Available online at www.sciencedirect.com

ScienceDirect

Composites: Part A 38 (2007) 1852–1859

composites
Part A: applied science and manufacturing

www.elsevier.com/locate/compositesa

# Effect of silane as coupling agent on the dielectric properties of $BaTiO_3$-epoxy composites

L. Ramajo *, M.S. Castro, M.M. Reboredo

*Institute of Research in Materials Science and Technology (INTEMA), CONICET – University of Mar del Plata, Juan B Justo 4302, B7608FDQ Mar del Plata, Argentina*

Received 15 September 2006; received in revised form 19 March 2007; accepted 11 April 2007

## Abstract

The influence of silane coupling agents on the microstructure and dielectric behaviour of epoxy/$BaTiO_3$ composites was studied. Epoxy was diluted using tetrahydrofuran as solvent in order to facilitate the mixing step. Methoxy silane was applied onto ceramic particles. Different diluted aqueous solutions with 0.25, 0.35 and 0.50 wt% of silane/$BaTiO_3$ were used. Dipping technique was utilised to obtain composite films. Dielectric measurements were performed from 25 Hz to 1 MHz and from 20 °C to 120 °C. Composites presented good dielectric properties and a strong dependence with the silane concentration.

*Keywords:* A. Polymer–matrix composites (PMCs); B. Electrical properties; E. Surface treatments; Ceramic particles

## 1. Introduction

Embedded capacitors are specially printed portions within the printed-wiring-board (PWB) laminations that provide the charge storing function without using precious surface space of the boards. With the use of passive elements (capacitors, resistors, and inductors) embedded into PWBs, significant reductions of parasitic impedance, assembly cost, and device size become possible. Those applications need capacitances as high as $50\,nF/cm^2$ [1] for successful implementation. For this reason, one major challenge is the development of new dielectric materials that possess good dielectric and mechanical properties [2].

Polymer-ceramic materials are an encouraging choice for embedded thin-film capacitors. In these composites, high content and good dispersion of ceramic particles assure better and homogeneous packaging, resulting in higher dielectric permittivities and uniform properties of the film. However, it can be envisaged that an optimum amount of polymer may be necessary to completely wet the particles [3,4]. Low polymer volume fractions result in a low dielectric constant, presumably because of the residual porosity of the composites.

To modify properties of a filled polymer, many additives have been developed. Among these additives, coupling agents have gained more attention because of their special structures, which have two different functional groups, one that is attracted to the resin and the other that is attracted to the surface of the filler [4]. There are many different commercial alkylsilanes, organozirconates and organotitanates that have been developed for the use with specific composites. Coupling agents are usually used for inorganic fillers-contained plastics to improve the adhesion between fillers and polymer, preferably via chemical bonds; their use improves the performance of composite materials [5].

Coupling agents are also adhesion promoters between substrate and adhesive, which can be applied directly to the substrate, similar to primers, or they can be mixed with the adhesive itself. When mixed with the adhesive, the coupling agents are capable of migrating to the interface and reacting with the substrate surface as the adhesive cures [5].

The objective of the present work is to study the influence of silane treatments on the microstucture and the

---

* Corresponding author. Tel.: +54 223 4816600; fax: +54 223 4810046.
*E-mail address:* lramajo@fi.mdp.edu.ar (L. Ramajo).

1359-835X/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compositesa.2007.04.003

dielectric properties of epoxy/$BaTiO_3$ composite materials. In order to optimise the dielectric behaviour, three different silane content were used. Measurements were performed as a function of frequency and temperature.

## 2. Experimental

A commercial epoxy resin, DER 325 (Dow Chemical) and a curing agent, triethylenetetramine (DEH 324, Dow Chemical), at 12.5 phr (part per hundred of resin) were employed. Also, tetrahydrofuran (THF, Dorwil Chemical, boiling point 66 °C) up to 75 wt% was added to reduce the resin viscosity.

Commercial barium titanate, $BaTiO_3$ (TAM, Ceramics Inc.) was used as 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 during 5 min. Afterwards, alcohol was eliminated by heating at 65 °C until constant weight. The powder was thermally treated at 1350 °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 until an average particle size of 1.4 μm was obtained.

Glycidoxy methoxy silane Z-6040 (Dow Corning) was applied onto ceramic particles as diluted aqueous solutions of 0.25, 0.35 and 0.50 wt% (respect to barium titanate) of silane in order to improve processability and increase filler wet-out and dispersion. Aqueous solution was prepared, adjusting the pH of the water to 3.5 with acetic acid and then introducing the silane. After the silane was added to the acidified water, the system was stirred for about 15 min before it hydrolysed and formed a clear and homogeneous solution. The fillers were mixed with the silane at low shear for several minutes without additional solvent. After applying the silane, the $BaTiO_3$ was dried briefly at 110 °C to avoid condensation of silanol groups at the surface. Residual silane was eliminated washing the particles in toluene at 25 °C and then, the resulting powder was dried and sieved through 40 μm mesh.

The detection of small quantities of silane in the products after the silanisation process was achieved by Fourier Transform Infrared Spectrometry (FTIR) in transmission mode, using a Mattson Genesis II in the range

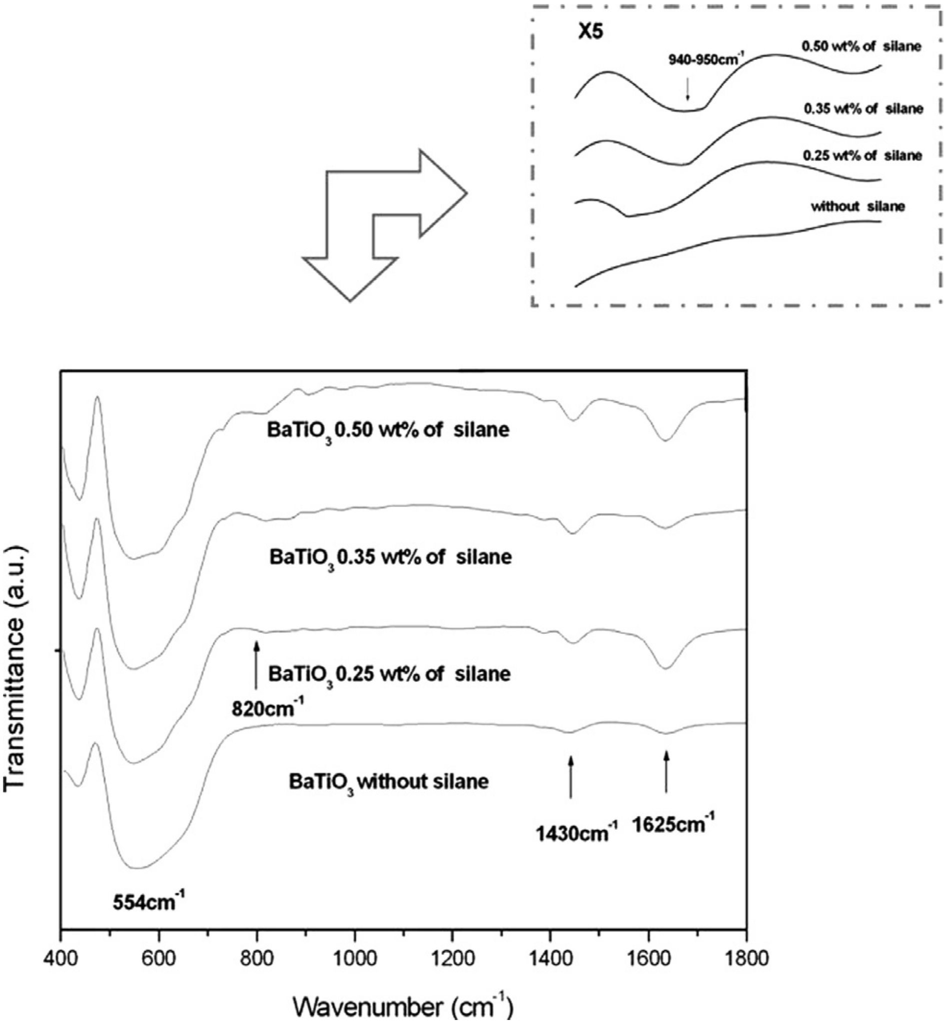

Fig. 1. FTIR spectra of $BaTiO_3$ powder untreated and treated with 0.25, 0.35 and 0.50 wt% of Z6040.

400–2000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$; and transmition electron microscopy (IEM), using a Philips CM200 with an acceleration of 200 KV.

The composite films were obtained using the dipping technique. First, a suspension containing 50 vol% of $BaTiO_3$ powder (treated and untreated), solvent (THF), epoxy and curing agent was prepared in a glass container. After that, agitation at 2000 rpm during 3–5 min was applied to avoid ceramic agglomerations. The suspension was placed on a glass substrate with gold electrodes previously deposited by dc-sputtering, using a dipping rate of 3 cm/min. The films were cured at 100 °C for 2 h. Top electrodes were deposited by dc-sputtering through a shadow mask.

Silane coated powders and their composites were analysed by thermogravimetry (TGA, Shimadzu TGA-50) under nitrogen atmosphere with a heating-rate of 10 °C/min from room temperature to 700 °C. Dispersion of $BaTiO_3$ particles into the composites was analysed through scanning electron microscopy (SEM, JEOL 6460LV), after the dipping and the curing processes. Thicknesses were measured employing a micrometer (Mitutoyo) and verified by SEM.

Dielectric measurements were performed using a Hewlett Packard 4284A Impedance Analyser in the frequency range from 20 Hz to 1 MHz. Temperature was varied from room temperature to 120 °C.

## 3. Results and discussion

### 3.1. FTIR analysis

Fig. 1 shows the FTIR spectra of the powders treated with silane from 0.25 to 0.50 wt%. The broad bands at 554 cm$^{-1}$ are due to Ti–O stretching modes of $BaTiO_3$ [6,7], while peaks at 1430 and 1625 cm$^{-1}$ are related to the $CO_2$ absorption [7]. Moreover, peaks at 820 and 1380 cm$^{-1}$ characteristic of C–C stretching modes and organic groups of silane, respectively, are observed [8,9]. These peaks increase with silane concentration.

Normalised and amplified spectra were used in order to obtain additional information about the coupling agents on the surface of the ceramic powder. The peak appearing at 950 cm$^{-1}$, assigned to the structural bridge of silane on the titanate surface (Ti–O–Ti), suggests that silane is linked or chemisorbed on the particle surface [9]. Again, silane peak increases when silane concentration increases.

### 3.2. Transmition electron microscopy (TEM)

TEM micrographs of powders treated with 0.35 and 0.50 wt% of silane are showed in Fig. 2. Both samples present particle agglomeration due to silane effects and some inhomogeneous organic material dispersion around the

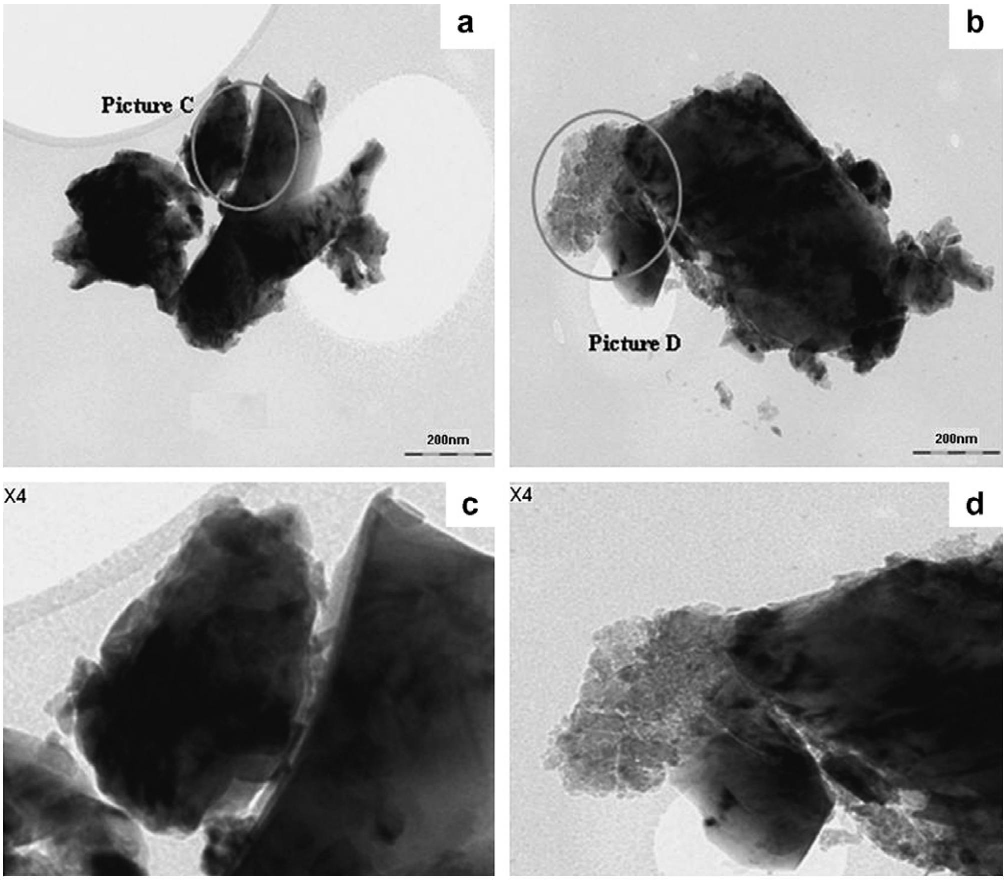

Fig. 2. TEM of particles with (a) 0.35 wt% and (b) 0.50 wt% of silane; and (c) enlargement of picture (a) and (d) amplification enlargement of picture (b).

$BaTiO_3$ particles. This behaviour increases with the silane content (Fig. 2b and d).

As it can be seen, the high silane content helps to link the particles, among themselves and thus, particle agglomeration increases. Then, the rheological behavior of the mixture is affected, modifying the composite final properties.

### 3.3. Thermogravimetric analysis (TGA)

In Table 1 and Fig. 3 the effective silane concentration and real $BaTiO_3$ volume fraction of composites, measured by thermogravimetric analysis are shown. It can be seen that certain silane content is retained in the particles after the treatment showing that silanisation process was effective (as already shown by FTIR and TEM). Also, it is observed that the silane amount does not affect the effective incorporation of filler. From Fig. 3 can be observed that silane does not change the degradation process of the composite.

Table 1
Silane concentration, $BaTiO_3$ volume fraction, and real permittivity of the composites

| Silane (wt%) | | $BaTiO_3^a$ (vol%) | $\varepsilon'$ |
|---|---|---|---|
| Initial | Final[a] | | |
| 0.00 | 0.00 | 49 | 37 |
| 0.20–0.30 | 0.25 | 50 | 39 |
| 0.30–0.40 | 0.35 | 48 | 29 |
| 0.50–0.60 | 0.50 | 51 | 21 |

[a] Determined by TGA.

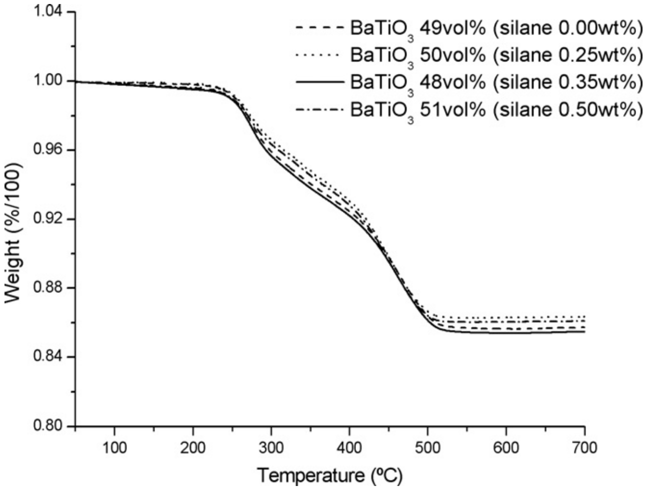

Fig. 3. Thermal gravimetric analysis (TGA) of composites with 0, 0.25, 0.35 and 0.50 wt% of Z6040 in current air.

### 3.4. Scanning electron microscopy (SEM)

SEM micrographs of transversally cut samples are observed in Fig. 4. It shows composites with silane concentration between 0 and 0.50 wt%. Areas without filler and small trails of micro-porosity are observed in samples made with high Z6040 amounts (Fig. 4c and d). In these samples, particle distribution is not homogeneous and some particle

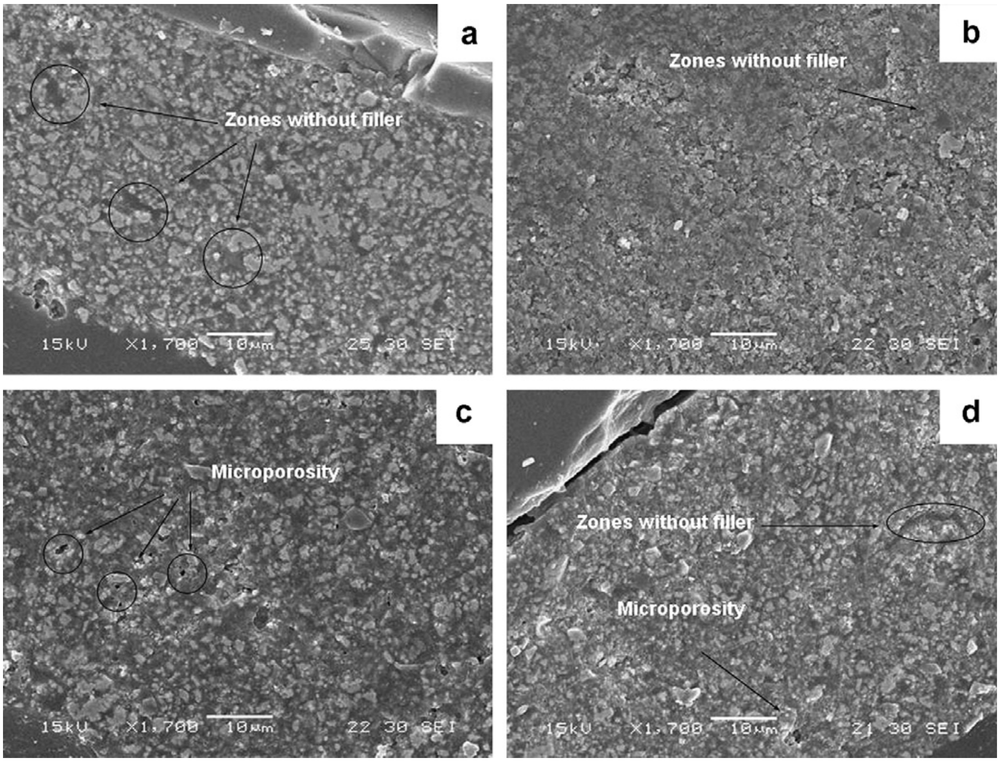

Fig. 4. SEM of composites with (a) 0 wt%, (b) 0.25 wt%, (c) 0.35 wt% and (d) 0.50 wt% of Z6040 (50 vol% of $BaTiO_3$). Bar 10 µm.

agglomeration appears. The addition of 0.25 wt% (Fig. 4b) of silane gives a more homogeneous distribution and a better microstructure.

TEM and SEM results confirm that fine powders form strong agglomerates which difficult the filler dispersion when a high solid loading is used (50 vol%). These agglomerates increase the effective particle size, restricting the filling of voids between bigger particles. Nevertheless, when $BaTiO_3$ is treated with 0.25 wt% of Z6040, a better dispersion is attained, providing easy deagglomeration and efficient packing of the particles mixture.

### *3.5. Electric behaviour*

Real permittivity as a function of silane at 30 °C and 2500 Hz is shown in Table 1. Temperature and frequency selected values were chosen in order to obtain more representative data diminishing measurement fluctuations. It can be seen that real permittivity is influenced by the coupling agent. The system with lower silane concentration (0.25 wt%) has a slightly improvement in the permittivity than the system without silane addition. Nevertheless, higher Z6040 amounts (0.35 and 0.50 wt%) present important reductions in the dielectric permittivity.

Frequency dependence of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) permittivity as a function of the percentage of silane at 30 °C are shown in Fig. 5. At low frequency, imaginary part of permittivity decreases when frequency increases due to the dc conductivity effect. Nevertheless, after 1000 Hz it increases and a soft loss peak at around 100 KHz, is formed. Real permittivity decreases monotonically as a function of frequency. Composites made of $BaTiO_3$ treated with 0.25 wt% of Z6040 have a highest dielectric constant than untreated filler all the over frequency range. It seems that silane act as molecular bridges between the polymer and the ceramic filler, resulting in the

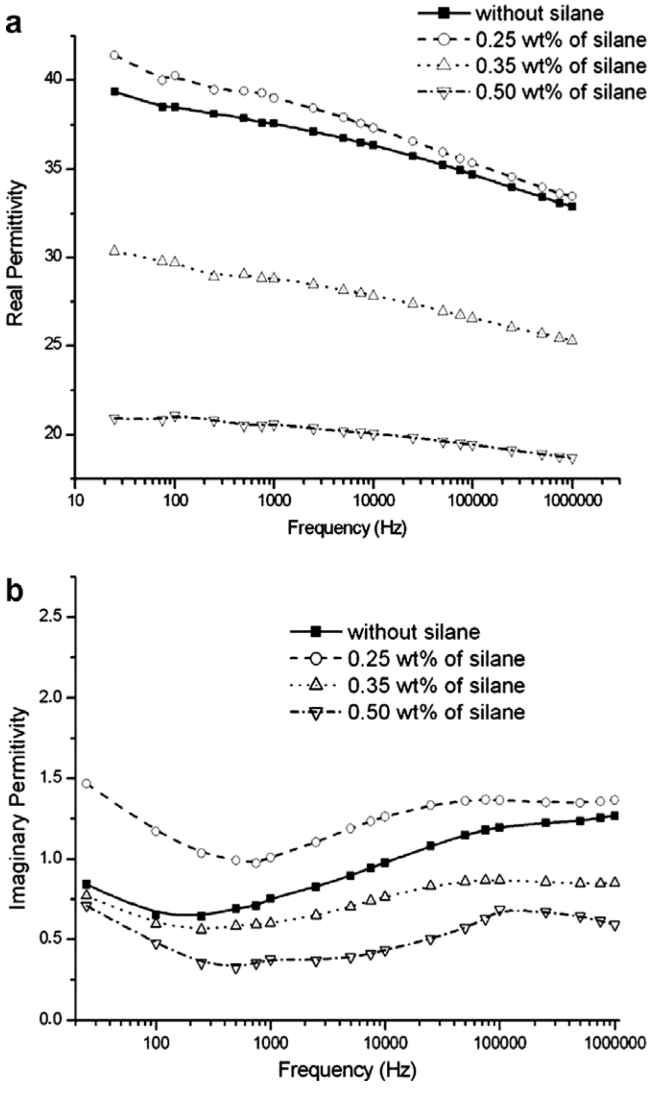

Fig. 5. Real (a) and imaginary (b) permittivity vs. frequency curves of the composites with different silane amount (at 30 °C and 50 vol% of $BaTiO_3$).

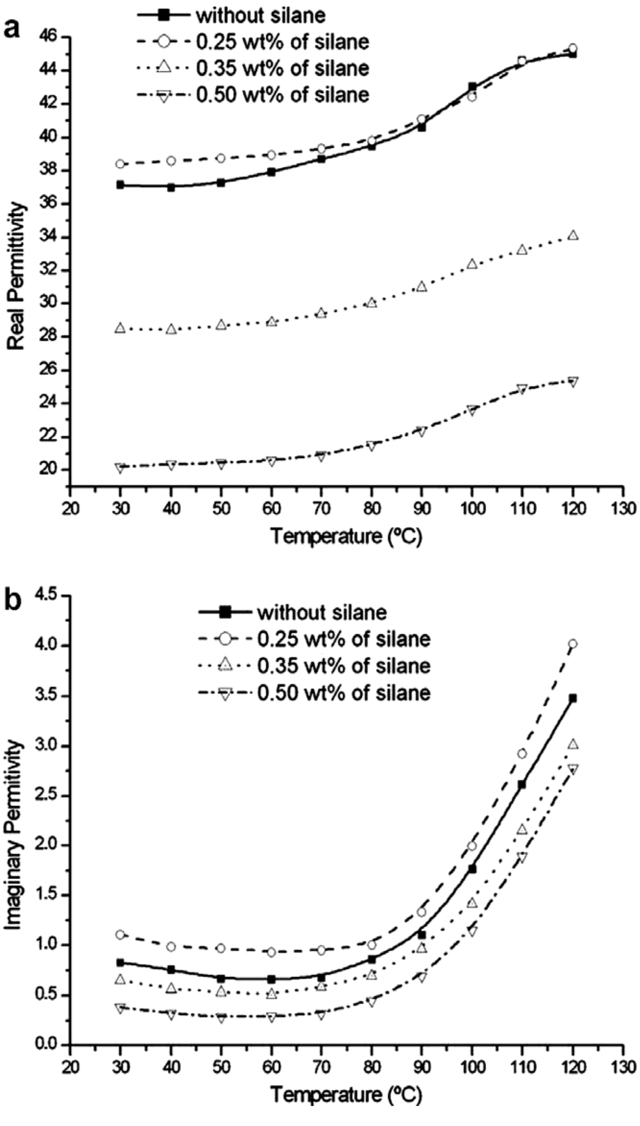

Fig. 6. Real (a) and imaginary (b) permittivity vs. temperature curves of the composites with different silane amount (at 2500 Hz and 50 vol% of $BaTiO_3$).

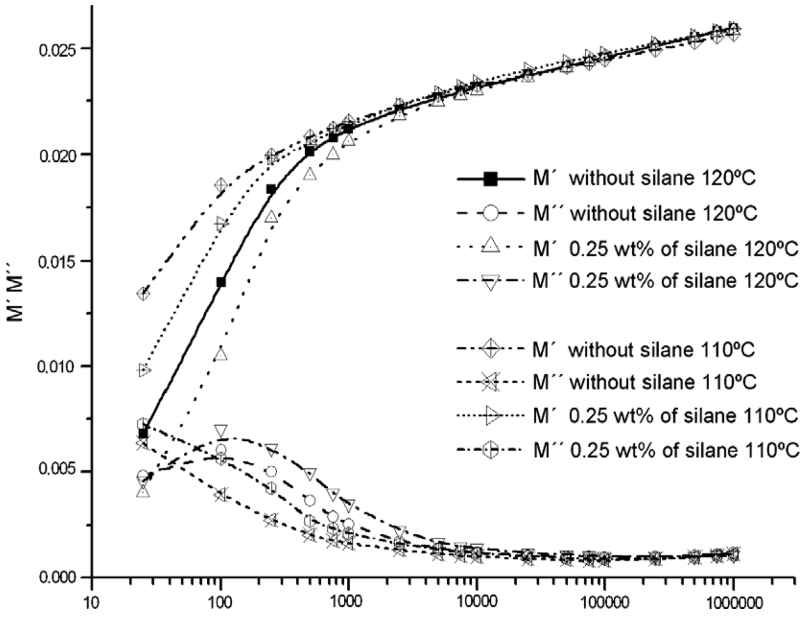

Fig. 7. Real part ($M'$) and imaginary part ($M''$) of electric modulus vs. frequency of samples untreated and treated with 0.25 wt% of Z6040 (50 vol% of $BaTiO_3$).

formation of covalent chemical bonds across the interface, which improve the dielectric properties, at least at these low concentrations. Besides the good microstructure obtained in these composites assures a good distribution of higher permittivity particles. Nevertheless, higher silane amounts tend to lower dielectric properties, because of the higher porosity, agglomeration particles and defect content.

Fig. 6 shows the real and imaginary permittivity at different temperatures and 2500 Hz. Real permittivity increases slightly with the temperature, while imaginary permittivity rises abruptly due to the higher segmental mobility of polymer near $T_g$. This relaxation associated with the glass transition is labelled α and it is referred as the primary or glass–rubber relaxation [10].

In order to understand the frequency relaxation process and electrical behaviour of the untreated and 0.25 wt% silane treated systems, electrical modulus and ac conductivity were used (Eqs. (1) and (2)). It is known that electric modulus (Eq. (1)) helps to observe bulk relaxation properties at low frequencies [11], while conductivity phenomena can be extracted from the dielectric loss by calculating the ac conductivity (Eq. (2)).

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

$$\sigma_{ac} = \varepsilon_0 \cdot \varepsilon'' \cdot \omega \quad (2)$$

Fig. 7 shows the real ($M'$) and the imaginary ($M''$) part of electrical modulus for composites untreated and treated with 0.25 wt% of silane. The figure shows that $M'$ values increase quickly with frequency until they reach a less pronouncing slope. A rise in temperature produces a diminution in the $M'$ values at low frequency range, without important changes at higher frequencies. Moreover, peaks in $M''$ curves at 120 °C are observed, indicating a

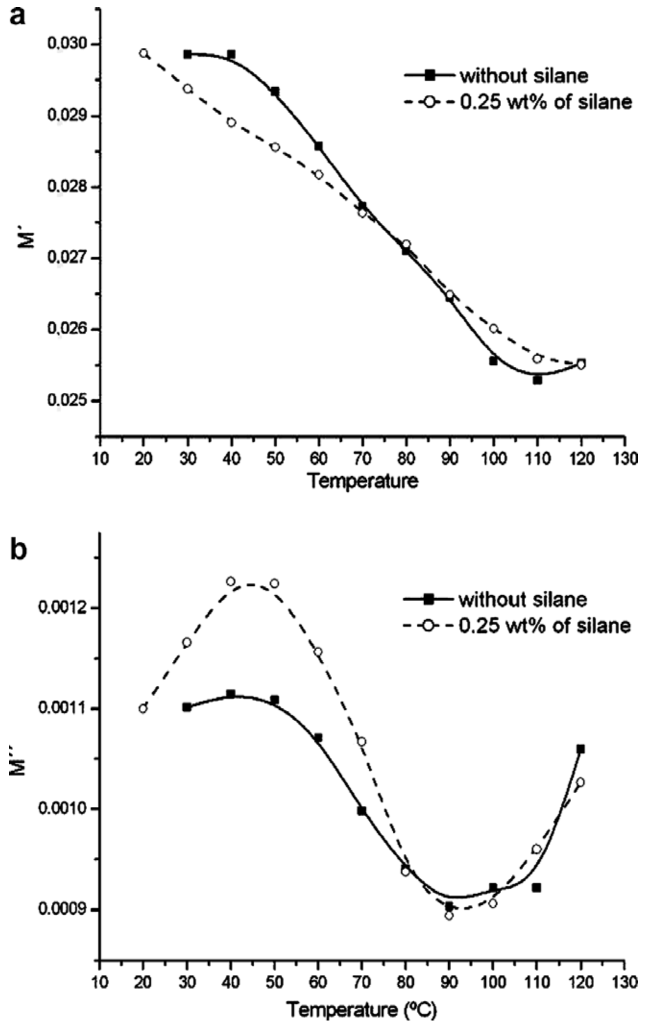

Fig. 8. Real part ($M'$) and imaginary part ($M''$) of electric modulus vs. temperature curves of samples untreated and treated with 0.25 wt% of Z6040 (at 500 KHz and 50 vol% of $BaTiO_3$).

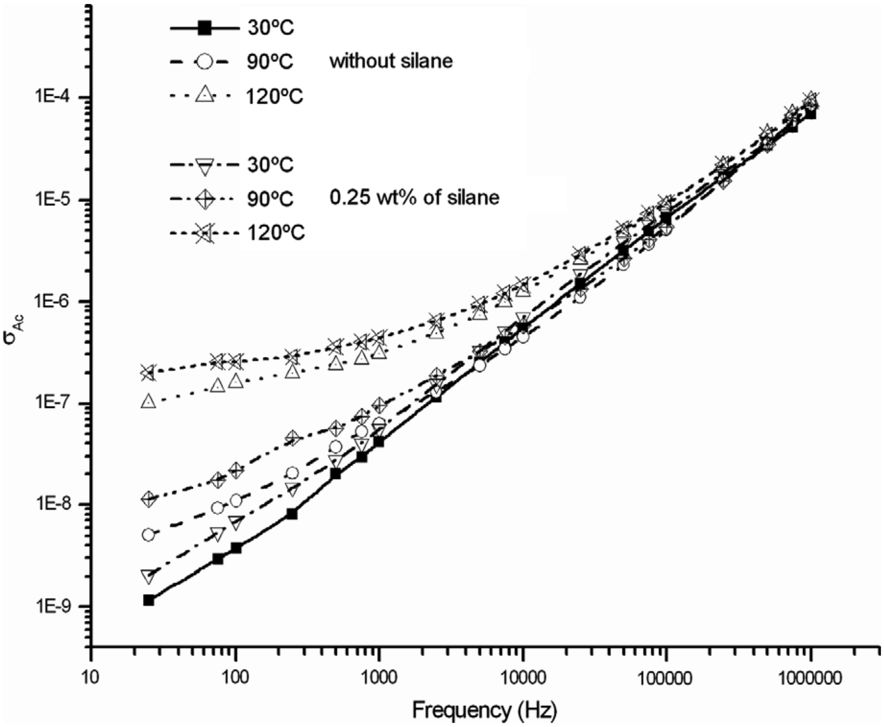

Fig. 9. The ac conductivity ($\sigma_{ac}$) versus frequency of composites with 0 and 0.25 wt% of Z6040 at 30, 90 and 120 °C (50 vol% of $BaTiO_3$).

relaxation process which is not evident in the loss tangent curve. 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 [12]. Also, silane dipole contribution modified the frequency of the α-relaxation. In general, both systems present similar behaviours; however untreated samples have smaller $M'$ and $M''$ than treated samples.

Fig. 8 shows the temperature effect on resin relaxation process of samples with 50 vol% of $BaTiO_3$ untreated and treated with 0.25 wt% of silane. A rise in temperature produces the $M'$ reduction. Peaks in imaginary modulus appear at lower temperature than α-relaxation peak, and they are related to a β-relaxation process. This mechanism is linked with localised rotational fluctuations of the dipoles and they are observed at higher frequency and lower temperature than α-relaxation [13].

In epoxy resin the β-peak is attributed to the relaxation of the hydroxyether units $–O–CH_2–CH(OH)–CH_2–$ created during the cross-linking reactions from the initial epoxy prepolymer [14]. In this way, samples with silane exhibit a more notorious peak of β-relaxation. The rise in the conductivity, caused by the silane influence on polymer-ceramic interface, could be responsible of the important β-relaxation peak [4,14].

The ac conductivity of the composites clearly depends on temperature and frequency, increasing as both rise (Fig. 9). At higher frequencies, conductivity dependence on temperature may be neglected. Nevertheless, at low frequencies, relaxation processes are influenced by temperature and conductivity. The dependence on frequency could be expressed according to a power law $\sigma_{ac} \sim w^s$ $(0 \leqslant s \leqslant 1)$ [15]. At constant temperature, ac conductivity can be expressed as $\sigma_{ac}(\omega) = \sigma_{dc} + A \cdot \omega^s$, where $\sigma_{dc}$ is the $\omega \to 0$ limiting value of $\sigma_{ac}(\omega)$, $A$, and $s$ parameters depend on temperature and filler content [16]. This equation is often called "the ac universality law" since it has been found to satisfactorily describe the ac response of numerous different types of materials [16]. In general, conductivity was higher in treated samples suggesting that silane helps to increase the electric charge transference at the interfaces.

On the other hand, a considerable increase of conductivity appears as temperature is raised, at constant conductive filler content. Conductivity values are altered by almost four orders of magnitude with temperature, indicating a thermally activated process. In this way, at low frequency the effect is more notorious, due to an effect of molecular mobility near $T_g$.

## 4. Conclusions

Silane influence on dielectric properties and microstructure of highly loaded epoxy/ceramic composites have been investigated. It was confirmed that the addition of silane helped to wet particles and improved the interface contact. Low silane concentration modified interfaces and helped to retain the electrical properties of composites. However, higher silane concentrations increased the porosity and defects, and impoverished the dielectric properties.

From a practical point of view, a reasonably good trade-off between silane amount, final microstructure and dielectric properties is obtained at 0.25 wt% of Z6040.

## Acknowledgements

This work was supported by the 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.

## References

[1] Windlass H, Markondeya Raj P, Balaraman D, Bhattacharya S, Tummala R. Polymer-ceramic nanocomposite capacitors for system-on-package (SOP) applications, Part B: advanced packaging. IEEE Trans 2003;26:10–6.

[2] Shrout TR, Hackenberger W, Jang SJ, Zhang QM, Randall CA. Novel dielectric materials, IMAPS 3rd advanced technology workshop on integral passives technology, Pennsylvania, April 17–18, 1998.

[3] Ramesh S, Shutzberg BA, Haung C, Gao J, Giannelis EP. Dielectric nanocomposites for integral thin film capacitors: materials design, fabrication, and integration issues. IEEE Trans Adv Pack 2003;26:17–24.

[4] Tan F, Qiao X, Chem J, Wang H. Effects of coupling agents on the properties of epoxy-based electrically conductive adhesives. Int J Adhes Adhes 2006;26:406–13.

[5] Plueddemann EP. Silane coupling agents. New York: Plenum Press; 1982, Chapter 5.

[6] Duran P, Gutierrez D, Tartaj J, Banares M, Moure C. On the formation of an oxycarbonate intermediate phase in the synthesis of $BaTiO_3$ from (Ba, Ti)-polymeric organic precursors. J Eur Ceram Soc 2002;22:797–807.

[7] Durán P, Capel F, Tartaj J, Moure C. Heating-rate effect on the $BaTiO_3$ formation by thermal decomposition of metal citrate polymeric precursors. Solid State Ionics 2001;141:529–39.

[8] Nakamoto K. Infrared and raman spectra of inorganic and coordination compounds. 4th ed. New York: Wiley; 1986, p. 231.

[9] Lenza RFS, Vasconcelos WL. Synthesis of titania–silica materials by sol–gel. Mater Res 2002;5:497–502.

[10] McCrum NG, Read BE, Williams G. Anelastic and dielectric effects in polymeric solids. Dover Publication; 1991, Chapter 5.

[11] Schönhals A. Dielectric spectroscopy on the dynamics of amorphous polymeric systems. Novocontrol. Application Notes Dielectrics I 2003:10.

[12] Kwan Chi Kao. Dielectric phenomena in solids. Elsevier, Academic Press; 2004, p. 110–112.

[13] Mangion BBR, Johari GP. Relaxations in thermosets. 7. Dielectric effects during the curing and postcuring of an epoxide by mixed amines. Macromolecules 1990;23:3687–95.

[14] Lestriez B, Maazouz A, Gerard JF, Sautereau H, Boiteux G, Seytre G, et al. Is the Maxwell–Sillar–Wagner model reliable for describing the dielectric properties of a core-shell particle-epoxy system. Polymer 1998;38:6733–42.

[15] Psarras GC, Manolakaki E, Tsangaris GM. Electrical relaxations in polymeric particulate composites of epoxy resin and metal particles. Composite Part A 2002;33:375–84.

[16] Psarras GC. Hopping conductivity in polymer matrix–metal particles composites. Composite Part A 2006;37:1545–53.