Design, Synthesis and Characterization

CERAMIC-POLYMER DIELECTRIC COMPOSITES PRODUCED VIA DIRECTIONAL FREEZING

E.P.Gorzkowski, and M.-J. Pan
Naval Research Laboratory
4555 Overlook Ave., SW
Washington, DC 20375

ABSTRACT

The freeze casting method was successfully used to create ceramic-polymer composites with the two phases arranged in an electrically parallel configuration. The result is a novel composite that exhibits dielectric constant (K) of up to 4000 for PMN-10PT while maintaining low dielectric loss (< 0.05). The finished composites not only exhibit the high dielectric constant of ferroelectric ceramics but maintain the flexibility and ease of post-processing handling of polymer materials. Graceful failure of these samples was observed during dielectric breakdown testing as well as high d_{33} and good hysteresis behavior. In fact the PZT-5A samples had a d_{33} value of ~250 pC/N and a remnant polarization of 15 $\mu C/cm^2$.

INTRODUCTION

A recent article in Science[1] demonstrates the fabrication of nacre-like laminar ceramic body using a novel ice template process. This technique entails freezing an aqueous ceramic slurry uni-directionally along the longitudinal axis of a cylindrical mold to form ice platelets and ceramic aggregates. Given the proper conditions, which include slurry viscosity, percentage water, temperature gradient between the top and bottom of the mold, and starting temperature, the ice platelets are aligned in the temperature gradient direction. The proper starting temperature and temperature gradient must be maintained so that homogeneous freezing occurs and hexagonal ice is formed. This allows the ice front to expel the ceramic particles in such a way to form long range order for both the ceramic and the ice. Upon freeze drying, the ice platelets sublime and leave a laminar ceramic structure with long empty channels in the direction of the temperature gradient. Subsequently the green ceramic body is sintered to form the final microstructure.

This article focuses only on the mechanical properties of the ceramic body, but a ceramic-polymer composite with excellent dielectric properties may be possible by adapting the technique. The adaptation involves 1) using a high K material as the ceramic phase, 2) infiltrating the space between ceramic lamellae with a polymer material, and 3) applying electrodes perpendicular to the ceramic-polymer alignment direction to form an electrically parallel composite dielectric. In this way, the resultant material should exhibit a dielectric constant up to two orders of magnitude higher than that of existing polymer-based dielectrics.

EXPERIMENTAL PROCEDURES

Ceramic slurries were prepared by mixing purified water with 2 wt% of the ammonium polymethacrylate dispersant, Darvan C, (R.T. Vanderbilt Co., Norwalk, CT), 1 wt% of polyvinyl alcohol (Alfa Aesar, Ward Hill, MA), and 68 wt% PZT-5A ceramic (Morgan Electroceramics, Bedford, OH) or 72 wt% PMN-10PT ceramic (made via the Columbite method). Slurries were ball-milled in a high density polyethylene bottle for 12 h with zirconia milling media and de-aired in a vacuum desiccator.

Freezing of the slurries was accomplished by pouring them into a Teflon mold (1.5 in. diameter, 0.75 in. tall) and cooled using a custom built freezing setup. The mold is placed between two copper rods that are cooled by liquid nitrogen to – 60 °C at 5 °C/min. There are band heaters attached to the copper rods in order to control the cooling rate and temperature gradient between the copper rods (10 °C). The samples were freeze-dried (Freeze Dryer 2.5, Labconco, Kansas City, MO) for 24 h. Samples were then removed from the mold for annealing.

Binder burnout and bisque firing was done by heating the samples at 1.2 °C/min to 300 °C, 0.1 °C/min to 350 °C, 0.6 °C/min to 500 °C, 5 °C /min to 900 °C , and finally, a 1 h dwell at 900°C. The samples were then sintered at 1150 °C for 2 h. Each cylindrical sample was then infiltrated with Epotek 301 Epoxy (Epoxy Technology, Billerica, MA) under vacuum creating a composite that is 25 vol% ceramic 75 vol% polymer. Smaller cylindrical plate capacitor samples were cut and prepared for dielectric testing. This entailed lapping the samples using 400 and 600 grit SiC slurry to create flat parallel faces. Some samples were gold coated for capacitance measurement, while others were masked for breakdown and d_{33} measurements. The dielectric constant and loss were measured using an HP 4284A at 0.1, 1, 10, and 100 kHz from 150 down to -60 °C. The breakdown measurements were made using a Hipot tester (QuadTech) at 100 V/s. The d_{33} measurements were performed on the PZT-5A samples using a Berlincourt piezo d_{33} meter (Channel Products INC., Hesterland, OH) after being poled at 80 °C for 5 min. at 30 kV/cm.

Pieces from each of the various samples were mounted onto a stub, carbon coated and masked with conductive tape for Scanning Electron Microscopy (SEM). Images of these surfaces were obtained using a Leo 1550 SEM. Light Optical images were taken with a Nikon microscope (Nikon Instruments, Melville, NY).

RESULTS AND DISCUSSION

After freeze-drying the green samples were fragile but easily transportable. The sample shrinks approximately 2 % in all dimensions after the binder burnout and bisque firing, but the strength of the sample increases dramatically. Once sintered the samples shrink in the lateral and longitudinal directions by ~40%. This is due to the reduction of porosity in the ceramic platelets as the size of the channels between the plates does not decrease after sintering. The SEM image in Figure 1 shows that there is alignment of the PZT-5A ceramic lamellae. It is important to note that the PMN-10PT microstructure looks similar to the PZT-5A, and was not included to avoid repetition.

The microstructure of the sintered samples which consists of ceramic plates aligned in the direction of the temperature gradient. In previous studies,[2] interconnects formed between the ceramic plates, but better care was taken to make sure that the cooling rate was controlled. By controlling the cooling rate the ice front does not reach supersaturation of the ceramic and thus no particle repulsion which causes the local ice crystal front to split leaving behind an agglomerate of ceramic particles.[3] In addition the platelets are not exactly parallel to the temperature gradient. This is due to the differences between the imposed and the preferred growth directions. The preferred growth direction is controlled by the system i.e. interfacial energies while the imposed growth direction is highly dependent on the temperature gradient.[4,5] If the temperature gradient is too low then the preferred growth direction dominates and thus the platelets grow a few degrees off of the temperature gradient direction. A larger temperature gradient can correct this problem and will be used in future experiments.[3]

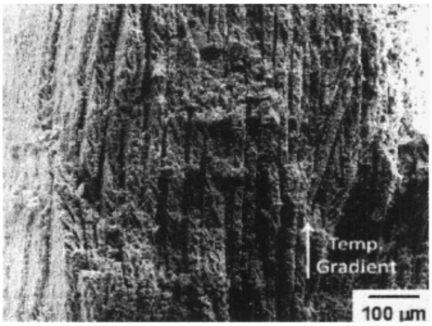

Figure 1 SEM image of the microstructure of freeze-cast PZT-5A sample.

In order to determine the dielectric properties of this composite the fired ceramic was infiltrated with epoxy and cut into smaller pieces perpendicular to the freezing direction. After polishing and electroding with gold the dielectric properties were measured. The dielectric constant versus temperature can be found in Figure 2 for (a.) the PZT-5A and (b.) the PMN-10PT samples. The peak value of dielectric constant for the PZT-5A was 500 and 4000 for the PMN-10PT. In both cases the dielectric constant is 2 orders of magnitude higher than conventional composite capacitors and about 50% lower than that of the sintered ceramic of the same compositions. Additionally, the dielectric loss of these samples is less than 0.05 for most frequencies which is lower than sintered ceramics but not as good as polymers. This means that the ice template method is a viable way to produce high dielectric constant composite capacitors.

The epoxy used in these experiments were not flexible enough to bend by hand, but any thermoplastic or mixable thermoset polymer can be infiltrated. Therefore, the composite can maintain the flexibility and ease of post-processing handling of polymer materials. In fact, flexible polymer/ceramic capacitors with high dielectric constant and high breakdown strength can be produced.

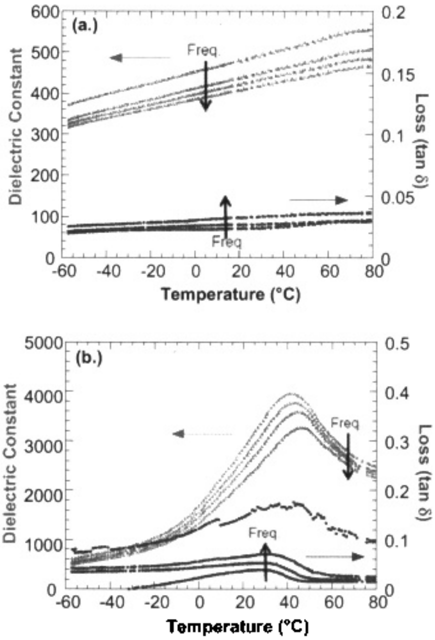

Figure 2 Dielectric constant versus temperature data for (a.) the PZT-5A and (b.) the PMN-10PT samples.

In order to be confident that the alignment of the particles caused the higher dielectric constant, a fully dense ceramic and a random composite sample was created. The ceramic sample was created from the same powder batch as the aligned composite as well as pressure less sintered at the same temperature and time. The random composite was created by mixing the same volume of ceramic powder that was in the aligned composite in epoxy and allowed to cure. Figure 3 shows the dielectric constant versus temperature of the various samples for comparison purposes. It can be seen that the ceramic value as expected is the highest and the random composite is the lowest. In fact the ceramic sample is two orders of magnitude higher than the aligned composite (freeze-cast sample) and the random composite is two orders of magnitude higher than the aligned composite. This shows that the alignment is responsible for the increase in the dielectric constant.

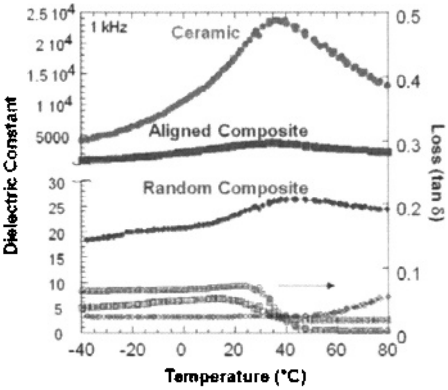

Figure 3 Dielectric Constant at 1 kHz versus temperature plot that compares PMN-10PT ceramic, freeze-cast, and random composites.

Another verification that the alignment process works well was found by observing other properties of these samples. Figure 4 shows the polarization versus field plots for the (a.) PZT-5A and the (b.) PMN-10PT samples. Both samples show a ferroelectric behavior as would be expected. The values for the coercive field, remnant polarization, and peak polarization are comparable to commercially available ceramic samples with the same respective compositions.

Breakdown measurements were also taken of these samples. These tests were done by increasing the voltage on the sample until a breakdown event occurred. The same sample was ramped up again until another breakdown event occurs and this process was repeated up to 50 times, which can be seen in Figure 5. No catastrophic failure or fail-short was observed for either composition over this testing range. Since the area around the breakdown is healed like in most polymer capacitors, voltage can be re-applied. This means that these composites fail in a graceful manner though the mechanism was not studied further. In the case of the PMN-PT/Epoxy composite the breakdown strength increased as the number of breakdown events increased. This is most likely due to the established "weakest link" theory, where breakdown occurs at the weakest point of the sample. Since the next weakest spot, the area where the next breakdown occurs is stronger than the first the breakdown voltage goes up.

The last property that was measured for the PZT-5A composites was the piezoelectric coefficient, d_{33}. In this case the value was ~250 pC/N. The ceramic value is 300-450 pC/N so the composite sample performs very well. Overall it seems that the freeze-casting method provides a viable way to make composite capacitors with excellent dielectric and piezoelectric properties. The only drawback to make this process viable for large scale manufacturing is the freeze-drying step. This may be avoided by using non-aqueous slurries. For example, camphene has been used to make slurries like this because camphene sublimes at room temperature and is liquid at 50 °C. Therefore, future studies will include the study of non-aqueous slurries.

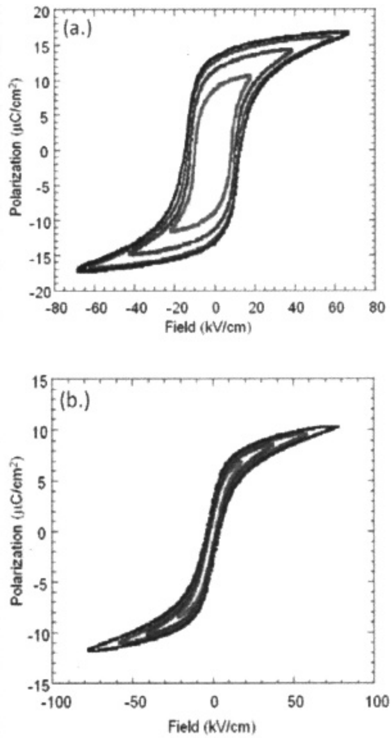

Figure 4 Polarization versus Field curves for (a.) the PZT-5A and (b.) the PMN-10PT samples.

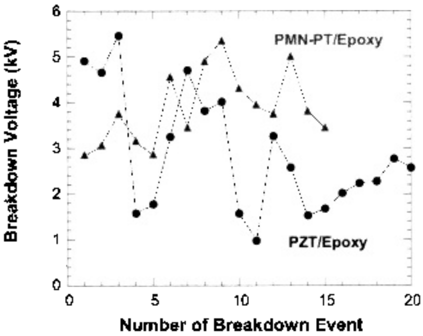

Figure 5 Breakdown voltage results for PZT-5A and PMN-10PT freeze-cast samples showing graceful failure.

CONCLUSION

The freeze casting method was successfully used to create ceramic-polymer composites with the two phases arranged in an electrically parallel configuration. The result is a novel composite that exhibits dielectric constant (K) up to two orders of magnitude higher than that of composites with ceramic particles randomly dispersed in a polymer matrix while maintaining low dielectric loss (< 0.05). The finished composites not only exhibit the high dielectric constant of ferroelectric ceramics but maintain the flexibility and ease of post-processing handling of polymer materials. Graceful failure of these samples was observed during dielectric breakdown testing as well as high d_{33} and good hysteresis behavior.

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