Cellular polyethylene-naphthalate ferroelectrets: Foaming in supercritical carbon dioxide, structural and electrical preparation, and resulting piezoelectricity

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Polymer foams with electrically charged cellular voids, the so-called ferroelectrets, are soft piezoelectric transducer materials. Several polymers such as polyethylene terephthalate or cyclo-olefin copolymers are under investigation with respect to their suitability as ferroelectrets. Here, the authors report an additional ferroelectret polymer, cellular polyethylene-naphthalate (PEN), which was prepared from commercial uniform polymer films by means of foaming in supercritical carbon dioxide, inflation, biaxial stretching, electrical charging, and metallization. Piezoelectric d_{33} coefficients of up to 140 pC/N demonstrate the suitability of such cellular PEN films for transducer applications. Their piezoelectricity is partially stable at elevated temperatures as high as 100 °C. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2738365]

Polymer ferroelectrets with large piezoelectric d_{33} coefficients are a major area of research on soft transducer materials.[1] Their piezoelectricity arises from the combination of internally separated and trapped charges and an anisotropic cellular polymer matrix with very low elastic stiffness. A number of polymers, such as polypropylene (PP),[2,3] polyethylene terephthalate (PET),[4] and cyclo-olefin copolymers (COC),[5] have been investigated, and some device applications of PP ferroelectrets, such as touch pads (Screentec Company) and bed sensors (Emfit, Ltd.) are already on the market. However, a relatively low thermal stability of the piezoelectricity sometimes limits their usefulness. For example, the maximum long-term operating temperature of PP ferroelectrets is about 60 °C; PET and COC ferroelectrets exhibit slightly higher stabilities but usually at the price of smaller piezoelectric d_{33} coefficients. Although COC ferroelectrets can be thermally stable at 110 °C, the corresponding d_{33} is relatively small.[5]

Our starting material is a biaxially oriented PEN film (Teonex® Q51 from DuPont Teijin Films™) with a thickness of 100 μm and a density of 1.45 Mg/m^3. PEN is a high-performance thermoplastic polyester. Its chemical structure is the same as that of PET, except that the single-ring terephthalate is replaced by the double-ring naphthalate, which enhances the thermal, mechanical, and barrier performance of PEN in comparison with PET.

A two-step process is employed for foaming the non-voided PEN film. First, the film samples are exposed to supercritical carbon dioxide (CO_2) for 5 h in a steel chamber (Sigmar Mothes Hochdrucktechnik, Berlin) at a pressure of 150 bars so that the polymer is saturated with the supercritical fluid. Second, the sample undergoes a heat treatment for 10 s at 130 °C, well above the glass-transition temperature[6] T_g of PEN, and the sudden volume increase of the CO_2 upon its phase change leads to voiding of the PEN. Subsequently,

the voided samples are inflated[7] in a separate process in order to improve the cellular geometry. To this end, the samples are exposed to CO_2 at 150 bars for 19 h. When the high pressure is suddenly removed, the cellular PEN films are further inflated, and the change of the foam geometry is stabilized by another heat treatment at 130 °C for 10 s. In comparison to chemical foaming with a blowing agent, the present physical foaming process does not cause any pollution or impurities.

After voiding and inflation, the PEN films are biaxially stretched on a laboratory-scale film stretcher (KARO IV from Brückner Maschinenbau) at a ratio of about 1.5. Internal charging of the voids is achieved in a point-to-plane corona discharge either in air at atmospheric pressure with a voltage of −21 kV or in sulfur hexafluoride (SF_6) at a pressure of 3 bars with the much higher voltage of −50 kV. The charging process takes 15 s. Finally, aluminum electrodes are deposited onto both sides of the PEN films under high vacuum. The resulting piezoelectric d_{33} coefficients are determined dynamically: The sample is loaded with a static force of 3 N plus a sinusoidal force of 1 N (peak to peak) at a frequency of 2 Hz, and the electrical response is measured.

Figure 1 shows the scanning electron microscope (SEM) image of the cross section of a cellular PEN sample that is suitable as a ferroelectret after electrical charging. The SEM image demonstrates that it is possible to form lenslike voids inside the PEN films by means of voiding with supercritical CO_2, additional inflation, and biaxial stretching. Figure 2 shows d_{33} as a function of foam density for the two different charging processes. The film density ranges from 0.95 to 1.25 Mg/m^3 and the d_{33} coefficient increases with density up to a maximum at a density of approximately 1.1 Mg/m^3 and then decreases again to zero. Samples with small voids, corresponding to a high density, are relatively stiff and therefore show only low piezoelectricity. Controlled inflation decreases the sample density, resulting in a lower elastic stiffness and higher piezoelectricity. If the PEN films
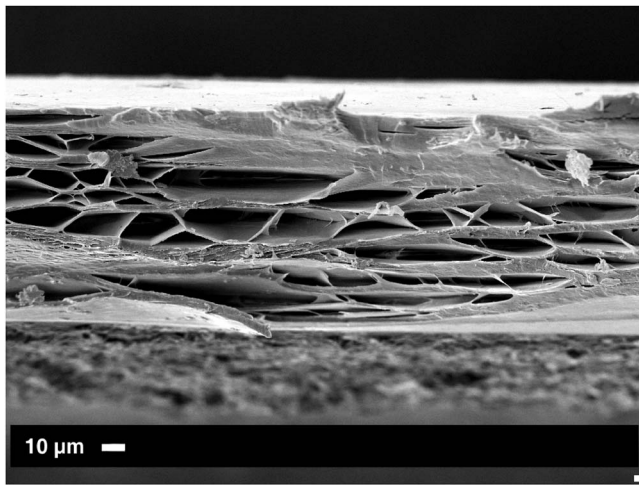
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FIG. 1. SEM image of voided, inflated, and biaxially stretched PEN (thickness of 97 μm, density of approximately 1.0 Mg/m^3).

FIG. 3. Short-term test. Decay of d_{33} after annealing for 1 h at selected temperatures.

are inflated even more to a still lower density, the voids become more and more spherical, and the elastic stiffness strongly increases and the piezoelectricity decreases again. This behavior is qualitatively the same as on PP and PET ferroelectrets.[7,8]

The experimental error of the d_{33} coefficient measurement is 7%. It should be noted that some steps of the complex, nonstandard foaming process are not yet completely reproducible. In particular, the shape and size distributions of the voids could not be very well controlled yet. Therefore, the scattering in the piezoelectric coefficients of Fig. 2 is large, and some samples show no piezoelectricity at all, even though they have an almost optimal overall density.

d_{33} coefficients between a few and around 100 pC/N are observed. The highest d_{33} coefficient of 140 pC/N is found on a PEN film charged in SF$_6$. Here, the higher charging voltage results in a higher charge density on the external film surface and thus in a higher internal electric field. In addition, SF$_6$ inside the voids leads to higher breakdown strength. Consequently, more charges are separated and trapped on the internal surfaces of the voids, which yield higher piezoelectricity.[9,10] Similar results were already obtained on PET ferroelectrets.[4]

Short- and long-term tests of the thermal stability were also performed. For the short-term test, the initial d_{33} coefficient is measured at room temperature, and then the samples are kept for 1 h at the given elevated temperature, and d_{33} is

measured again at room temperature. Figure 3 shows the decay of d_{33} as a function of the annealing temperature. After annealing at 60 or 80 °C for 1 h, there is only a slight decay of d_{33}. Annealing at 100 °C, however, leads to a significant decrease of d_{33}. At higher temperatures, charges can be detrapped more easily, and some piezoelectric activity is lost. Above 120 °C, the samples show no more piezoelectricity. The reported glass-transition temperature T_g of PEN is about 123 °C. If samples are heated above T_g, the molecular chains have sufficient mobility for rather large movements, and the charges on the internal void walls are compensated or detrapped. The double-ring naphthalate structure in the PEN monomer enhances its thermal stability which results in a higher T_g than that of PET (around 80 °C). This is the main reason why PEN ferroelectrets are thermally more stable than PET ferroelectrets.

In the long-term test at 100 °C, as shown in Fig. 4, d_{33} decreases from 23 to 12 pC/N ($\approx 50\%$) after one day for the sample charged at −21 kV, and from 27 to 16 pC/N ($\approx 60\%$) for the sample charged at −50 kV. After 5 days, the remaining d_{33} values are 6 pC/N ($\approx 25\%$) and 11 pC/N ($\approx 40\%$). d_{33} decays rather quickly during the first day. After 5 days, the piezoelectric activity can be considered approximately stable. This means that PEN ferroelectrets are still piezoelectric at 100 °C. Compared to PP ferroelectrets, whose d_{33} coefficient is almost completely lost after only a few hours at 100 °C,[11] the piezoelectricity of properly prepared PEN ferroelectrets is much more stable.

In conclusion, cellular ferroelectrets have been prepared from nonporous PEN films by means of foaming, inflation,
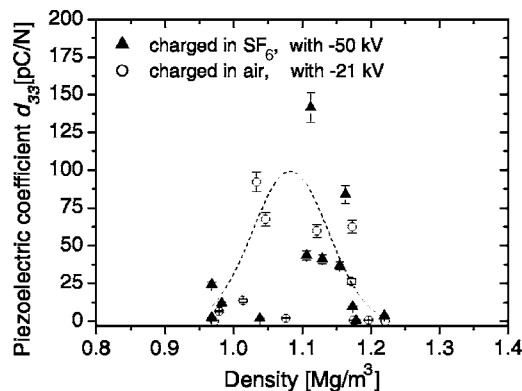

FIG. 2. Dependence of d_{33} on sample density for two different charging processes (the line indicates the observed behavior qualitatively).
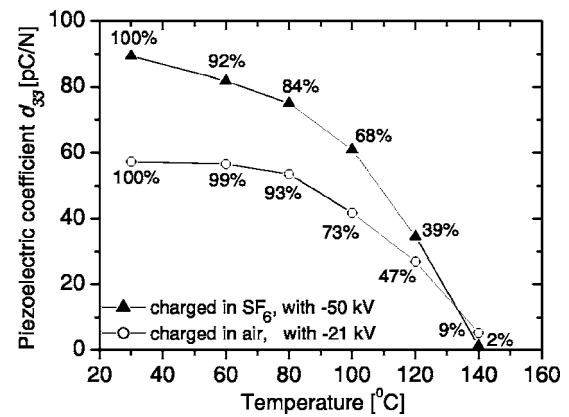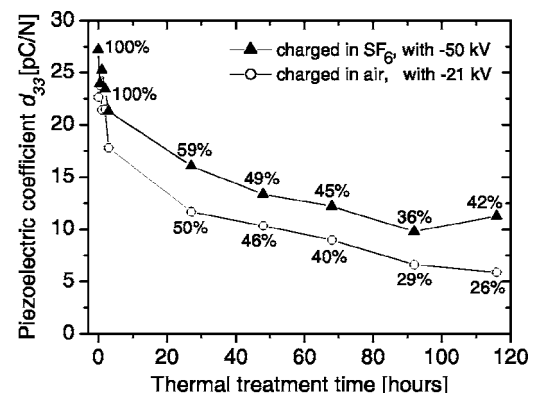

FIG. 4. Long-term test. Decay of d_{33} at 100 °C over 5 days.

biaxial stretching, charging, and metallization. The resulting piezoelectric activity is strongly influenced by the polymer structure. Relatively high d_{33} coefficients are only achieved on samples with an optimal density. Higher charging voltage results in stronger piezoelectricity, samples charged at -21 kV show d_{33} coefficients up to 80 pC/N, while those charged at -50 kV exhibit up to 140 pC/N. In short-term tests, the piezoelectricity of PEN ferroelectrets is rather stable at elevated temperatures up to at least 80 °C. There is an obvious decrease of d_{33} at 100 °C, but PEN ferroelectrets are still piezoelectrically active to a considerable extent even at this temperature.

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