

Controlled inflation of voids in cellular polymer ferroelectrets: Optimizing electromechanical transducer properties

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When exposed to sufficiently high electric fields, polymer-foam electret materials with closed cells exhibit ferroelectric-like behavior and may therefore be called ferroelectrets. In cellular ferroelectrets, the influence of the cell size and shape distributions on the application-relevant properties is not yet understood. Therefore, controlled inflation experiments were carried out on cellular polypropylene films, and the resulting elastical and electromechanical parameters were determined. The elastic modulus in the thickness direction shows a minimum with a corresponding maximum in the electromechanical transducer coefficient. The resonance frequency shifts as a function of the elastic modulus and the relative density of the inflated cellular films. Therefore, the transducer properties of cellular ferroelectrets can be optimized by means of controlled inflation.

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Application-relevant properties of cellular materials strongly depend on the shape and the size of the voids.¹ In cellular polypropylene (PP) films,² highly anisotropic voids lead to ferroelectric-like poling behavior³ and, after bipolar charging of the internal void surfaces,⁴ to unusual electromechanical properties.⁵ Consequently, these materials, with their internal electret charge, hysteresis, and switching behavior, may be called ferroelectrets.⁶ In recent years, the understanding of the charging process and of the resulting electromechanical behavior in such cellular ferroelectrets has been significantly advanced. The importance of void shapes and sizes for the electromechanical properties is, however, still far from clear.

It is known that the elastic properties of cellular materials (foams) strongly depend on the relative density and the shape anisotropy of the voids.¹ Therefore, we attempted to vary these parameters by means of controlled inflation of the voids. From our results, connections between these parameters and the mechanical and thus also the electromechanical behavior are developed. The observed correlations permit the optimization of the transducer properties of ferroelectric foams.

Cellular PP films are routinely prepared by stretching filler-loaded PP under suitable conditions.⁷ Here, two PP films with thicknesses of (A) 37 and (B) 70 μm and different cell sizes are inflated by means of pressure treatments in order to vary the cell shapes and sizes systematically. Two routes were chosen for the controlled inflation of voids, as shown schematically in Fig. 1.

(1) In the isothermal process I, the external pressure is reduced from the ambient pressure p_0 to a well-controlled

value so that the higher internal gas pressure inside the closed cells leads to their controlled inflation at room temperature. This process can be performed on charged samples *in situ*. It should be noted, however, that the inflation is not permanent when the pressure is again increased to ambient pressure.

(2) In the alternative nonisothermal process II, the external pressure is raised and kept at a certain high value so that the internal pressure inside the cells becomes equal to the externally applied pressure because of gas diffusion through the cell walls. Subsequently, the external pressure is reduced to its original value, and the higher internal pressure again inflates the cells in a controlled manner,⁸ but at a suitable elevated temperature. This inflation procedure leads to a permanent change of sample density. With this process, the samples can be charged only after the treatment.

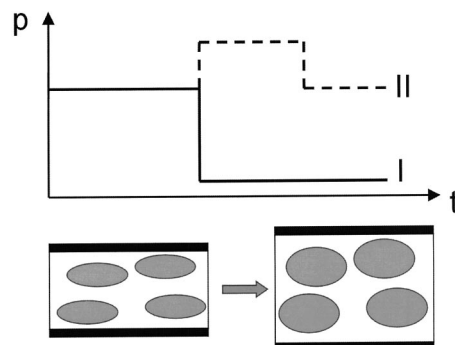


FIG. 1. Two routes for the controlled inflation of voids in cellular polymers. Route II permits an irreversible inflation of the voids that is long-term stable at ambient pressure.

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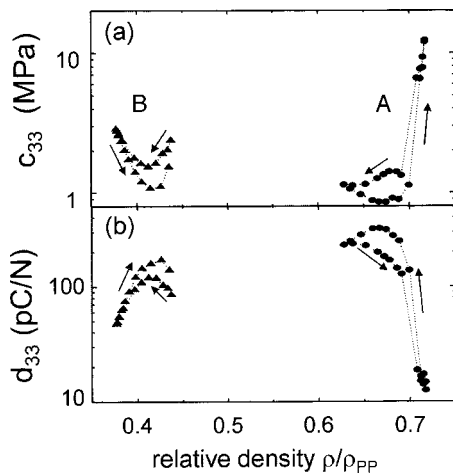


FIG. 2. Elastic modulus c_{33} (a) and electromechanical transducer coefficient d_{33} (b) as calculated from dielectric resonances as functions of the relative density of originally (A) 37- and (B) 70- μm -thick cellular PP films inflated according to scheme I.

Both treatments lead essentially to the same effect (inflation of the cells because of the higher internal pressure), but the biasing external pressure and the sample temperature during inflation are different.

All experiments were done in closed chambers under nitrogen at pressures between 1 kPa and 2.5 MPa. For monitoring the inflation-related property changes, dielectric resonance spectroscopy was employed in the frequency range around the thickness-extension resonance of the respective film.^{9–11} From the frequency-dependent real and imaginary parts of the capacitance $C(\omega)$, the antiresonance frequency f_p , the electromechanical coupling factor k_t , the elastic modulus c_{33} , and the electromechanical transducer coefficient d_{33} follow according to Eqs. (1) to (3) for the thickness-extension mode of a freely vibrating sample:

$$C(\omega) = \frac{\varepsilon_r^S \varepsilon_0 A}{h} \frac{1}{1 - k_t^2 \frac{\tan(\omega/4f_p)}{\omega/4f_p}} - iC_{\text{loss}}, \quad (1)$$

$$f_p = \frac{1}{2h} \sqrt{\frac{c_{33}}{\rho}}, \quad (2)$$

$$k_t^2 = \frac{d_{33}^2 c_{33}}{\varepsilon_r^S \varepsilon_0}. \quad (3)$$

In Eq. (1), the term $-iC_{\text{loss}}$ describes the inherent dielectric loss of the sample. h , A , ρ , ε_r^S and ε_0 are the sample thickness, the electrode area, the density of the polymer, the relative permittivity of the sample under constant strain and the vacuum permittivity, respectively.

In Figures 2, 3, and 4, the abscissae are given in relative densities calculated from the respective film thicknesses before and immediately after the pressure treatment. The film thicknesses were determined with electrical capacitance measurements between the evaporated sample electrodes, with mechanical profilometry of the step at the film edge or with a thickness gauge under constant spring loading.

In order to investigate inflation at reduced external pressures (process I), previously charged cellular PP films were employed. Figure 2(a) shows the elastic modulus c_{33} as a

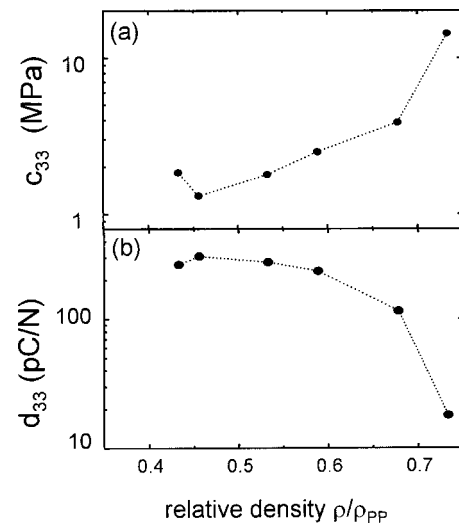


FIG. 3. Elastic modulus (a) and electromechanical transducer coefficient (b) as a function of the relative density of cellular PP films inflated according to scheme II. Note the local minimum and the local maximum in c_{33} and d_{33} , respectively.

function of the relative film density ρ/ρ_{PP} , where ρ and ρ_{PP} are the densities of the foam and of the bulk polymer, respectively. Even though the relative density lies only between 0.37 and 0.43 (for the initially 70- μm -thick film) and between 0.62 and 0.72 (for the 37- μm -thick film), the elastic modulus varies by about one order of magnitude. In contrast to the standard scaling behavior of foams,¹ a minimum elastic modulus around 1.5 MPa is observed at a relative density of 0.41 for the initially 70- μm -thick film. Although a relative density of 0.41 is rather large for a foam, the elastic modulus is by about three orders of magnitude smaller than in bulk PP. The low value is caused by the extreme anisotropy of the voids within the polymer, whereas the local minimum of c_{33} is probably caused by the unavoidable changes of the void shape during inflation. Stronger inflation changes the typically lens-like voids into spherical voids and also enhances the stiffness. Since the electromechanical transducer coefficient d_{33} is inversely proportional to c_{33} ,^{12,13} its density dependence [Fig. 2(b)] is inverted in comparison to that of the elastic modulus [Fig. 2(a)]. Therefore, a local maximum of d_{33} is achieved. The optimum is, however, not permanent (Fig. 2), since the voided film must be brought back to ambient pressure. At ambient pressure, similar values for c_{33} and d_{33} are achieved before and after the inflation cycle. However, it is important to note the hysteresis in the elastical and electromechanical properties during the decrease and increase of the pressure in the chamber.

In order to achieve a lasting optimum of the d_{33} coefficient, an irreversible inflation according to process II must be effected. Figure 3 shows c_{33} and d_{33} as functions of the relative density for foams inflated from 37- μm -thick cellular PP films. Within the applied pressure range from 0.5 to 2.5 MPa, the density varies between 0.73 and 0.43, respectively. The irreversible inflation has been performed at a temperature of 90 °C.¹⁴ Analogously to the results in Fig. 2, a minimum elastic modulus and a maximum transducer coefficient are observed at a relative density of 0.43 [Figs. 3(a) and 3(b)]. The softest cellular PP film with the highest long-lasting dynamic electromechanical transducer coefficient of

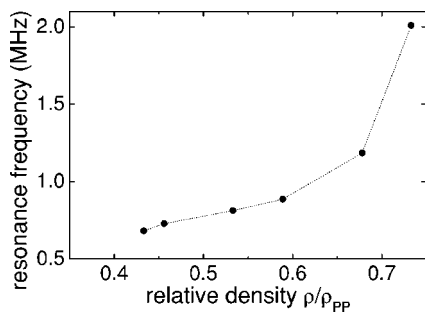


FIG. 4. Thickness-extension resonance frequency as a function of the relative density for differently inflated cellular PP films.

$d_{33} = 306$ pC/N was achieved after inflation at 2 MPa, an improvement by a factor of 2 over earlier findings.¹⁰ However, the maximum electromechanical coefficient of 306 pC/N is lower than the transducer coefficients reported in¹⁴ for similar inflated cellular films. In Ref. 14, the direct transducer coefficient was measured by means of a dynamical method at rather low frequencies, typically a few hertz. The electromechanical transducer coefficient of cellular PP strongly depends on the frequency of mechanical excitation. Higher frequencies of the applied pressure correspond to lower electromechanical transducer coefficients.

In transducer applications, the frequency response and, in particular, the thickness-extension resonance frequency $f_{\text{res}} = (1/2h)\sqrt{c_{33}/\rho}$ of an electromechanical film are essential.^{9,11} An adjustable resonance frequency is advantageous for resonant devices as well as for transducers operated far from resonance.¹⁵ The presented inflation process also enables one to modify the resonance frequency as shown in Fig. 4. Through controlled inflation, the resonance frequency may be shifted by a factor of three from 2 down to 0.6 MHz.

In conclusion, we have shown that the elastic modulus exhibits a local minimum upon increasing inflation of the voids in cellular PP. Furthermore, its value is well below that expected from scaling models. In internally charged PP foams, the local minimum translates into a local maximum

of the electromechanical transducer coefficient d_{33} . A detailed theoretical treatment of the underlying density and anisotropy changes of the voids will probably allow for a quantitative explanation of the observed behavior, and for the prediction of the elastic modulus and the electromechanical transducer coefficient of foams.

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