J Mater Sci (2007) 42:3685–3691
DOI 10.1007/s10853-006-1408-6

Characterisation of epoxy/$BaTiO_3$ composites processed by dipping for integral capacitor films (ICF)

Leandro Alfredo Ramajo · Maria Marta Reboredo · Miriam Susana Castro

Received: 17 November 2005 / Accepted: 17 February 2006 / Published online: 30 January 2007

Abstract Polymer composites of epoxy resin and Nb_2O_5 doped $BaTiO_3$ were prepared in the form of film (thickness 30–300 μm) using a dipping technique. Samples containing various amounts of ceramic filler were examined by thermal analysis and SEM analysis. Dielectric measurements were performed from 20 Hz to 1 MHz and 20 °C to 120 °C. It was found that the final materials had high permittivities increasing with the filler concentration. Electrical relaxations were assigned to interfacial phenomena due to the particles and α-relaxation because of the resin.

Introduction

Polymeric composite materials, consisting of an epoxy resin and dielectric ceramic particles, have been reported to posses interesting properties for many varieties of applications, like passive electronic devices. Polymer-ceramic materials have arisen much attention mainly for uses in microelectronic packaging, because of their good performance and low cost, size and weight [1]. However, for optimal operation, matrix must have very low dielectric losses.

Composite dielectric behaviour can be affected by the presence of porosity and filler distribution. Besides the necessary amount of filler has to be enough to obtain a rather high composite permittivity. However the processing step is more difficult when high filler amounts are incorporated [2]. A possible solution to this problem is adding a solvent in order to decrease matrix viscosity. The diluted resin allows the incorporation of higher filler concentrations without increasing too much the viscosity and making thin films with higher capacitances.

It is known that the dipping process is an effective method to prepare coatings and films. This process has potential applications not only in electronic, magnetic, and electro-optical small thickness devices, but also in thermal, chemical and wear resistance coatings. The practical advantages of the method are raw materials and equipment costs. Using this technique, thickness of 10–50 μm can be easily achieved against other processing methods [3].

This paper reports the microstructure characterisation and dielectric properties evaluation of composite materials made of epoxy resin—barium titanate obtained by dipping process. In order to improve processing conditions, polymeric viscosity was reduced by adding tetrahydrofuran (THF). Composite relaxation phenomena as a function of frequency and temperature in samples with different filler amounts were analysed.

Experimental

A commercially available bisphenol based epoxy resin (DER 325, Dow Chemical) was chosen because of its good dielectric properties ($\varepsilon = 4.18$, $\tan\delta = 0.0082$). A triethylenetetramine, (DEH 324, Dow Chemical) at

L. A. Ramajo (✉) · M. M. Reboredo · M. S. Castro
Instituto de Investigaciones en Ciencia y Tecnología de Materiales, INTEMA, CONICET-UNMdP, J.B. Justo 4302, Mar del Plata, Buenos Aires B7608FDQ , Argentina
e-mail: lramajo@fi.mdp.edu.ar

12.5 phr (part per hundred of resin) was employed as curing agent. Tetrahydrofuran (THF, Dorwil Chemical, boiling point 66 °C) up to 60 wt% was added to reduce the resin viscosity. The chemical systems were characterised by differential scanning calorimetry (DSC, Shimadzu DSC-50) in nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 200 °C. The reaction temperature (T_r) and the glass temperature (T_g) of the systems were determined. The retained solvent mass could be determined by weighting the sample before and after the temperature scanning. Finally, viscosity measurements were made using a Brookfield viscometer model LVRD at 20 °C.

Commercial barium titanate, $BaTiO_3$ (TAM Ceramics Inc.), was used as the filler. It was doped with 0.6 mol% of Nb_2O_5 to modify its dielectrical properties. Powders were mixed in isopropilic alcohol by agitation at 6,000 rpm during 5 min. Afterwards, alcohol was eliminated by heating at 65°C until constant weight was achieved. The powder was thermally treated at 1,350 °C for 180 min using a heating and a cooling rate of 3 °C/min. The powder was milled using a planetary mill with ZrO_2 balls (Fritsch, Pulverisette 7) for 90 min, in isopropilic medium. An average particle size of 1.4 μm was determined employing a Micromeritics equipment.

Fabrication procedure of epoxy/$BaTiO_3$ composites films is shown in Fig. 1.

First, a suspension containing $BaTiO_3$ powder (fractions around 20–50 vol%), solvent (THF), epoxy and curing agent were prepared in a glass container. After that, agitation at 2000 rpm during 3–5 min was applied to avoid ceramic agglomeration. Each mixture was analysed by thermal gravimetric technique (TGA, Shimadzu TGA-50) in nitrogen atmosphere and a heating rate of 10 °C/min from room temperature to 800 °C. DSC was used at this time to find out the real volume fraction of particles and the final concentration of retained solvent after the curing process. Finally, the mixed solution was placed on a glass substrate with gold electrodes deposited by dc-sputtering, using dipping technique (at a rate of 3 cm/min) and cured at 100 °C for 2 h.

Scanning electron microscopy (SEM, JEOL 6460LV) was used to analyse the dispersion of $BaTiO_3$ particles into the composites, after the dipping and the curing processes. Thicknesses were measured by employing a micrometer and verified by scanning electron microscopy. The film thickness varied from 50 μm to 300 μm depending on the concentration of $BaTiO_3$.

The roughness was measured using a profilometer Surtronic 3t with 0.8 mm of cut-off. The parameters were obtained by Talyprofile software, taking the averaged values for each sample on longitudinal and transversal direction of processing.

Top electrodes were deposited by dc-sputtering through a shadow mask. Dielectric measurements were performed using a Hewlett Packard 4284A Impedance Analyser in the frequency range 20 Hz to 1 MHz. Temperature was varied from room temperature to 120 °C.

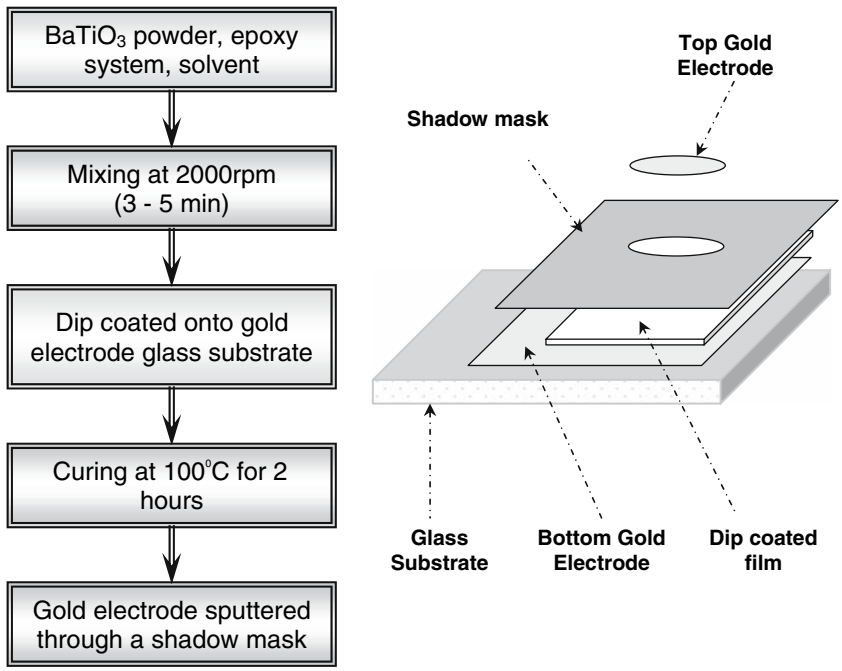

Fig. 1 Fabrication procedure of epoxy/$BaTiO_3$ composite film

Results and discussion

Thermal analysis

The influence of solvent on viscosity and thermal properties of the resin is shown in Table 1 for samples containing between 0 wt% and 60 wt% of THF. Viscosity decreases quickly up to a value of around ≈5 cp as THF concentration increases. Nevertheless, a little fraction of solvent is retained into the resin after the curing step. Systems with 9 wt% of THF only conserve ≈4.5 wt%, while specimens with 60 wt% conserve around 16 wt%. The reaction temperature (T_r) was shifted to higher values when THF content increased because of the required energy for the THF evaporation increased (Table 1 and Fig. 2). In the same way, the glass transition temperature (T_g) was also influenced by the presence of the retained THF, it decreases from 92 °C for pure resin to around 72 °C for systems with 8.6 wt% and 15.7wt% of retained THF (Table 1 and Fig. 2). These changes in glass transition temperature indicated that somehow the solvent swelled the polymeric network (increasing the free volume) producing plastification.

The diluted epoxy system used for practical purposes was the one containing an initial THF content of 60 wt% mainly due to its low viscosity which allows to incorporate easily higher particle contents.

DSC composites results did not show significant differences in the reaction temperature (≈110 °C) as filler content increased, because of the high filler concentration (18–52 vol%). On the other hand, T_g was not determined as the resolution of this technique was drastically reduced due to the presence of the particles.

The percentage of solvent retained for composites with different filler amounts is shown in Table 2. Samples with higher filler concentration impeded the solvent elimination and retained more THF.

The real $BaTiO_3$ volume fractions, determined by TGA analysis are also shown in Table 2 and Fig. 3. The real $BaTiO_3$ volume fraction was detected from this analysis, being more accurate the preparation of composites with higher ceramic content.

Table 1 Solvent influence on the epoxy resin system

THF initial (wt%)	η (cp)	T_r (°C)	T_g (°C)	THF retained (wt%)
0	1950 ± 50	104	92	0
9	245 ± 5	107	80	4.44 ± 0.45
25	17.5 ± 2.5	114	76	8.60 ± 1.42
60	5.5 ± 0.5	124	72	15.7 ± 1.71

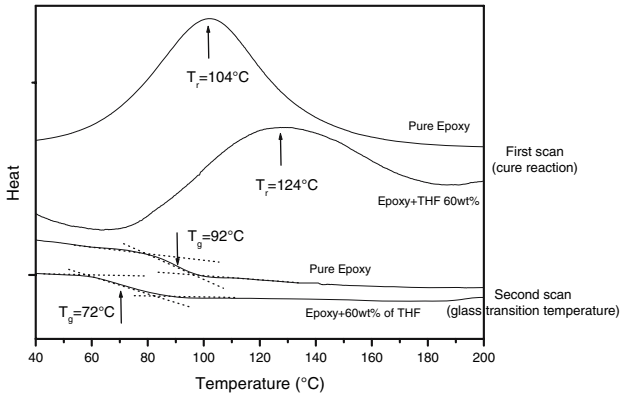

Fig. 2 Differential scanning calorimetry (DSC) of pure resin and resin with 60 wt% of THF

Table 2 Real $BaTiO_3$ and retained THF percentages for composites with different filler concentrations (determined through [x]TGA; [§] DSC). THF initial = 60%wt

Initial $BaTiO_3$ (vol%)	Real $BaTiO_3^x$ (vol%)	Retained THF[§] (wt%)
25	18	16
35	27	20
45	38	30
55	52	35

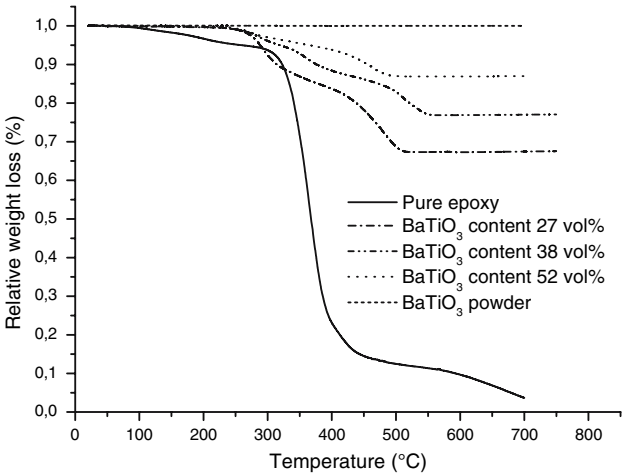

Fig. 3 Thermal gravimetric analysis (TGA) of pure resin, $BaTiO_3$-epoxy composites and $BaTiO_3$ powder

SEM analysis

Micrographs obtained by scanning electron microscopy of the transversal area of the sample are shown in Fig. 4. Figures (a) and (b) show areas without filler, but there are not trails of micro-porosity. It can be clearly observed that the particle distribution is not homogeneous. Even though some agglomeration of particles

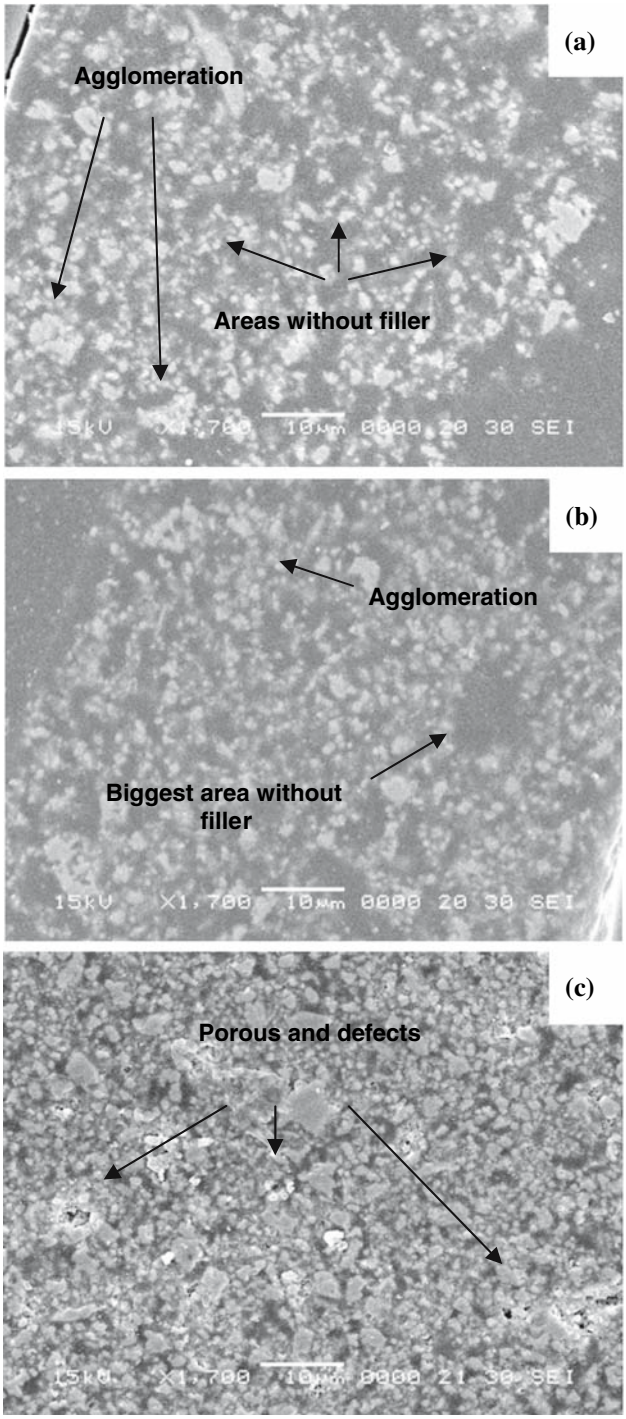

Fig. 4 SEM of composites with 18 (**a**), 27 (**b**) and 52 vol% (**c**) Bar 10 μm

appears in both composites, it is more evident in the sample with less $BaTiO_3$ content (18 vol%). Figure (c) shows a better particle distribution, nevertheless there are only few areas without filler and some trails of micro-porosity, being more significant on the surface. Although high filler concentration generates some defects, due to solvent effect and higher viscosity during the mixing step, it was possible to increase the $BaTiO_3$ content and obtain homogeneous materials.

Surface roughness

It is known that the distribution and the amount of surface peaks of most materials depend on the structure and the type of processing used [4]. The typical parameters for roughness are R_a and R_t. R_a is the arithmetic average surface roughness or average deviation of all points from a fixed plane to the test surface over the sample length. R_t is the maximum peak to valley height over the sample surface, which is the summation of the maximum peak and valley heights.

The roughness parameters R_a and R_t for composites with different $BaTiO_3$ percentages are shown in Table 3. The roughness measurements in composites show that R_a values are similar to particle radius (diameter = 1.4 μm) for all the samples, while the R_t values are greater in samples with higher ceramic concentration (>18 vol%). On the other hand, for both directions the resin has smaller values of R_a and R_t. It means that the average roughness is given by the particle radius, and that irregularities are influenced by the filler concentration as R_t increases with particle content. Since higher particle concentrations restrain the THF evaporation from the epoxy, the number and size of faults increase and thus the roughness of the films. This fact is in accordance with DSC results (Table 2) where the retained THF increased with the amount of particles. The tendency is the same on longitudinal and transversal directions meaning that the films have been deposited homogeneously onto the substrate.

Dielectric behaviour

Real (ε') and imaginary (ε'') permittivity values for composites as a function of frequency and percentage of ceramic at 30°C are plotted in Fig. 5(a) and (b). Both, real and imaginary parts of the permittivity are influenced by filler amount and frequency. Real and imaginary parts rise with the ceramic amount. Permittivity as high as 42 ε_0 at 1,000 Hz is obtained by adding 52 vol% of particles. Imaginary part of permittivity increases with frequency while real part decreases.

Figures 6 and 7 show real and imaginary permittivity parts as a function of temperature and frequency, respectively. As it can be seen in Fig. 6 (frequency 2,500 Hz), real permittivity increases slightly when temperature rises, nevertheless imaginary permittivity rises abruptly as a result of the higher mobility of

Table 3 Surface roughness values measured in longitudinal and transversal direction

Sample	Longitudinal		Transversal	
	R_a (μm)	R_t (μm)	R_a (μm)	R_t (μm)
Epoxy-THF	0.1714 ± 0.0508	1.578 ± 0.9435	0.143 ± 0.02858	1.233 ± 0.1569
18 vol%	0.8398 ± 0.1122	5.688 ± 1.5152	0.7663 ± 0.1935	5.230 ± 1.3216
27 vol%	0.8284 ± 0.2318	8.911 ± 4.9158	0.8053 ± 0.2125	8.983 ± 2.2081
38 vol%	0.8170 ± 0.1238	7.328 ± 1.6538	0.8763 ± 0.2258	9.456 ± 2.8651
52 vol%	0.8070 ± 0.0973	9.094 ± 4.3829	–	–

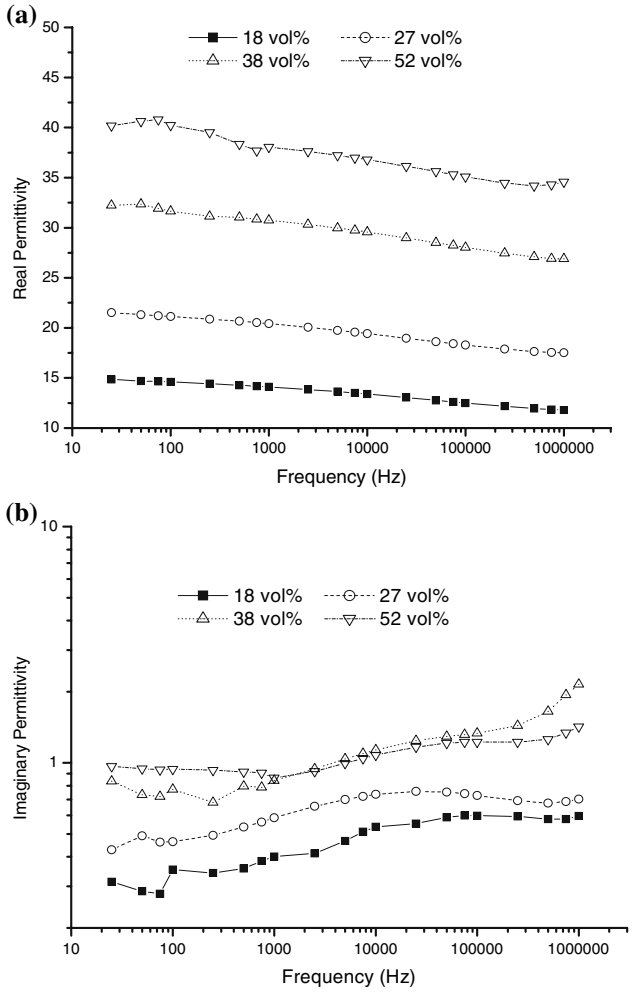

Fig. 5 Real (**a**) and imaginary (**b**) permittivity for composites vs. frequency and $BaTiO_3$ volume fraction (Temp. 30 °C)

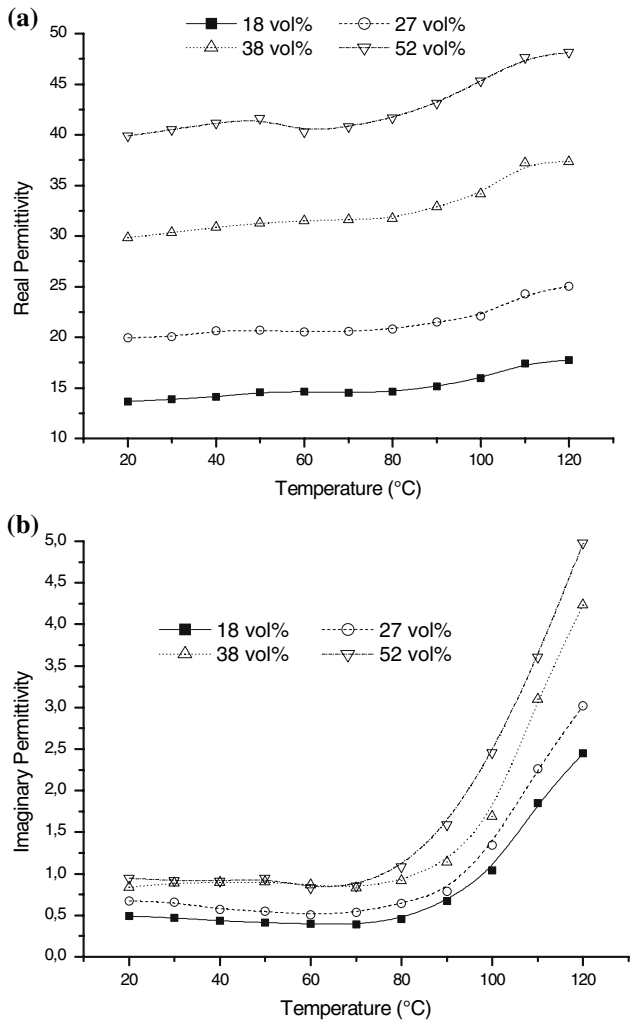

Fig. 6 Real (**a**) and imaginary (**b**) permittivity versus temperature and volume fraction (Freq. 2,500 Hz)

polymeric chains. This segmental mobility corresponds to the α relaxation associated to T_g and which appears around 80 °C.

Figure 7(a) shows that real permittivity remains constant with frequency at lower temperatures and it presents an important variation at higher temperature. On the other hand, it is observed that imaginary permittivity increases and then decreases slightly at high frequency when temperature is low (Fig. (b)). This behaviour can be produced by modifications in the total dipolar alignment among the polymer molecular rearrangement process [5].

The changes in the permittivity are attributed to dielectric relaxations. These are more pronounced at low frequencies and high temperatures due to micro-Brownian motion of whole chain (segmental movement). Nevertheless, these are also affected by the

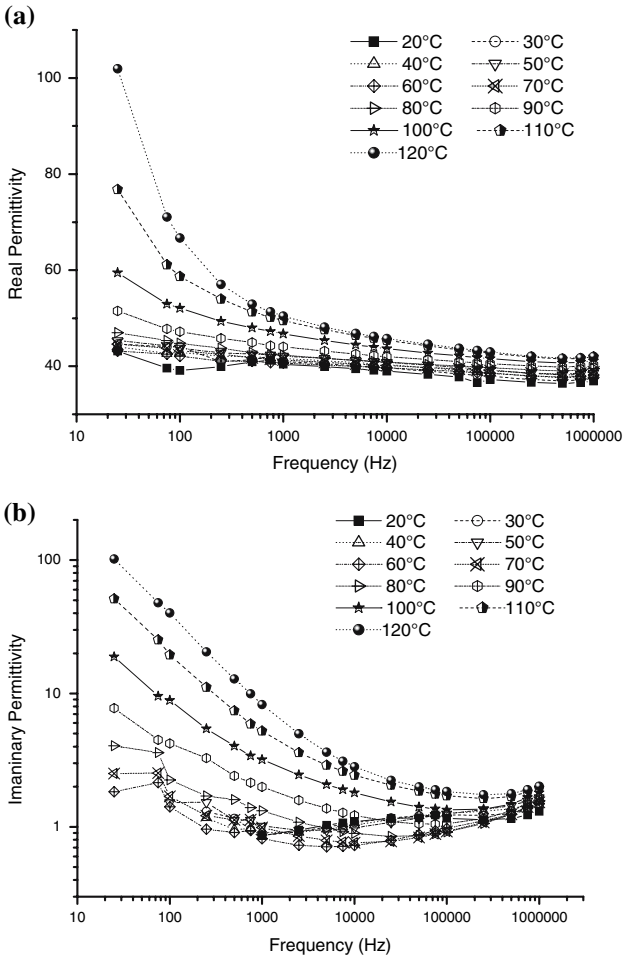

Fig. 7 Real (**a**) and Imaginary (**b**) permittivity versus log frequency and temperature of the sample with 52 vol% of $BaTiO_3$

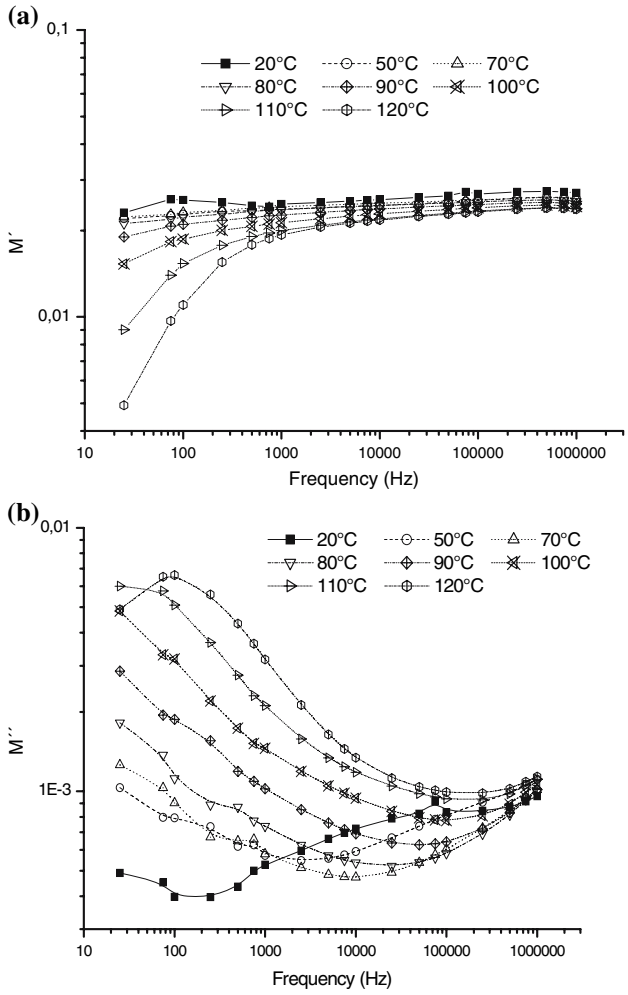

Fig. 8 Real part (M') (**a**) and imaginary part (M'') (**b**) of electrical modulus versus frequency (sample of 52 vol%)

interfacial polarisation process known as Maxwell–Wagner–Sillar, which exists in heterogeneous dielectrics and it is produced by charge carriers travelling [6]. This polarisation process is also responsible of the real permittivity variation at low frequency and high temperature.

In order to study the frequency and temperature dependence of relaxation processes, electrical modulus was analysed. Figures 8 and 9 show the real and imaginary parts of the electrical modulus obtained through equation 1 [7] as a function of frequency and temperature, respectively.

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + j.M'' \quad (1)$$

In Fig. 8 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 Ḿ values at low frequency range. Nevertheless, peaks in M'' values are developed at this same frequency range, indicating the apparition of a relaxation process (α relaxation) which is not completely visible in the frequency range analysed [8].

In order to understand the resin relaxation process, samples with low $BaTiO_3$ concentration (18 vol%) were analysed. Figure 9 shows the behaviour of these samples versus temperature and frequency. A rise in temperature produces a reduction in M', while at low frequency a plateau formation is observed (Fig. 9(a)). This behaviour is associated to the presence of two relaxation processes.

In Fig. 9(b) two peaks can be observed in the imaginary modulus at low frequency. These peaks are shifted to higher frequency when temperature increases and they correspond to β and α relaxations. β relaxation is attributed to the movement of side groups or small units of main chain and is observed at higher frequency and lower temperature than α relaxation [5].

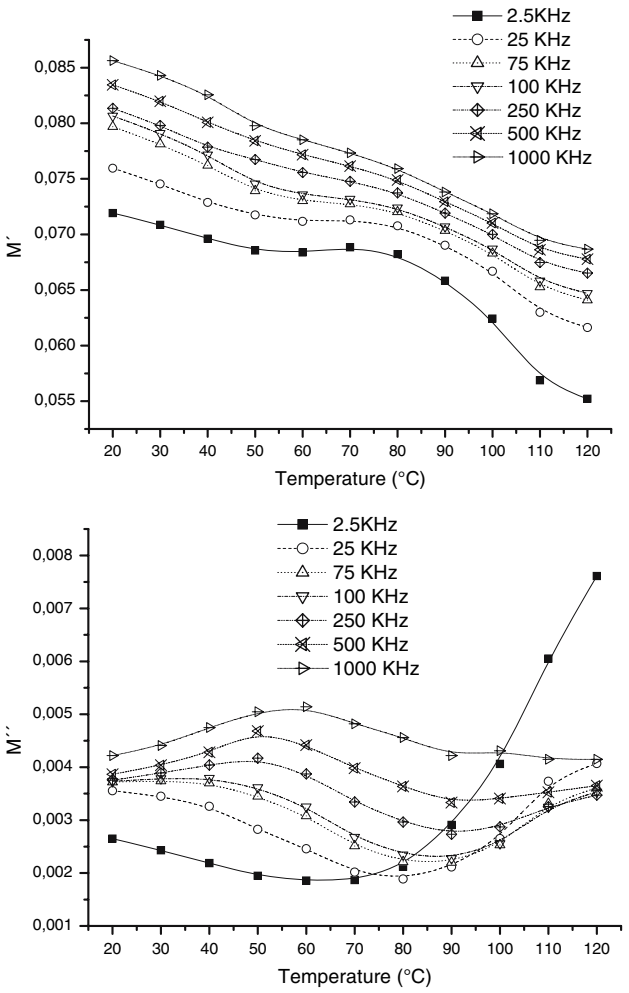

Fig. 9 Real part (M') (**a**) and imaginary part (M'') (**b**) of electric modulus versus temperature (sample of 18vol%)

Finally, in order to compare this processing method with reported data for roll coater and hand poured, some bibliographic references are mentioned. Composites by roll coater were made [9] using similar materials ($BaTiO_3$ and epoxy resin) finding 15 μm film thickness and permittivities around 40, while composites made by hand poured [10] using the same materials had 3,000 μm film thickness and permittivities around 37. It can be seen that the dipping process had good permittivity performance ≈40. Nevertheless, composites processed by roll coater could form thinner films (15 μm), against the 50–300 μm obtained by dipping (for 18 to 52 vol% of $BaTiO_3$).

Conclusions

Microstructure characterisation and dielectric properties of epoxy/$BaTiO_3$ composites obtained by dipping process have been investigated. The following conclusions were reached.

1. Solvent helped to reduce the resin viscosity (<10 cp) and to increase the amount of incorporated particles into the composite. Nevertheless, solvent was retained into the resin after curing and generated swelling of the polymeric structure, changing the resin properties (diminishing T_g).
2. Surface roughness and SEM analysis showed that tetrahydrofuran increased the number and size of faults in samples with high filler concentration. From roughness measurements, it was determined that films were longitudinally and transversally homogeneous.
3. The epoxy matrix had influence on composite relaxation processes. The presence of α- and β-relaxations were observed. Nevertheless, interfacial polarisation processes known as Maxwell-Wagner–Sillar were generated by particle incorporation.
4. Composites processed by dipping had good dielectric performance compared to other techniques. However, it must be improved to achieve the typical film capacitors of 10μm.

Acknowledgements This work was supported by Antorchas Foundation and National Council of Science and Technology of Argentina (CONICET) and ANPCyT/FONCyT PICT 14738 (BID 1201/OC-AR). Also it was achieved thanks to material donation from Dow Chemical Argentina due to management of Ariadna Spinelli and Alfredo Fahnle and roughness measurements by Ing. María Dolores Echeverría and Ing. Osvaldo J. Moncada from Metrology Laboratory of Mechanical Engineering Department (UNMdP).

References

1. Thongvigitmanee T, May GS (2000) Twenty Sixth IEEE/CPMT. International Electronics Manufacturing Technology, USA, p 47
2. Kuo DH, Chang CC, Su TY, Wang WK, Lin BY (2004) Mat Chem Phys 85:201
3. Lee BI, Zhang J (2001) Mat Research Bull 36:1065
4. Narayan P, Hancock BC (2003) Mater Sci Eng A 355:24
5. CHI KAO K (2004) Dielectric Phenomena in Solid, Elsevier Academic Press, p 110
6. Psarras G, Manolakaki E, Tsangaris GM (2002) Comp Part A 33:375
7. Suzhu Y, Hing P, Xiao H (2000) J App Phys 88:398
8. Tsangaris G, Psarras GC (1999) J Mat Sci 34:2151
9. Cho SD, Lee JY, Hyun JG, Paik KW (2004) Mat Sci Eng B 110:233
10. Ramajo L, Reboredo MM, Castro MS (2005) Comp Part A 38:1267