BARIUM TITANATE-POLYMETHYLSILOXANE NANO/MICRO -COMPOSITES: DEVELOPMENT, CHARACTERIZATION, FUNCTIONALITY AND ENERGY STORARE

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Abstract

Ceramic–polymer composites incorporating ferroelectric and piezoelectric crystal particles, randomly distributed within the polymer matrix represent a novel class of materials. Composites including ferroelectric and/or piezoelectric particles are expected to exhibit functional properties because of the varying polarization of the ceramic particles. In the present study elastomer matrix PDMS/$BaTiO_3$ micro- and nano-composites were prepared, in different filler concentrations and sizes. The dielectric response of all samples was studied by means of Broadband Dielectric Spectroscopy (BDS), over a wide temperature (from 30°C to 200°C) and frequency (from 10^{-1} Hz to 10 MHz) range. In the dielectric spectra two relaxation processes were detected, namely α-relaxation and Interfacial Polarization (IP). Dielectric permittivity increases with filler content, size and diminishes rapidly with frequency. Finally, the energy density of all systems was evaluated. Composite systems with embedded micro-$BaTiO_3$ exhibit higher energy storing efficiency, while thermally induced structural changes in ferroelectric particles provide functional behaviour to barium titanate composites.

1. Introduction

Composites are materials in which the micro/nano-sized dispersed phase in a suitable matrix can enhance some of the existing properties, as well as give rise to new ones. Elastomers micro/nano-composites are of great interest because the addition of filler improves electrical, mechanical and thermal response and can also modify other properties. Polydimethylsiloxane (PDMS) elastomer is an electrorestrictive polymer having excellent electrical, elastic, mechanical and thermal properties [1, 2]. The composites derived from PDMS elastomer can be used in various applications including actuation, sensing, artificial muscles, biocompatibility and microfluidics, exhibiting also good environmental stability. Elastomer matrix composites incorporating ceramic nanoinclusions receive enhanced scientific and technological interest, because of their advanced performance. 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. Barium titanate is a wide band gap semiconductor with ferroelectric properties. Ferroelectric particles are considered as active dielectrics, since they undergo a structural transition from the polar ferroelectric phase to the non-polar paraelectric phase, at a critical temperature. Polar oxides/elastomer dielectrics exhibit tunable polarization, related to the piezoelectric and/or ferroelectric behaviour of the filler. The electrical response of these composites can be suitably adjusted by controlling the type and the amount of the ceramic inclusions [3-6], addressing the engineering demands for suitable dielectric properties in tandem with improved mechanical strength and ease processing at a relative low cost.

The produced polymer composite system purposes to combine the three desirable characteristics that is high dielectric constant, low dielectric loss and high breakdown field strength. The electrical response of elastomer matrix/particulate composites depends on various factors like the permittivity and conductivity of the constituent phases, the shape, size and the type of distribution of the inclusions. The interface between the elastomer matrix and the ceramic filler consists another crucial factor, due to the interactions among of them [5-10]. In this study, various ceramic polar oxides are embedded in an elastomer matrix. The employed fillers are micro- and nano- $BaTiO_3$ particles, for each size of filler a series of composites is prepared varying the ceramic content. Dielectric response are investigated by means of Broadband Dielectric Spectroscopy (BDS) in a wide frequency and temperature range [10]. Data analysis is focused in realizing the optimum type and amount of reinforcing phase with respect to dielectric behaviour, functionality and energy storage efficiency.

2. Experimental

2.1 Materials and micro/nano-composites preparation

Composite specimens were prepared by employing commercially available materials. In particular, polydimethylsiloxane (PDMS) belongs to a group of polymeric organic silicon compounds that are commonly referred to as silicones. The chemical formula for PDMS is $CH_3[Si(CH_3)_2O]nSi(CH_3)_3$ provided by Dow Corning. Aiming to study the effect of the filler's size upon the dielectric properties two different powder sizes of $BaTiO_3$ were used both provided by Sigma Aldrich. The first one with a mean particle diameter less than 2 μm and another one that has mean particle diameter in the range of 30-50 nm.

The preparation procedure is constituted by the following steps:

- Mixing PDMS + 50 ml toluene for 20min (hand stirring),
- Mixing nano-powder +50 ml toluene for 30 min (magnetic stirring) 300 rpm, at T= ambient temperature,
- Pouring both mixtures into a single container and magnetically stirring them for 30 minutes at 400 rpm, at T= ambient temperature,
- Continuous stirring for 4 hours at T=50 °C and 300 rpm followed by stirring for 1 hour at T=50°C and 100 rpm,
- Adding the curing agent, hand stirring for 20 min at T= ambient temperature,
- Pour solutions into molds,
- Applying a degassing procedure,
- Finally cure for 20 min at T=110°C

The main goal of the preparation procedure was to achieve fine dispersed particles with no extensive cluster and voids. The $BaTiO_3$ content of the prepared specimens expressed in parts per hundred resin (phr) per weight was the following: 0 (unreinforced PDMS), 1, 5 and10 phr.

2.2 Dielectric Measurements

Broadband Dielectric Spectroscopy (BDS) was employed for the electrical characterization of all manufactured micro/nano-composites. The frequency range varied from 0.1Hz to 10^6 Hz and an Alpha-N Frequency Response Analyzer was used, supplied by Novocontrol Technologies. The applied Vrms was constant at 1V, while the temperature was controlled by Novotherm system (Novocontrol Technologies) with ±0.10^{o}C accuracy. A two electrodes dielectric cell BDS 1200, also supplied by Novocontrol, was used. The specimens were placed between the gold-plated metal electrodes and isothermal frequency scans were conducted for every specimen, from 30^{o}C to 200^{o}C with a temperature step of 5^{o}C/min. Data acquisition was conducted automatically in real time via suitable software (Windeta). All AC measurements were performed according to the ASTM D150 specifications.

3. Results and Discussion

Dielectric spectra of composite systems are very complex, due to the interactions among molecules and/or particles and the concurrence of electric dipoles both permanent and induced. The $BaTiO_3$ micro/nano-composites systems were electrically characterized via Broadband Dielectric Spectroscopy BDS. Three dimensional (3-D) dielectric plots of the real part of dielectric permittivity (ε') and loss tangent (tanδ) are represented in Fig. 1 and Fig. 2 respectively, for the composites with 1 nano and 1micro phr content, as a function of frequency and temperature. Similar spectra have been recorded for all studied composites. The micro/nano $BaTiO_3$ reinforced systems exhibit higher values of ε' in comparison with the neat PDMS in all frequency and temperature range. Dielectric permittivity reaches high values in the low frequency and high temperature regions, conditions in which the maximum of polarization is accomplished, since permittivity is proportional to polarization. The real part of dielectric permittivity (ε') increases while the frequency of the applied field diminishes. This is because dipoles attain adequate time to orient themselves in the direction of the alternating field. Under isothermal conditions the real part of dielectric permittivity is decreasing rapidly at increment of the frequency. As the frequency increases dipoles fail to follow the rapid orientation of the applied field, resulting in low polarization level and (ε') values. The polarization process is accommodated by temperature, due to the thermal agitation of the dipoles and (ε') gets high values in the low frequency and high temperature range [11-13]. Fig. 1a shows a two step-like transition in the permittivity spectra, implying the presence of dielectric relaxation processes. The relaxation processes are more evident in the loss tangent versus temperature and frequency (Fig. 1b). Two relaxation are recorded, the first one in the the intermediate frequency region and the second one corresponding at the high frequencies. At intermediate frequencies and temperature, a stronger relaxation process is recorded, which refers to the transition of the amorphous elastomeric matrix, from the glassy to the elastomeric phase (α-relaxation). This transition is characterized by the glass transition temperature T_g, which is related to the location of the loss peak. 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.

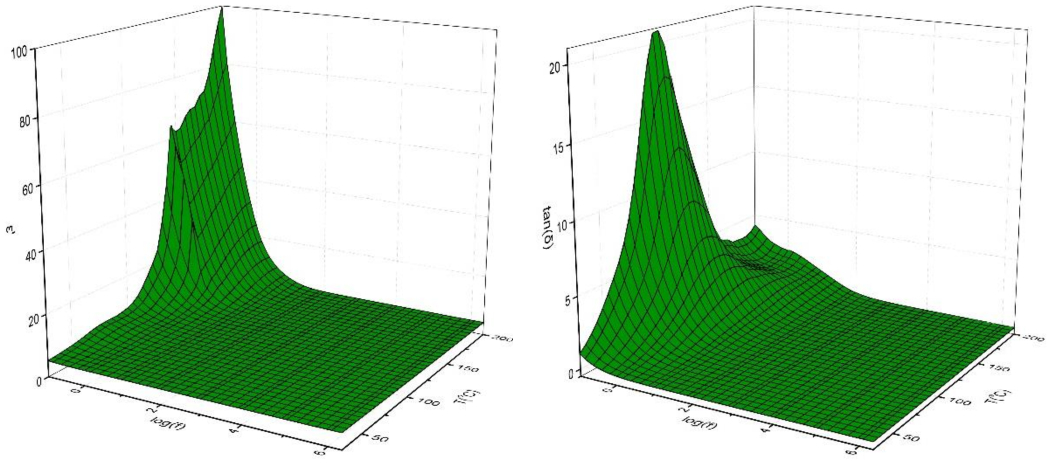

Figure 1. Dielectric spectra of the 1 phr $BaTiO_3$ microcomposite as a function of temperature and frequency, for the (a) real part of dielectric permittivity (left) and (b) loss tangent (right).

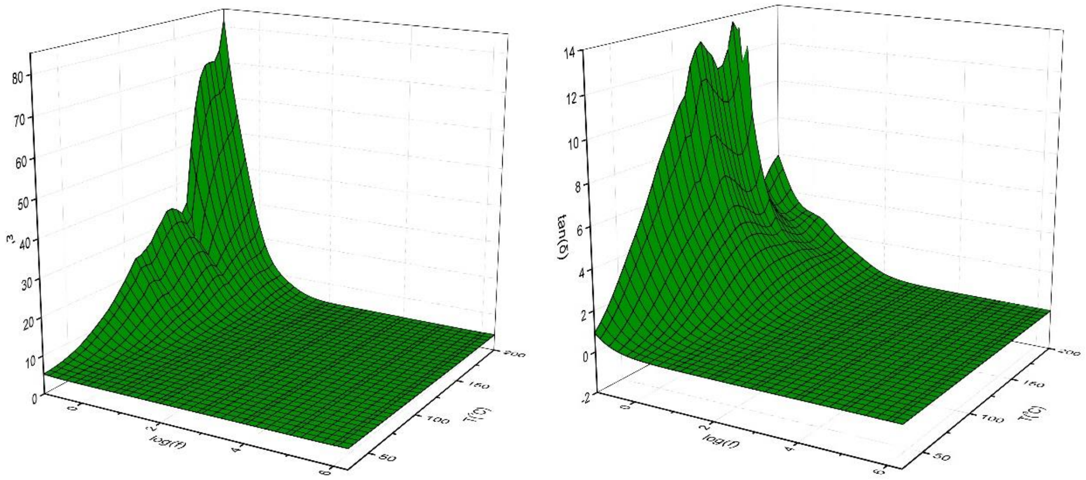

Figure 2. Dielectric spectra of the 1 phr $BaTiO_3$ nanocomposite as a function of temperature and frequency, for the (a) real part of dielectric permittivity (left) and (b) loss tangent (right).

Large parts of the macromolecular chains relax simultaneously because of the existence of cross links between the polymeric chains [16, 17]. The second relaxation occurs at low frequency and high temperature and is attributed to interfacial polarization (IP) process. Interfacial polarization process is observed in electrically heterogeneous systems of two or more phases. Since dipoles exhibit time delay in their orientation parallel to the field when the frequency of the applied field increases, the appearance of the IP process is enhanced at low frequency edge and at high temperatures [1, 8, 14-16, 18]. Real part of dielectric permittivity increases with frequency diminishing and with rise of temperature.

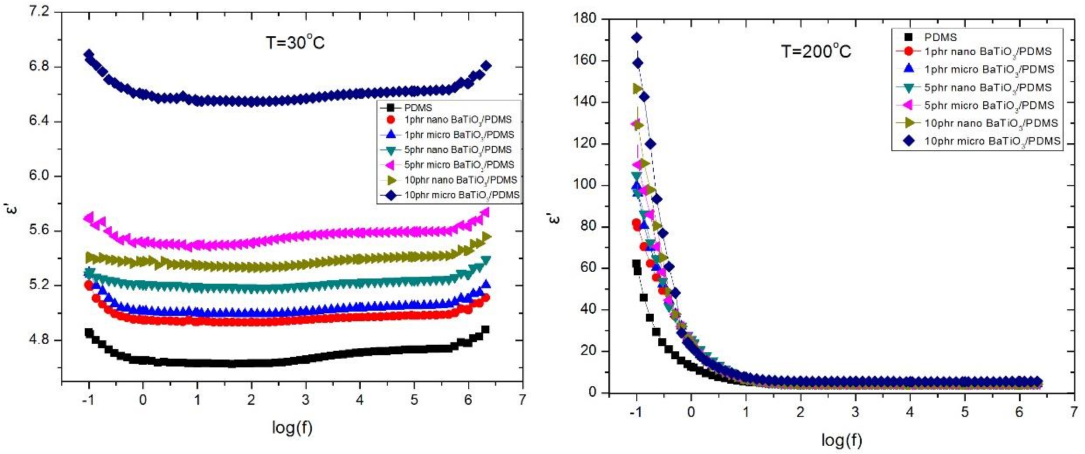

Figure 3: Real part of permittivity (ε´) as a function of frequency for all the examined composites at (a) 30° C (left) and (b) 200° C (right).

This is expected, since (ε´) reflects the level of the achieved polarization. When frequency is low, permanent and induced dipoles acquire sufficient time to align themselves parallel to the applied field further higher temperatures offer thermal agitation which facilitates the orientation of the dipoles. Values of (ε′) increase with filler content, since the composites become more conductive, their heterogeneity raises, charges accumulate at the interfaces of the system and thus interfacial polarization enhances [19]. Fig. 3(a) and (b) denotes that the effect of microsize $BaTiO_3$ inclusions is more pronounced with respect to the effect of nanosize $BaTiO_3$ particles. In the case of the micro-nano $BaTiO_3$/PDMS composites there is a systematic increase of (ε′) part with filler content. Dielectric permittivity in both micro- and nano-particles, (ε′) increases with filler content. Since dielectric permittivity of $BaTiO_3$ is much higher than that of PDMS the recorded behaviour for the filler concentration up to 10 phr, in Fig. 3 is quite understandable [10, 21-23]. The effect of $BaTiO_3$ size on the real part of the dielectric permittivity can be seen in Fig. 3. For the same filler content and at the same temperature it becomes evident that microcomposites exhibit higher permittivity than nanocomposites, denoting a higher level of polarization. The latter most probably is related to the higher polar nature (pure tetragonal lattice) of the micro-particles. Fig.4 presents the variation of dielectric permittivity as a function of temperature for all the examined systems at constant frequency 0.1 Hz. Reinforced systems attain higher values compared to pure PDMS, because of the presence of barium titanate, which exhibits high values real part of dielectric permittivity. The variation of permittivity with temperature becomes significant in the range of 120-140°C. At lower temperatures (ε′) attains rather constant values, while at temperatures higher than 120°C increases rapidly with temperature. At this temperature range the increase of (ε′) is attributed to the enhanced mobility of large parts of the polymer chains and to the co-operating contribution of IP effect in the composite systems. Permittivity curves form or tend to form two peaks, at 0.1Hz. $BaTiO_3$ is a typical ferroelectric material, exhibiting a ferroelectric to paraelectric phase transition at the characteristic temperature of ~140°C [20], which is known as Curie temperature (T_C). Below T_C, $BaTiO_3$ is consisted by domains showing spontaneous polarization, due to the lower symmetry of the crystal unit cell (tetragonal) in comparison to the unit cell in the paraelectric phase (cubic). Under the influence of the electric field the dipole moment, at least of a part, of these domains will be able to follow the applied field contributing to the overall polarization of the system. However, as the temperature is approaching T_C a disorder to order transition takes place in the crystal structure of ceramic filler, which becomes evident through the formed peaks in Fig. 4.

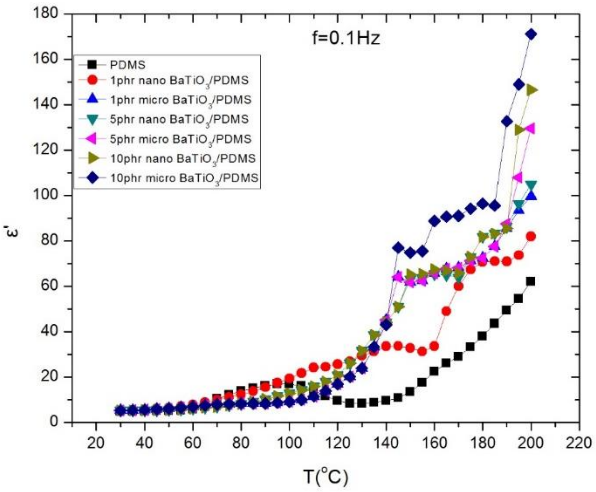

Figure 4: The real part of permittivity (ε΄) as a function of temperature for all the tested specimens at f=0.1Hz.

The influence of the size of $BaTiO_3$ particles on the real part of dielectric permittivity can be seen in Fig. 4, by comparing the values from the composites with 10 phr micro- and nano-particles respectively. The micro-composite exhibits higher values of permittivity in the whole temperature and frequency range, implying a higher level of polarization. $BaTiO_3$ micro-particles are in the polar ferroelectric phase (100% tetragonal lattice) below T_C, while both polar tetragonal and non-polar cubic phases coexist in nano-particles [24]. Consequently, dielectric permittivity is higher in micro-$BaTiO_3$ particles and electrical heterogeneity of the composites' constituents is enhanced in the case of the micro-composite due to their polar structure.

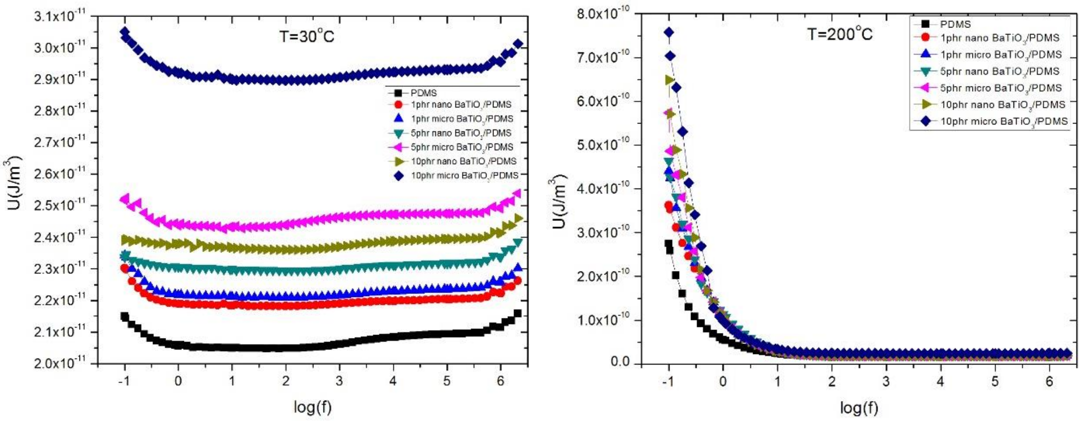

Figure 5: Energy density (U) as a function of frequency for all the examined composites at (a) 30° C (left) and (b) 200° C (right).

The electric energy density of a dielectric material is given by Eq. (1):

$$U = \frac{1}{2}\varepsilon_o \varepsilon' E^2 \qquad (1)$$

where ε_o is the permittivity of vacuum and E the field's intensity. Using Eq. (1) and experimental data the function of energy density for all the examined systems can be determined. It should be noted that energy density changes with both dielectric permittivity and applied field [25, 26]. However, the effect of field's intensity is more rapid, since it appears in

Eq. (1) in the second order. Maximum energy density is achieved at the material's breakdown strength. In this study the applied field was low, focusing upon the influence of the materials properties on the energy storing efficiency. Materials properties are expressed in equation (1) via the real part of dielectric permittivity. Isothermal plots of the function of energy density are depicted in Fig. 5, at two different temperatures. Further, energy density increases steadily with microsize $BaTiO_3$ content.

Conclusions

Elastomer matrix PDMS/barium titanate micro- and nano-composites were prepared and studied. From the conducted analysis results, that the recorded relaxation phenomena include contributions from both the polymer matrix and the micro- and nano-particles. Dielectric permittivity increases with $BaTiO_3$ particles content and temperature and reduces rapidly with frequency, following the variation of the achieved systems' polarization. The tan(δ) spectra include two relaxation phenomena. The first one, recorded at intermediate frequencies (α-relaxation), is related to the glass to rubber transition of the polymer matrix. The second relaxation which is the slower one, appearing at low frequencies and high temperatures originates from interfacial polarization due to the accumulation of unbounded charges at the interface of the system. The tendency to form peaks in the $\varepsilon'=F(T)$ plots and the corresponding variation of polarization can be used as the basis for developing smart systems and nano-devices because it provides the possibilities of controlling the energy storage efficiency at the nanoscale and of tuning the achieved polarization. Addition of $BaTiO_3$ to PDMS increases the ability of the material to store energy in the whole frequency and temperature range.

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