Induced Anisotropy in Electrically Modified Polymer/Ceramic Nanocomposites

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Abstract: Polymer/Ceramic composites with controlled spatial distribution of fillers are synthesized, and the corresponding changes in their properties are studied. Using dielectrophoretic assembly we create anisotropic composites of aligned $BaTiO_3$ particles in silicone elastomer, and study their electrical properties as a function of ceramic volume fraction, connectivity and composite morphology. We investigate these composites for a variety of electrical properties i.e. permittivity, d.c. conduction, dielectric breakdown and energy density. The energy density of these electric-field-structured composites is found to be highly dependent on the anisotropy present in the system. This study emphasizes the important role of conductivity, permittivity, and particularly local cluster distribution in controlling high field dielectric behavior. Designed anisotropy in dielectric properties can provide new paradigms for the development of high energy density materials and gain important insights into the mechanisms that control dielectric breakdown strengths and non-linear conduction at high fields in polymer/ceramic composites.

INTRODUCTION

There is an immediate need for small size, lightweight, low cost and fast-response capacitors for pulsed power applications and power distribution systems [1]. The electrostatic energy density that can be stored in a material is directly proportional to its dielectric permittivity at the local field and the square of the operational electric field. This necessitates that modern materials for high energy density should not only posses high dielectric permittivity, but also provide high operational electric fields with low dissipation factors. The apparent absence of one single phase material exhibiting such a combination of properties emphasize the need to integrate two or more materials with complimentary properties; thus in turn creating a composite with performance far better than of its constituents. The large permittivity ferroelectric based ceramics and the apparent high breakdown strength of polymers makes the polymer-ceramic composite concept very appealing at first sight and enormous efforts have been devoted to their development [2-8]. However, limited by the low permittivity of polymer these composites often require high filler loadings and thus suffer from problems associated with dispersion, brittleness, porosity and high-field conduction etc. A majority of research for the development of high energy density materials has primarily focused on randomly dispersed nano or micron-sized ceramic particulates in a polymer matrix. Connectivity of phases, known to govern many of the final properties of composites such as effective permittivity, dielectric response and electrical conduction, has not captured any attention extensively in this area. In this study we investigate the role of spatial distribution or connectivity of present phases in improving the dielectric breakdown strength and charge storage polymer-ceramic composites.

EXPERIMENTAL

Fabrication of Model Composites:

Polymer/ceramic composite samples are prepared by adding the desired volume fraction of ceramic particulate filler ($BaTiO_3$) to polydimethylsiloxane resin (PDMS), and dispersing by high shear mixing until no sedimentation or agglomerates are visible. Subsequently, cross-linker is added and the sample is degassed under vacuum in order to remove air voids that are trapped during the mixing process. The degassed suspension is divided into three equal parts: The first two parts are processed in alignment cells, shown elsewhere, to design structured composites (1-3 parallel (z-aligned) and perpendicular (x-y aligned), while the third is subjected to a similar thermal cycle but in absence of an electric field [9]. The cells are connected to a high voltage power supply (Trek Power Amplifier model 620A), utilized to amplify the input signal from a Lock-in amplifier (SRS 830), and placed on a hot plate. An electric field (1.6kV/mm at 100 Hz) is then applied to the suspension, while it is held squeezed between the cell plates, concurrently with the application of heat (sample temperature is approximately 80˚C) in order to accelerate the curing process. The samples are kept on the hot plate with the field applied, until full crosslinking is obtained (~ 60 min).

Characterization:

For the electrical characterization, the films were cut into small square ($1 cm^2$) pieces; a gold circular electrode is sputtered in the center of the top surface, while the bottom was completely electroded. Fringing field effects were minimized by keeping the electrode diameter to thickness ratio of the order of 10^3. Composite films with volume percentage of ceramic filler ranging from 5% to 25%, were characterized by Scanning Electron Microscopy (SEM) showing a good filler dispersion within the composite. Excellent alignment is observed, well-defined particle chains with individual particles separated by a small distance (~20 nm), in spite of the small $BaTiO_3$ particle size, as shown in figure 1. At higher loadings, due to the strong dipole interactions between the polarized $BaTiO_3$ spheres, a more pronounced particle aggregation is observed, giving rise to a column-like alignment structure.

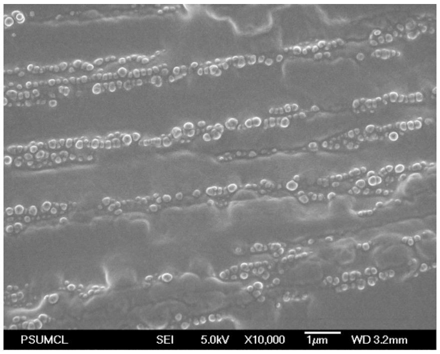

Fig 1. SEM micrographs of aligned $BaTiO_3$ (10 V%) particles in cured PDMS. A 1.6 kV/mm a.c field at 100 Hz is used for alignment. The frequency is chosen to minimize the space charge at the electrodes that screens the applied field and to limit electrophoretic transport of the filler phase.

Low-Field Characterization: The experiment values of the effective permittivity for the random composites (0-3) are summarized in figure 2a, along with the theoretical predictions according to various models [10]. The best fit to the experimental data obtained by the Wakino et al. model that considers the influence of dielectric and/or infringing of the electric flux due to discontinuity at the boundary of constituent phases [11] and is given by the expression,

$$\varepsilon_r = \exp\left[\ln\{V_c \varepsilon_c^{(V_c - V_0)} + (1 - V_c)\varepsilon_p^{(V_c - V_0)}\} / (V_c - V_0)\right] \quad (1)$$

where V_c is the ceramic volume fraction, ε_c and ε_p are the ceramic and polymer permittivities respectively. V_0 is the critical volume fraction corresponding to the point of intersection of the logarithmic and Wakino mixing models and found to be 0.39. Figure 2b shows that for any filler concentration, the 1-3 parallel (z-aligned) composites have the highest permittivity while the permittivity difference of 1-3 perpendicular (x-y aligned) and 0-3 (random) is relatively small. This anisotropy difference in the effective permittivities is found to increase with the ceramic filler content. Although low field characteristics of composites could be insightful, the high field behavior (applied voltages ~ 10 kV) is more important for pulsed power application.

High-Field Characterization:

I-V Characteristics: The current voltage characteristics at high field not only separate the d.c. conduction from dielectric losses, but also dictates the charge storage capacity of the material. The leakage current recorded at a given voltage should represent the steady-state d.c. leakage and should not include the depolarization currents. This was achieved by fitting the I(t) response to an expression which combined a Curie-von Schweidler decay with a constant term, i.e., $I(t) = I_0 t^{-n} + I_{d.c}$. The characteristic curves comparing the pure Siloxane matrix with aligned composites, thus obtained, are plotted and shown in figure 3. The z-aligned composites, at all filler loadings, are found to demonstrate much higher d.c conduction when compared to the randomly dispersed composites. On the other hand x-y aligned composites show similar or lower d.c conduction as compared to randomly dispersed (0-3) composites. The low values of conductivities in x-y aligned composites are not easily explained. To further explain such behavior, a better 3-D field computation of fillers arranged in x-y and z direction is required.

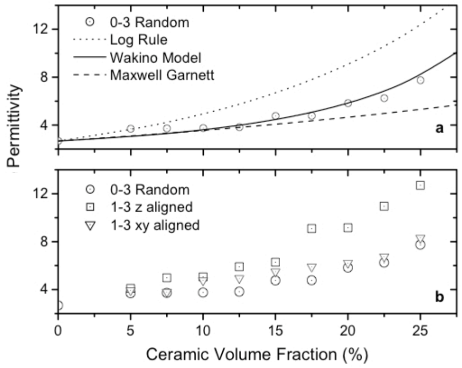

Fig 2. (a) Effective permittivity values *versus* filler volume fraction for the randomly dispersed system, fitting curves derived by using various models are also indicated on the plot. (b) Permittivity values at parallel and perpendicular directions compared to the randomly dispersed composite morphologies. The 1-3 parallel (z-aligned) composite shows an increase in permittivity compared to the 0-3 (random), whereas the 1-3 perpendicular (x-y aligned) systems show comparable permittivity values.

Displacement-Electric Field Loops: The dependence of electrical properties of filled composites on the applied electric fields is well established [2,13]. As filler particles become points of local field increase, due to the large differences or contrast between permittivity and conductivity at the filler-matrix interface, it is crucial to understand the high field losses present in the system arising due to the various contributions, *i.e.*, dc conduction and space charge. Also, both the breakdown strength and the amount of recoverable energy stored, should directly depend on the hysteresis phenomena exhibited by these ferroelectric ceramic-powder filled composites. The shape of polarization-electric field loops can be used to quantify the behavior of these systems at high fields.

A series of polarization-electric field (P-E) loops as a function of increasing electric field, comparing the

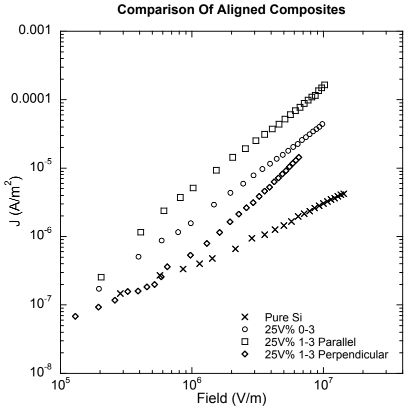

Fig 3: Current-Voltage characteristics of aligned composites. It is evident that the conduction is highest in the case of z-aligned composites while x-y aligned shows a slightly lower conduction compared to 0-3 composites.

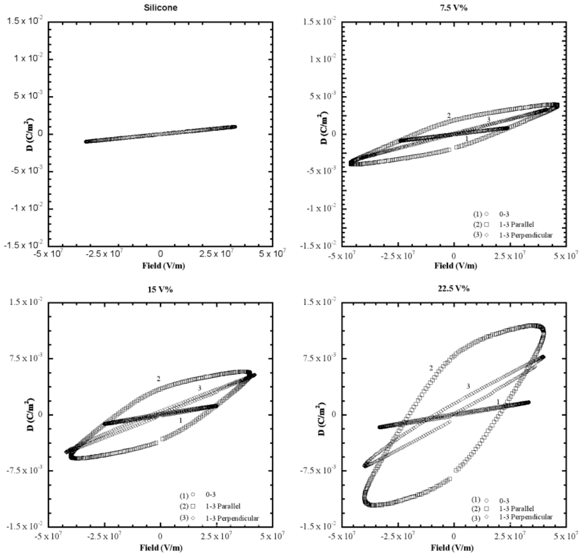

Fig 4: A comparison between the polarization-electric field loops, obtained at 10 Hz, for various volume fractions of structured and randomly dispersed composites. The z-aligned composites clearly indicate higher losses compared to 0-3 and x-y aligned.

siloxane matrix and various composites, are presented in figure 4. The widening (or opening) of loops shows a deviation from the linear behavior of dielectric displacement with electric field ($D = \varepsilon_0 \varepsilon' E = \varepsilon_0 E + P$, where P is the polarization) and can be related to the losses present in the system. A linear behavior of dielectric displacement with applied field was observed, figure 4, in the $BaTiO_3$-free matrix at all field levels. However, the losses present in all ceramic filled composites, represented by their wide loops, increased as a function of the field. As expected the z-aligned composites show the highest dielectric losses when compared to 0-3 or x-y aligned composites. This can arise from the development of large local fields in the gap between neighboring $BaTiO_3$ particles in the z-aligned composites. However, the x-y aligned composites developed the lowest losses, and illustrated the least dependence on magnitude, at all volume fractions, of the applied field. The behavior of these composites indicates that the interface between the ceramic and filler governs the distribution and/or origin of losses, space charge and conduction, present at high fields.

CONCLUSIONS

Modern materials for pulsed power application should not only satisfy the high permittivity and breakdown criteria but also possess a large recoverable energy density. An improvement in the recoverable energy density can be achieved by minimizing the high field losses present in the polymer/ceramic composite. The final properties of such composites are influenced by the spatial distribution of the filler in addition to the polymer-filler interactions. By designing the spatial distribution of fillers inside the polymer matrix, one can significantly enhance the dielectric properties of 0-3 composites. Polymer/ceramic composites with engineered spatial distribution of fillers show anisotropy in their electrical properties. The z-aligned composites demonstrate high permittivity values at low fields when compared to 0-3 composites. However, the benefit of this enhancement is lost due to large losses present in the system at high fields. Our results indicate that the x-y structured composites reduce the problems associated with high field losses and improve the low dielectric strength observed in 0-3 composites.[14] The improvement in dielectric strength of x-y composites, and their comparable permittivity values to 0-3 composites, can be exploited for high enegy density materials. This study has demonstrated that high field dielectric losses, polarization, and ultimate breakdown strength all demonstrate a clear dependance on the spatial distribution of the filler in the polymer matrix. Future work will focus on identifying good candidates for high permittivity polymers and nano-fillers with different shapes and textures, and on developing theoretical models for the permittivity and breakdown mechanisms of such anisotropic composites.

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