19th International Conference on
Adaptive Structures and Technologies
October 6-9, 2008
Ascona, Switzerland

PVDF Particle-stabilized Polymeric Foams as Piezoelectric Space-charge Electrets

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ABSTRACT

This conference proceeding accompanies a poster presentation which introduces cellular electrets produced from dried and consolidated PVDF particle-stabilized wet foams. Ultra-stable particle-stabilized wet foams provide a process by which bulk porous materials with tailored microstructures can be produced from a variety of polymers, including those considered intractable. The influence of the foam microstructure on the charge hysteresis diagrams and remnant charges is investigated. The trends observed in the behavior of the charges conform to Paschen's law for the electrical breakdown of gases.

Keywords: Particle-stabilized foams, piezoelectric, space-charge electrets, remnant charges, PVDF

1. INTRODUCTION

Polymeric foams are common materials with important applications in light-weight structures, thermal and electrical insulation, shock and vibration damping, and packaging. As passive materials, their low density and ability to dissipate longitudinal waves make them common materials in high frequency damping applications. However in the last twenty years, the study of porous cellular polymers as functional materials has generated much interest. In particular, piezoelectric behavior observed in poled cellular polymers suggests that active or 'smart' materials based on polymeric foams are possible. Such smart materials would find useful applications in soft sensors and actuators like ultrasonic transducers, large area pressure sensors, and active noise damping sensors.

The piezoelectric behavior of cellular space-charge electrets comes from macroscopic dipoles that form across the pores in a cellular polymer when the air between ionizes under high electric fields [1]. In good electret materials, these dipoles are considered quasi-permanent. Although many polymers will hold electric charges temporarily, these charges tend to dissipate over time and especially rapidly at elevated temperatures. Fluoropolymers are known to be exceptionally good electrets materials but unfortunately, some high temperature polymers cannot be foamed using conventional methods of physical or chemical blowing due to unfavorable polymer melt properties [2]. Therefore, alternative foaming processes are needed when dealing with such intractable polymers.

By using particle-stabilized wet foams as intermediaries, porous materials with controllable microstructures can be obtained, even from intractable polymers. Unlike-surfactant-stabilized foams, particle-stabilized foams are highly stable and resist coarsening even under drying and sintering conditions [3]. This novel technique for polymer foam processing allows novel porous materials that may have advantageous properties for applications in cellular electrets to be manufactured [4,5].

In this poster presentation, PVDF porous materials produced from dried and consolidated particle-stabilized wet foams are examined as electret materials. The effects of the foam microstucture on measured charge displacement under high electrical fields are investigated. Initial results showing that such foams behave as piezoelectric materials are presented.

2. MATERIALS AND METHODS

2-1. PVDF Foams

Highly stable PVDF particle-stabilized wet foams were made by mechanically frothing suspensions of mono-dispersed spherical sub-micrometer PVDF particles (Polysciences Inc.) in ethanol-water solutions with a two-pronged hand mixer (Braun Multimix 350W). By changing the parameters of the initial suspension and frothing conditions such as the ratio of ethanol to water, the concentration of particles in the suspension, and the speed of duration of frothing, different wet foam microstructures were obtained. Strong correlations between the parameters and the bubble size distribution and air content were found. This allowed wet foams with tailored macroporous microstructures to be made. These wet foams were ultra-stable and retained their microstructure when dried. The dried foams were then sintered into bulk porous materials and used in the following electrical investigations.

The foaming and consolidation processes along with the characterization of the stable wet foams and the obtained porous materials are all described in detail in a journal article currently in progress [6].

2-2. Sample Preparation

Samples for electrical characterization were prepared by cutting the bulk foams made using the particle-stabilized foam process into 1 mm thick slices. To prevent short circuits through the sample due to large or broken pores, a layer of 55 μm thick polyimide tape was applied to each side. Circular electrodes with diameters of 1 cm were patterned on both sides by depositing 45 nm of sputtered platinum. The electrodes were patterned as mirror images so that they would overlap only within the circular area to obtain a very well defined sample test area. Figure #1 shows a photograph of a standard sample. Precise measurements of the sample thicknesses were taken using a caliper and used to calculate the applied electrical fields.

The samples were connected to the testing apparatus through connecting wires were taped to the electrodes.

Figure #1. Photograph of a 1 mm thick slice of PVDF foam sandwiched between two layers of polyimide tape with patterned platinum electrodes. Samples like these were used in the charge and piezoelectric measurements.

2-3 Electrical Measurements

2-2-1. Charge Hysteresis

The sandwiched foam samples were tested for charge hysteresis under high electrical poling fields by applying a triangular wave function across the electrodes using a high voltage generator. To avoid dielectric breakdown of the polyimide tapes, the maximum voltage applied was ±12 kV. The samples were tested at frequencies of 10, 1, and 0.1 Hz. Only the results from the 0.1 Hz are presented here.

A highly sensitive current amplifier and integrator circuit that was constructed in-house was used to measure the charge displacement. The circuit was connected to an oscilloscope (Tektronix TDS5034B) that measured the current and charge signals as a function of the applied voltage.

2-2-2. Remnant Charges

Remnant charges are the charges that remain in the sample even after all external fields have been removed. These values were read from the charge hysteresis curves at the points when the applied field is zero and plotted against the peak electric field values.

2-2-3. Piezoelectric Measurements

To test for piezoelectric activity, changes in the thickness of the samples during the poling cycles were measured using a dynamic mechanical analyzer (DMA) operating in static mode. To consider possible viscoelastic effects, the poling cycle was chosen to have a long period of 5 min. A peak voltage value of ± 9 kV was selected because it is well above the value at which remnant charges emerge.

3. RESULTS & DISCUSSION

3-1. Charge Hysteresis

Figure #2 shows SEM images of consolidated PVDF foams with increasing average bubble size with their corresponding charge hysteresis diagrams plotted beside them. The charge hysteresis loops were measured at different peak-to-peak magnitudes in increasing order.

At low peak-to-peak voltages no hysteresis was observed. When the applied electrical fields were below 3 kV/mm, the charge displacement varied linearly with the field. Only at higher fields did closed hysteresis loops form.

As can be seen in Figure #2, the charge displacements fell within a similar range of values for all the samples when cycled through comparable peak-to-peak electrical fields. However, noticeable differences were observed in the shape of the curves. The samples with smaller average pore sizes had charge hysteresis loops that were more open and rounded, while those with larger average pore sizes produced narrower curves with sharp corners.

The differences in the hysteresis loops can be explained by Paschen's law of gaseous breakdown which states that the minimum voltage required to break down the gas between two parallel plates is a function of distance between the plates and the amount (or pressure) of the gas. Paschen's law is described by equation (1) in which p and d are the pressure and gap distance, respectively, and a and b are experimentally-determined gas-dependant constants.

$$V = \frac{a(pd)}{\ln(pd) + b} \tag{1}$$

According to Paschen's law, the air inside large pores breaks down at lower voltages than those in smaller pores and explains why hysteresis is first observed at lower fields in the samples with the larger average pore diameters. Perhaps, the larger pores are also prone to dissipate earlier than the smaller pores just as they broke down earlier. As a result, the hysteresis loops of the foam samples with the larger pores appear narrower because of the faster dissipating charges.

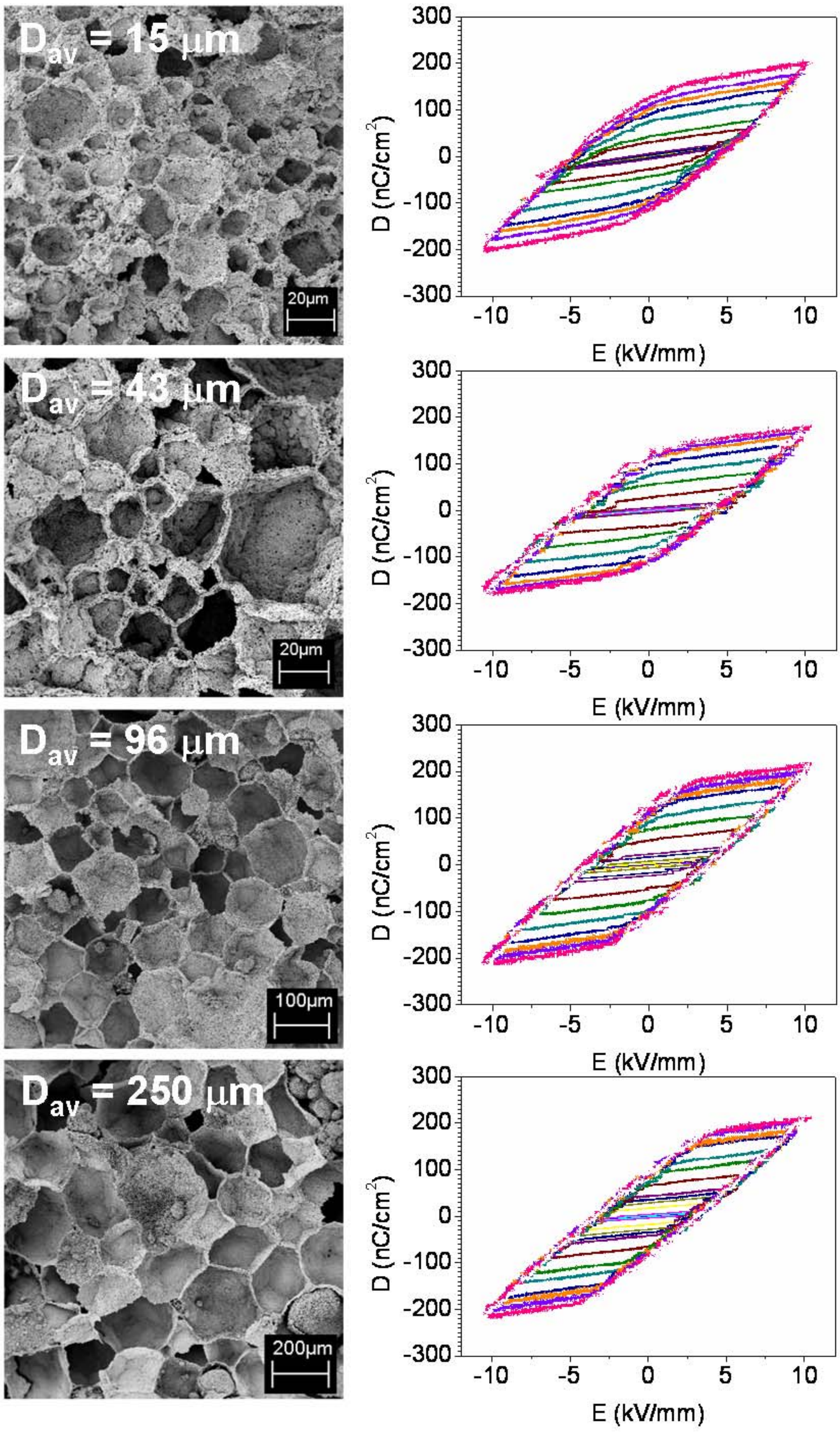

Figure #2. SEM images of various sintered PVDF foam microstructures *(left)*, with their corresponding charge hysteresis curves (*right)*. Hysteresis curves were measured at a frequency of 100 mHz cycling between electrical fields of increasing magnitude.

3-2. Remnant Charges

The presence of remnant charges indicates the presence of quasi-permanent charge dipoles due to the breakdown of the air inside the pores which get stuck in the dielectric polymeric pore walls. Figure #3 shows the remnant charges as function of the peak electrical field used to the pole the foam sandwiches. These values were read directly from the hysteresis loops presented in the previous section.

As explained earlier, Paschen's law states that the voltage required to break down the air in a pore increases as the size of the pore decreases. Therefore, the onset of the remnant charges should be a good indicator of the bubble size distribution within a porous material. With the exception of the remnant charge behavior of the sample with the smallest average pore diameter (15 μm), the electrical field required for the onset of remnant charges decreases as the average pore size increases. A possible explanation that the remnant charge onset occurs unexpectedly early in the case of the foam sample with an average pore size of 15 μm may be due to the presence of a few large voids that break down under lower fields. More experiments and statistical studies are required before further conclusions are drawn.

Another noticeable trend in the influence of the microstructure on the remnant charges is that at the highest peak poling fields, the total amount of remnant charge decreases with increasing pore size. This could again also be an indication that the larger pores are prone to reverse break down more than the smaller pores just as they broke down earlier.

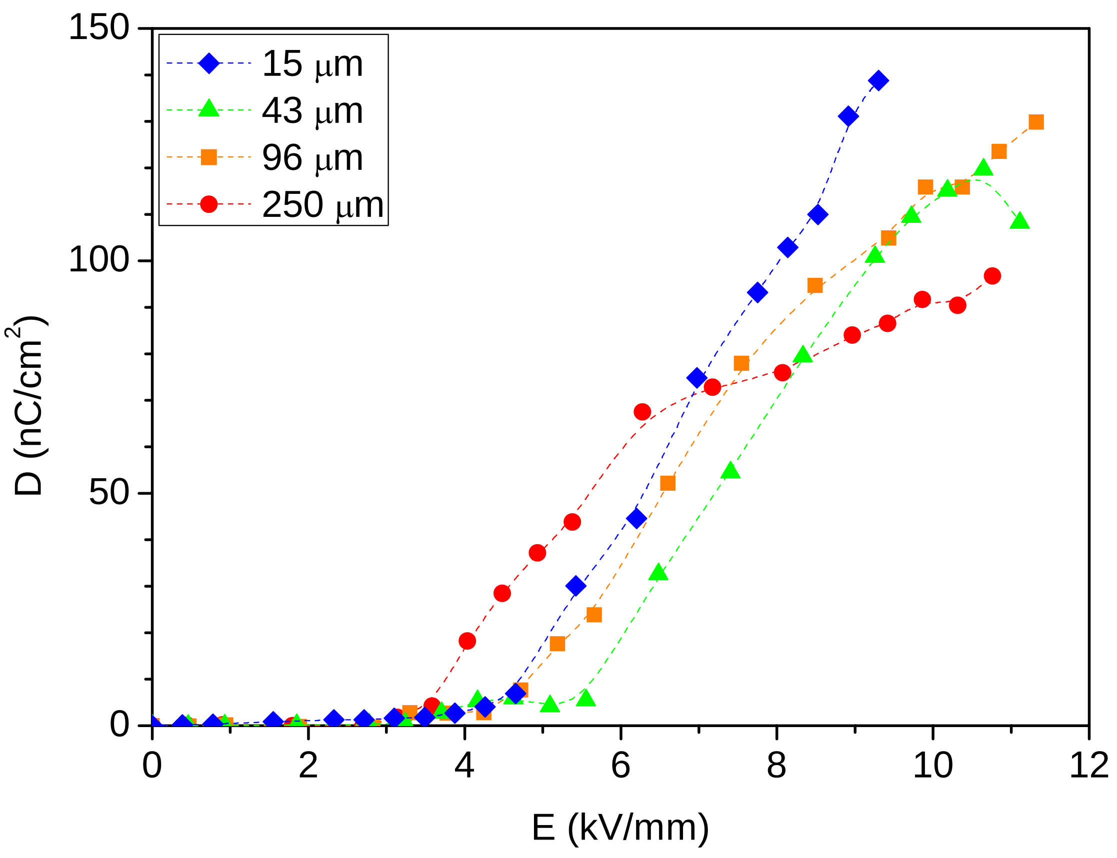

Figure #3. Remnant charges as a function of the electrical field used to pole the foam sandwiches.

3-3. Piezoelectric Activity

A typical ε-E curve obtained from the PVDF foam sandwiches is given in Figure #4 and provides evidence that the PVDF porous materials made from consolidated particle-stabilized foams can be used as materials for piezoelectric cellular electrets.

The d_{33} piezoelectric coefficient was measured as -121 pC/N, a value that is about 4 times greater than that of dense PVDF.

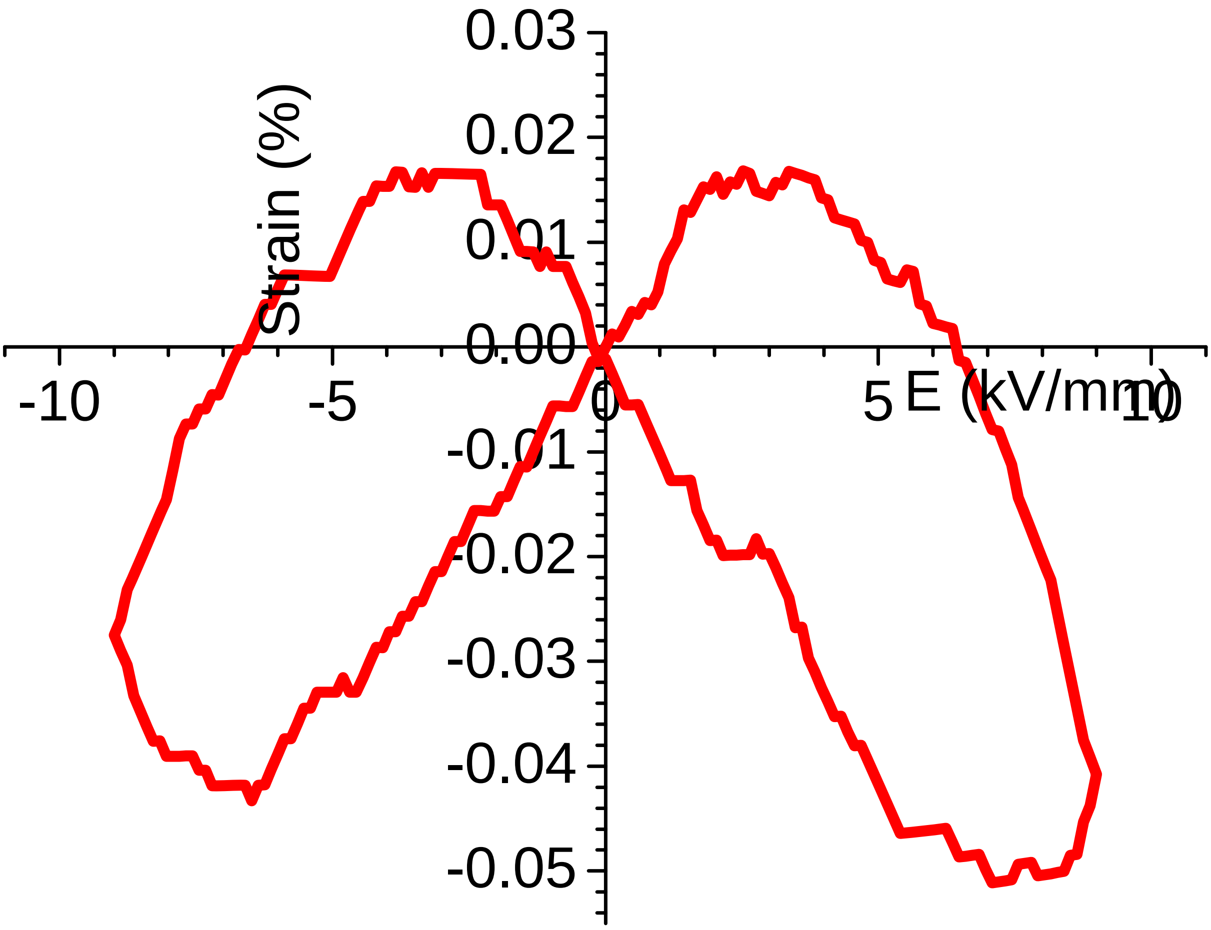

Figure #4. Typical ε-E butterfly curve of the piezoelectric cellular electrets produced from particle-stabilized foams. The sample was cycled between +8 kV/mm and -8 kV/mm in a period of 5 min.

4. OUTLOOK

In future work, particle-stabilized wet foams will be used to produce novel porous materials with properties that are advantageous to cellular electrets, for example by improving charge stability or piezoelectric activity. Such improvements may be brought about by investigating intractable polymers, composite foams, and other microstructures.

5. CONCLUSIONS

The microstructure of cellular electrets influences both the shape of the charge hysteresis curves and the electrical field at which remnant charges begin to occur. The electrical fields required for the onset of remnants charges can be largely explained by Paschen's law of gaseous breakdown. Initial investigations indicate that he poled foams exhibit piezoelectric behavior however further studies are needed to determine how the microstructure of the cellular electrets affect charge stability and piezoelectric activity.

ACKNOWLEDGEMENTS

The authors would like the thank the Swiss Competence Centre for Materials Science and Technology Surface, Coating & Particles Engineering Education Research Unit (CCMX-SPERU) for their financial support, Prof. Paul Smith of the Polymer Technology group at ETH-Zurich for use of his equipment, as well as Valerie Geiser for her contributions to the experimental work.

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