed.

The ceramic powders were added to the epoxy resin at different volume fractions and then suitably blended using an electric mixer at 2000 rpm. THF was introduced to reduce the viscosity of mixture with filler fractions between 20 and 50% v/v. Composites with low filler content (2–30% on volume) were mixed without addition of THF. Each mixture was poured into glass moulds and cured at 100 °C for 2 h. Density was measured by Archimedes's method and theoretical density (ρ_T) was calculated using Eq. (1).

$$\rho_T = (1 - V)\rho_p + V\rho_m \qquad (1)$$

where ρ_p is the filler density, ρ_m is the matrix density and V is the volume fraction of filler.

Microstructures of the polished samples were examined by scanning electron microscopy (Philips model SEM 505). Finally, for dielectric measurements, samples were painted with a silver paste and dielectric measurements were performed using a Hewlett Packard 4284A Impedance Analyser from 20 Hz to 1 MHz. Some samples showed a great dispersion in the capacitance at low frequency and then, in these samples data were acquired from 1 KHz.

3. Results and discussion

3.1. Materials characterisation

DSC analyses of epoxies with and without solvent are shown in Fig. 1. The transition temperature (T_g) of pure epoxy is 92 °C, while for the mixture epoxy-solvent is 80 °C, nevertheless reaction peaks were at 100 °C for both systems. It can be clearly seen that solvent remains into the material, changing the mobility of the molecules.

The particles size of powder after milling in the planetary mill were 0.65, 1.4, 2.6 μm for the particle diameters corresponding to 20, 50 and 80 vol.% of the distribution, D20, D50 and D80, respectively. From the values a smooth particle distribution is observed. On the other hand, the lattice parameters (c/a) of thermal treated powder and sintered and grounded disk are 1.0039 and 1.0033, respectively. From these results, it is observed that powders and disk ceramic disk show similar tetragonal parameters (c/a), which means that the filler

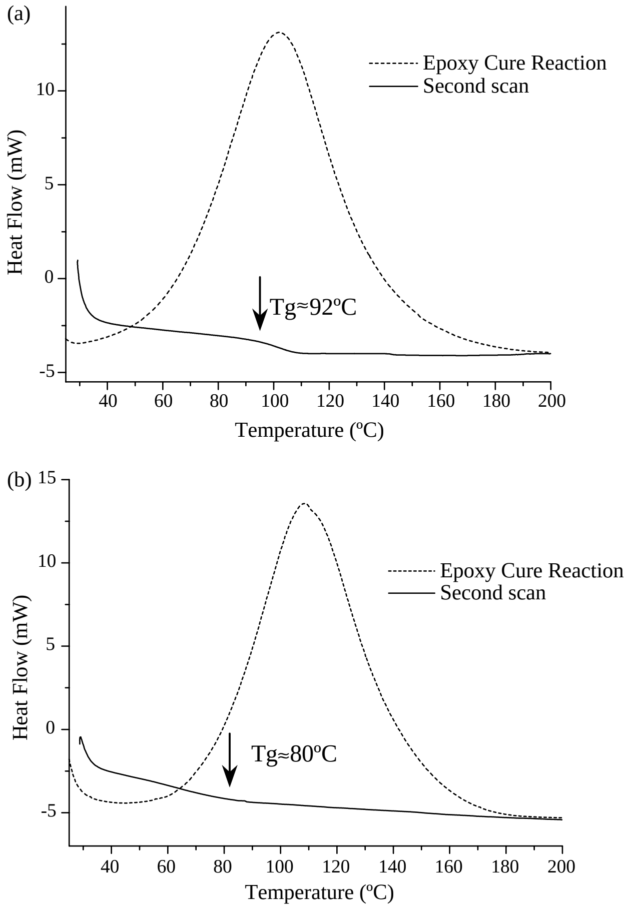


Fig. 1. Differential calorimeter analysis (DSC) of pure resin (a) and resin with THF (b).

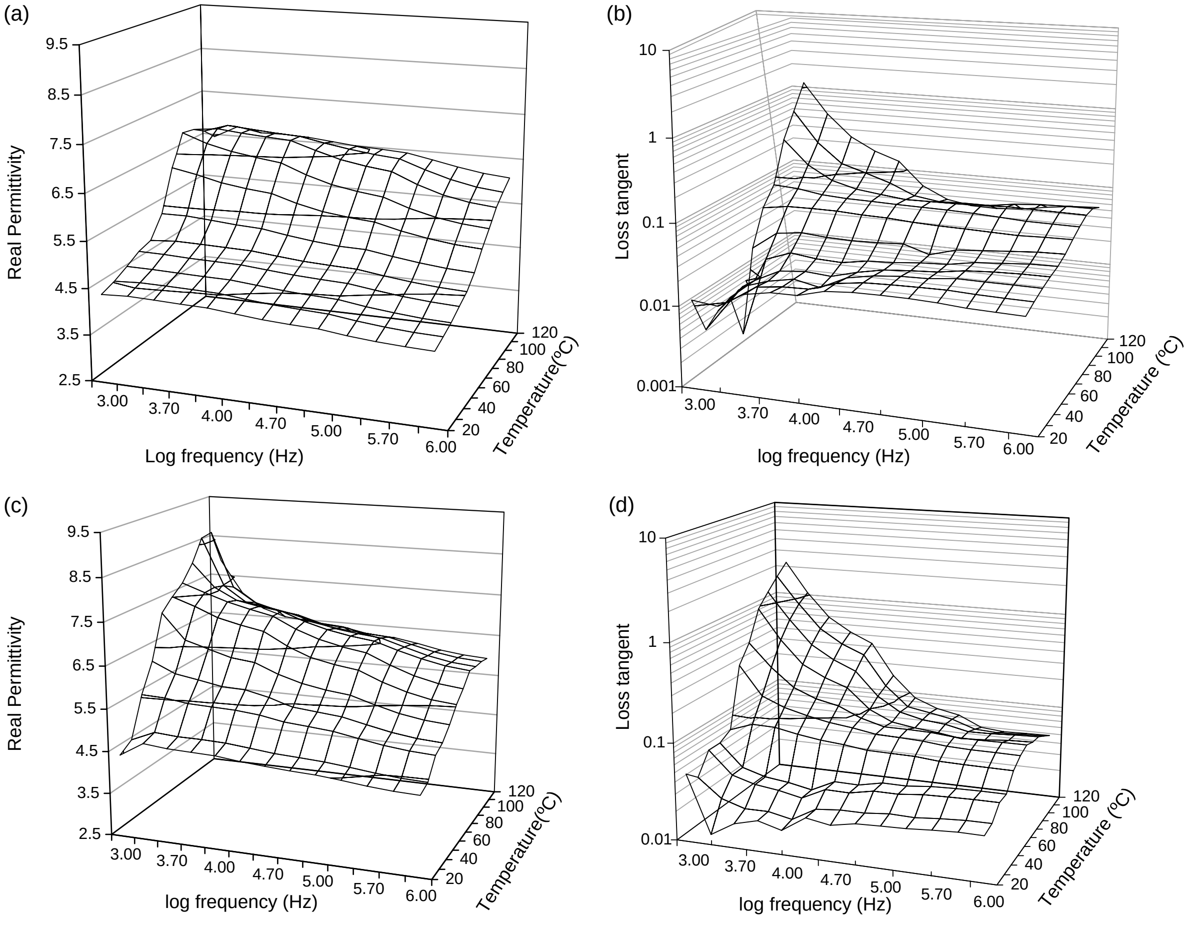


Fig. 2. Real permittivity (a) and (c); and loss tangent (b) and (d) for pure resin (a, b) and resin with THF (c, d) vs. log frequency and temperature.

has a pseudo-cubic structure and processing does not generate important microstructure changes.

Real permittivity and losses of epoxies (with and without THF) are plotted in Fig. 2 at different temperatures and frequencies. Loss tangent and real permittivity are influenced by the temperature and the frequency in both systems. At room temperature the permittivity at all frequencies has values around 4 and loss factors below 0.01. However, as temperature increases permittivity increases mainly around T_g. At temperatures near T_g the dipoles begin to have enough mobility to contribute to the permittivity, occurring first at the lowest frequency, indicating a relaxation process. The loss tangent has a similar behaviour; nevertheless losses are largest at high temperature and low frequency. Resin with THF (Fig. 2c and d) presents similar behaviour; but it appears at lower temperatures due to its lower T_g.

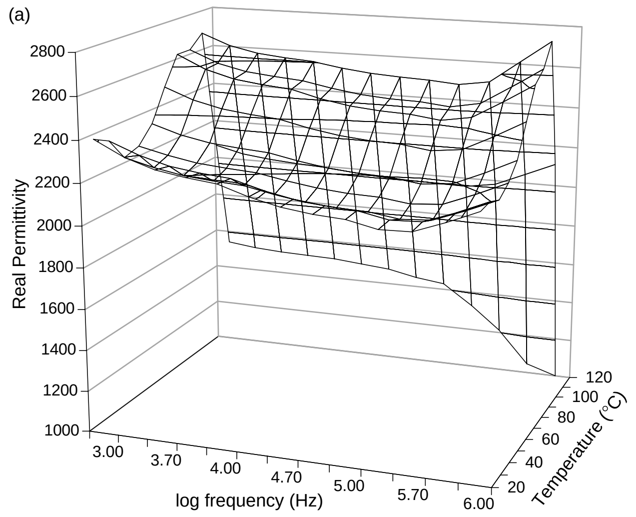
It is known that polymers in the amorphous state present a relaxation region associated with the glass transition. This relaxation process is usually labelled α and is referred as the primary or glass-rubber relaxation [5]. From a dipolar point of view it results from large-range motions 'dipole-elastic process' corresponding to microbrownian segmental motion of chain [6].

The dielectric behaviour of Nb_2O_5-doped $BaTiO_3$ is plotted in Fig. 3. Fig. 3(a) represents the permittivity response at different frequencies and temperatures, while Fig. 3(b) shows loss tangent for the same variables. Dielectric losses are low and constant for a long range of temperatures. On the other hand, permittivity is affected near the Curie temperature (≈ 90 °C). In the same way, dielectric losses raise when the temperature increases after Curie temperature. These changes are due to thermally activated conduction phenomenon, which are more visible in samples with a pseudo-cubic structure.

3.2. Microstructure analysis of composites

The experimental and theoretical densities of composites for different filler amount are shown in Table 1. Only fractions below 30% v/v could be added in pure resin, due to the high viscosity of the system (≈ 800 cp). The difference between the experimental and theoretical density values is fundamentally due to the presence of a porous microstructure, which is produced during mixing process when air liberation is restricted due to system viscosity. Composites up to 50% v/v of filler were obtained with the addition of 9% wt of THF. It helped to reduce the resin viscosity, decreasing the difference between the experimental and theoretical values.

Photographs obtained by scanning electron microscopy are shown in Fig. 4. Sample (a), (b) and (c) show composites with



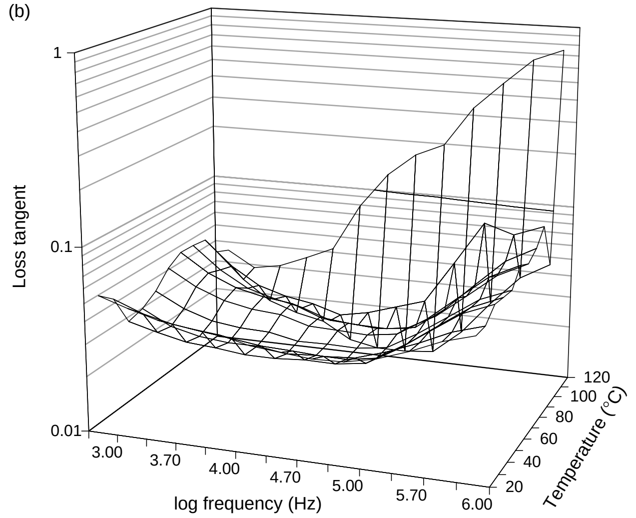


Fig. 3. Real permittivity (a) and loss tangent (b) for $BaTiO_3$ vs. log frequency and temperature.

8.5, 15 and 30% v/v of particles for pure resin and (d), (e) and (f) composites with 32, 41 and 50% v/v for epoxy with THF. Fig. 4f shows macro-pores; while smallest trails of micro-porosity could be seen in all samples. It can be observed that particle distribution is homogeneous with small trails of agglomeration. Finally, solvent did not affect the particle distribution but helped to increase the possible volume fraction of particles.

3.3. Dielectric behaviour of composites

Real permittivity and loss tangent values as a function of frequency and percentage of ceramic at 30 °C in a pure resin are plotted in Fig. 5a and b. The same properties for the resin with THF are shown in Fig. 5c and d. Real permittivity rises with volume fraction ceramic for both systems, although a break due to the high porosity in composites made with pure resin (Fig. 5a and Table 1, sample with 8.5% v/v). Permittivities as high as $40\varepsilon_0$ are obtained with the addition of 50% v/v of particles. Materials with higher filler amount have similar behaviour with frequency to pure resin. Loss tangent is practically constant at all filler volume fraction over the frequency range studied, even though differences could be seen related to porosity effect and dispersion of measurements.

Fig. 6 shows real permittivity and loss tangent of composites with 30% v/v of $BaTiO_3$ made from pure resin (a and b) and resin with solvent (c and d). Permittivity increases when the temperature rises. There are three competitive mechanisms: (a) segmental mobility of polymer is increased with temperature, which should increase permittivity; (b) thermal expansion of resin and ceramic disrupting the chains of contacting particles, which should decrease permittivity and; (c) changes in the ceramic structure produced by temperature increase (before Curie temperature), generate modification on dielectric response of the filler decreasing permittivity. As it will be explained below, loss tangent curves of resins and composites near T_g have a similar behaviour due to the influence of filler does not respond at a simple rule of mixtures. Frequency dependence of permittivity (ε') shows a decrease in permittivity with increasing frequency for composites and resins (with and without solvent, Figs. 2 and 6). This effect is more important at elevated temperature and low frequency. In the matrix a decrease in dipolar polarisation can be responsible for this behaviour, but in the composite systems another affecting term is present besides the dipolar polarization of polar groups: the interfacial or Maxwell–Wagner–Sillars (MWS), polarization due to the heterogeneity of the systems [7]. The piling of charges at the interface causes large-scale field distortion, in contrast to the other types of polarisations (atomic, electronic, dipolar),

Table 1
Variation of density at $BATiO_3$ fraction for pure and diluted resin

Pure resin			Diluted resin		
Volumetric fraction (V_p%)	Theoretical density (g/cm^3)	Experimental density (g/cm^3)	Volumetric fraction (V_p%)	Theoretical density (g/cm^3)	Experimental density (g/cm^3)
2	1.25	1.2	21	2.12	1.97
5	1.37	1.33	32	2.67	2.55
8.5	1.55	1.35	41	3.06	2.87
15	1.89	1.70	50	3.54	3.27
30	2.55	2.31			

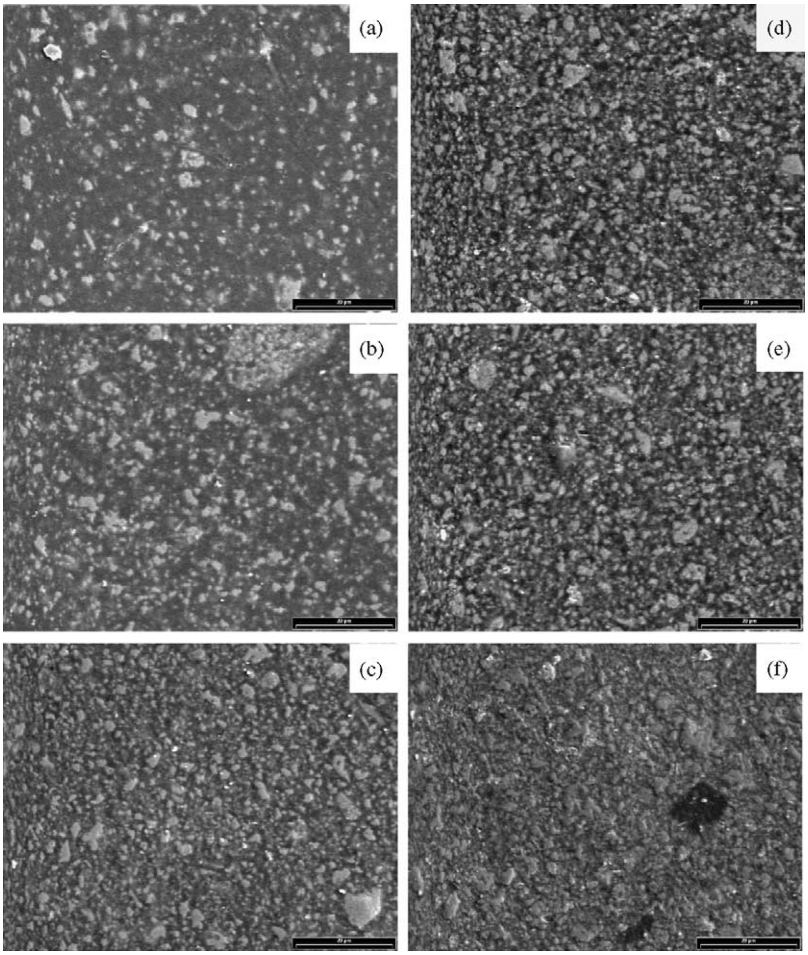


Fig. 4. SEM of composites made of pure resin with 8.5 (a), 15 (b) and 30% (c) of volume loading for pure resin and 32 (d), 41 (e) and 50% (f) of volume loading for resin with THF. Bar 20 μm.

being produced by the displacement or orientation of bound charge carriers [8].

Frequency dependent relaxation process is observed using electrical modulus (Eq. (2)), because it helps to understand bulk relaxation properties at low frequencies [9].

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + jM'' \tag{2}$$

Fig. 7 is obtained, giving the real (M') and the imaginary (M'') part of electrical modulus for composites counting $\approx 30\%$ v/v of $BaTiO_3$, made of pure resin and resin with solvent. It can be seen that M' values increased with frequency and reached a rather constant value. A rise in temperature produces a diminution in the M' values at the low frequency range, but did not change M' at higher frequencies. At the same frequency range, peaks in M'' values are developed, indicating a relaxation process which is not evident in values of loss tangent. These peaks correspond to α relaxation and start to be formed at high temperature near epoxy T_g, as mobility of polymer molecules is enhanced [10]. Experimental data showed a great dispersion in regions of low frequencies and low temperatures, so relaxations at lower temperatures were impossible to be detected.

The imaginary parts of electric modulus versus frequency are plotted for different ceramic volume concentration in Fig. 8 at 100 °C for both matrices. As it can be seen the temperature is almost the T_g of both polymeric systems, so there is some molecular mobility present. The maximum of M'' is diminished when filler amount increases, because the real permittivity ε' is increased. Relaxations peaks are displaced to higher frequencies, as expected because of relaxation processes. They are influenced by interfacial polarisation effect, known as MWS, which generates electric charge accumulation around the ceramic particles, displacing the relaxation peaks [7]. Also, the solvent displaces slightly relaxation peaks to higher frequencies, due to increases the dipolar mobility.

3.4. Experimental data fitting

In Fig. 9, series, parallel, Lichtenecker and Hashing–Shtrikman's models as a function of the filler volume

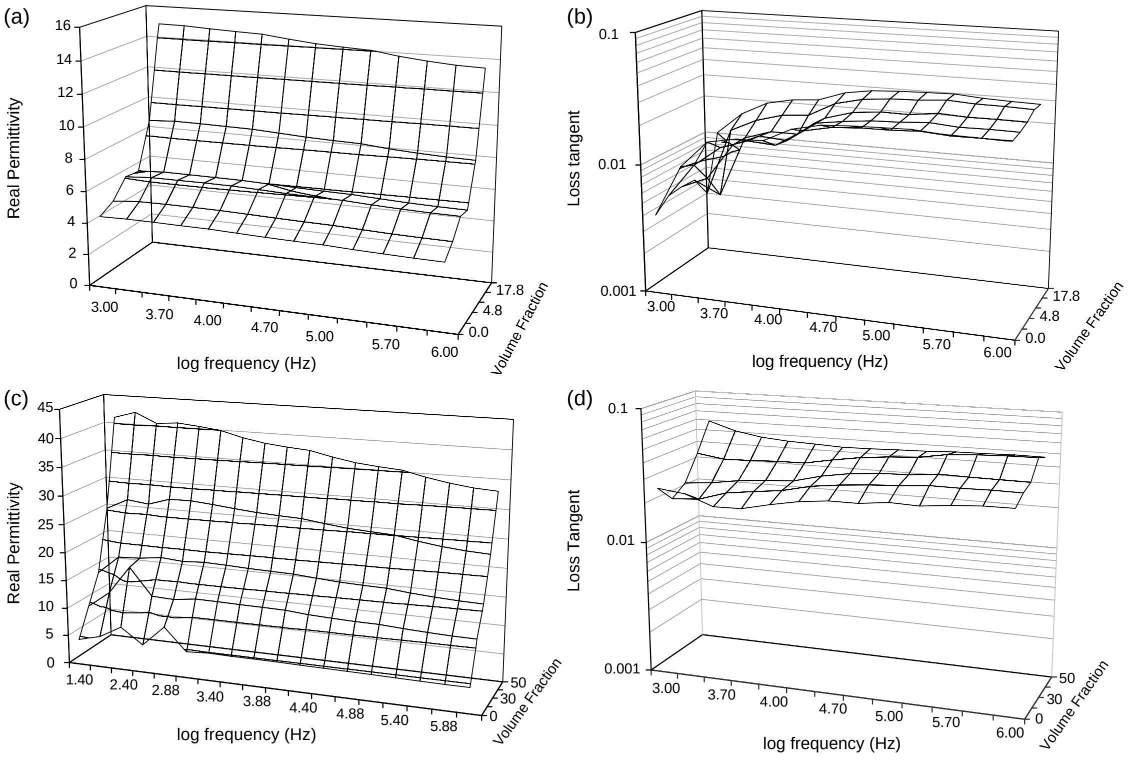


Fig. 5. Real permittivity (a) and (c); and loss tangent (b) and (d) for composites made of pure resin (a, b) and resin with THF (c, d) vs. log frequency and volume loading at 30 °C.

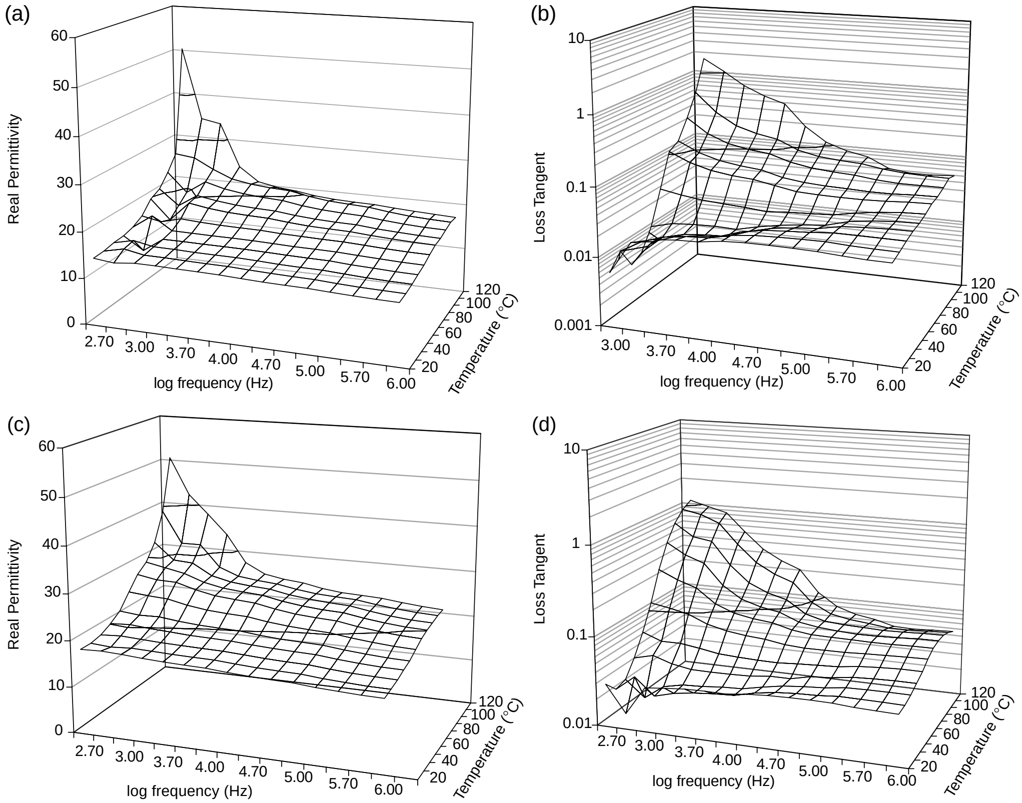


Fig. 6. Real permittivity (a) and (c); and loss tangent (b) and (d) of sample with 30% of volume loading made of pure (a, b) and resin with THF (c, d) vs. log frequency and temperature.

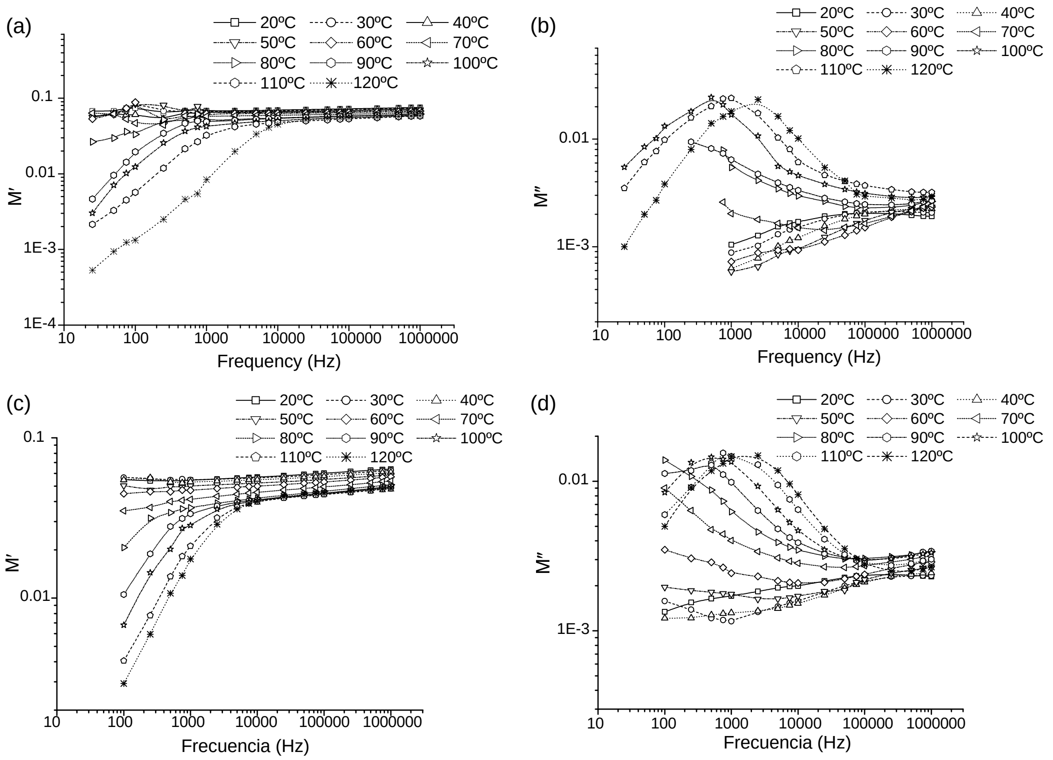


Fig. 7. Real part (M') (a) and (c); and imaginary part (M'') (b) and (d) of electric modulus of sample with ≈30% o volume loading made of pure (a, b) and resin with THF (c, d) vs. frequency.

fraction are plotted. In the fitting models the ceramic disk permittivity ($\varepsilon_f = 2280$) and the pure resin permittivity ($\varepsilon_m = 4.5$) were used. The experimental values were measured at 30 °C and 2500 Hz. Series and parallel mixing models represent the extreme cases where the model is alternated layers of each phase, perpendicular and parallel to the applied field, respectively. On the other hand, Hashin and Shtrikman's model employed the 'minimum energy' principle and introduced lower and upper bounds for effective magnetic permeability without requiring specific assumption about the phase geometry. This model may be considered for estimate the dielectric properties. The mathematical equations to each model are described as follows:

Series and parallel mixing modes

$$\text{Series} \quad \frac{1}{\varepsilon_c} = \frac{V_f}{\varepsilon_f} + \frac{V_m}{\varepsilon_m} \tag{3}$$

$$\text{Parallel} \quad \varepsilon_c = V_f \varepsilon_f + V_m \varepsilon_f \tag{4}$$

Hashin–Shtrikman bounds

$$\text{Lower bound :} \quad \varepsilon_c = \varepsilon_m + \frac{V_f}{1/(\varepsilon_f - \varepsilon_m) + V_m/3\varepsilon_m} \tag{5}$$

$$\text{Upper bound :} \quad \varepsilon_c = \varepsilon_f + \frac{V_m}{1/(\varepsilon_m - \varepsilon_f) + V_f/3\varepsilon_f} \tag{6}$$

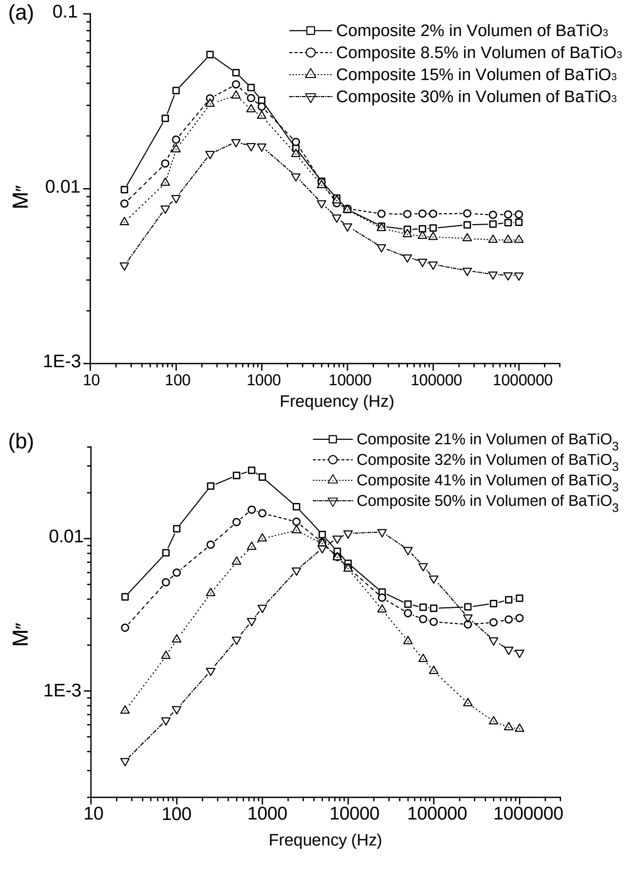


Fig. 8. Imaginary part (M'') of electric modulus for composites made of pure resin (a) and resin with THF (b) vs. frequency.

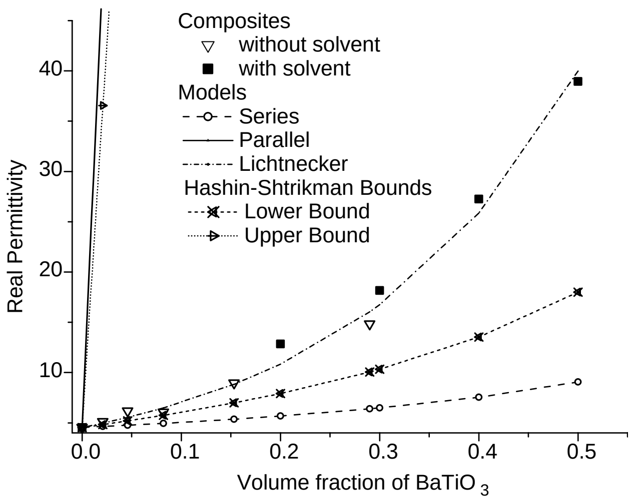


Fig. 9. Plot of theoretical mixing models and the measured real permittivity for different $BaTiO_3$ volume fractions at 100 °C and 2500 Hz.

Lichtenecker's mixing model

$$\log(\varepsilon_c) = V_f\varepsilon_f + V_m \log \varepsilon_m \qquad (7)$$

where V_f is the filler volume fraction and V_m is the matrix volume fraction.

The Lichtenecker's model shows the best tendency to fit the dates; due to it is an empirical relationship that presents a formula which considers the composite as a random mixture of nearly spherical inclusions [3]. The other models do not present a good agreement with the experimental data, because they are based in the simple rule of mixtures that do not consider appropriately particle distribution or interaction.

4. Conclusions

Both resins presented α relaxation processes, which are influenced by frequency. Resin diluted with THF had greater losses and relaxation peaks at lower temperatures than resin without THF, due to its higher molecular mobility.

Real permittivity is influenced by filler volume fraction. Ceramic particles produce a rise in permittivity and have more influence on samples with high volume fraction. In the same way, THF solvent helps to increase the permittivity by allowing an increase in the filler content. Nevertheless porosity is more important in composites with higher amount of filler, because of the higher viscosity of system.

Resins have influence on loss tangents and generate relaxation processes near their T_g on all composites, while ceramic content only influences the real permittivity. Interfacial polarisation processes known as Maxwell–Wagner–Sillar were generated by particles. It produced an accumulation of charges on the interface that helped to displace peaks to higher frequencies.

Dielectric mixing models such parallel, series and Hashin and Shtrikman bounds do not fit the experimental results. However, Lichtenecker fit the experimental results very good, for both matrices.

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References

[1] Uchino K, Takahashi S. Dielectric ceramic materials. Ceram Trans 1999;100:455–68.
[2] Thongvigitmanee T, May GS. Modelling and optimization of integral capacitor fabrication using neutral networks. Twenty sixth IEEE/CPMT international electronics manufacturing technology, Piscataway, USA 2000 [p. 47–54].
[3] Frost NE, McGrath PB, Burns CW. Effect of filler on the dielectric properties of polymers. Conference record of the IEEE international symposium on electrical insulation, Montreal, Quebec, Canada 1996 [p. 300–303].
[4] Yoon DH, Jianping Z, Burtrand I. Dielectric constant and mixing model of $BaTiO_3$ composite thick films. Mater Res Bull 2003;38: 765–72.
[5] McCrum NG, Read BE, Williams G. Anelastic and dielectric effects in polymeric solids.: Dover Publication; 1991 [chapter 5].
[6] Schönhals A. Dielectric spectroscopy on the dynamics of amorphous polymeric systems. Novocontrol application notes. Dielectrics 2003; 1.
[7] Psarras G, Manolakaki E, Tsangaris GM. Electrical relaxation in polymeric particulate composite of epoxy resin and metal particles. Compos Part A 2002;33:375–84.
[8] Tsangaris G, Kouloumbi N, Kyvelidis S. Interfacial relaxation phenomena in particles composites of epoxy resin with copper or iron particles. Mater Chem Phys 1996;44:245–50.
[9] Yu S, Hing P, Xiao H. Dielectric properties of polystyrene–aluminium-nitride composites. J Appl Phys 2000;88:398–404.
[10] Tsangaris G, Psarras GC. The dielectric response of a polymeric three-component composite. J Mater Sci 1999;34:2151–7.