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Microcellular polypropylene films with good piezoelectric properties

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Microcellular polypropylene films can be used to produce piezoelectric materials with improved properties, capacitance, and stored energy capacity.

Piezoelectricity is associated with the production of electrical charge by applying mechanical force to a material.[1] Piezoelectric materials are of interest in applications such as sensors, actuators, vibration control, energy conversion devices, speakers, microphones, as well as self-powered electromechanical conversion devices in healthcare monitoring systems,[2,3] biological-signal-detecting sensors,[2] and vibration energy harvesters.[4,5] Although several materials have intrinsic piezoelectric properties[1]—quartz and topaz are two examples—we and others have recently developed cellular thermoplastic films to produce 'ferroelectrets.' These are nonpolar materials with low permittivity and low thermal conductivity, but high flexibility. Moreover, because they have a gas-filled cellular structure, their acoustic impedance is closer to that of air than of compact materials, resulting in high charge-storage capacity.[1,6] Ferroelectrets also have greater piezoelectric properties than do classic piezoelectric materials.[6]

Our ferroelectrets are based on cellular polypropylene (PP) films, which in addition to flexibility also offer low material and processing costs and good fatigue resistance.[6,7] We have developed a novel continuous physical foaming process, using supercritical nitrogen (SC-N_2), to obtain thin cellular PP films having deformed (eye-like) cells.[8] Figure 1(a) schematically illustrates this foam extrusion process. It proceeds through several optimization steps: adjusting the temperature profile and N_2 pressure (as blowing agent) to optimize PP foaming; designing a proper extruder screw configuration to improve gas dispersion/saturation in the PP melt; accurately controlling and optimizing the N_2 content; optimizing the speed and temperature of the calendar (i.e., cooling rolls) post-extrusion to achieve a precise, eye-like cellular structure; and adding a nucleating agent (calcium carbonate, $CaCO_3$) and optimizing its concentration to improve cell uniformity.

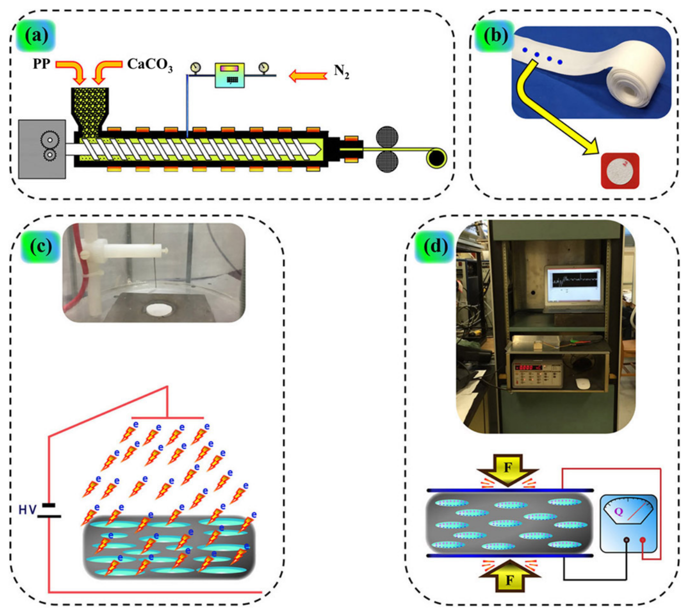

Figure 1. *(a) Schematic representation of the developed foam extrusion process to obtain thin polypropylene (PP) films with an eye-like cellular structure, (b) foamed PP film and sample for charging, (c) corona charging system, and (d) piezoelectric measurement system. $CaCO_3$: Calcium carbonate (nucleating agent). N_2: Nitrogen. HV: High voltage. e: Electron. F: Force. Q: Electrical charge.*

Following optimization, we obtain films having a thickness of around 500μm and density close to 700kg/m^3. Figure 2(a) presents a typical structure for these films. We then obtain the ferroelectret PP samples by electric poling of the gas inside a closed-cell structure, using a corona method. In this procedure, a discharge generator with a needle voltage of −21kV, charging needle distance of 4cm, and charging time of 60s are employed.[9] Figure 1(b) shows the obtained foamed

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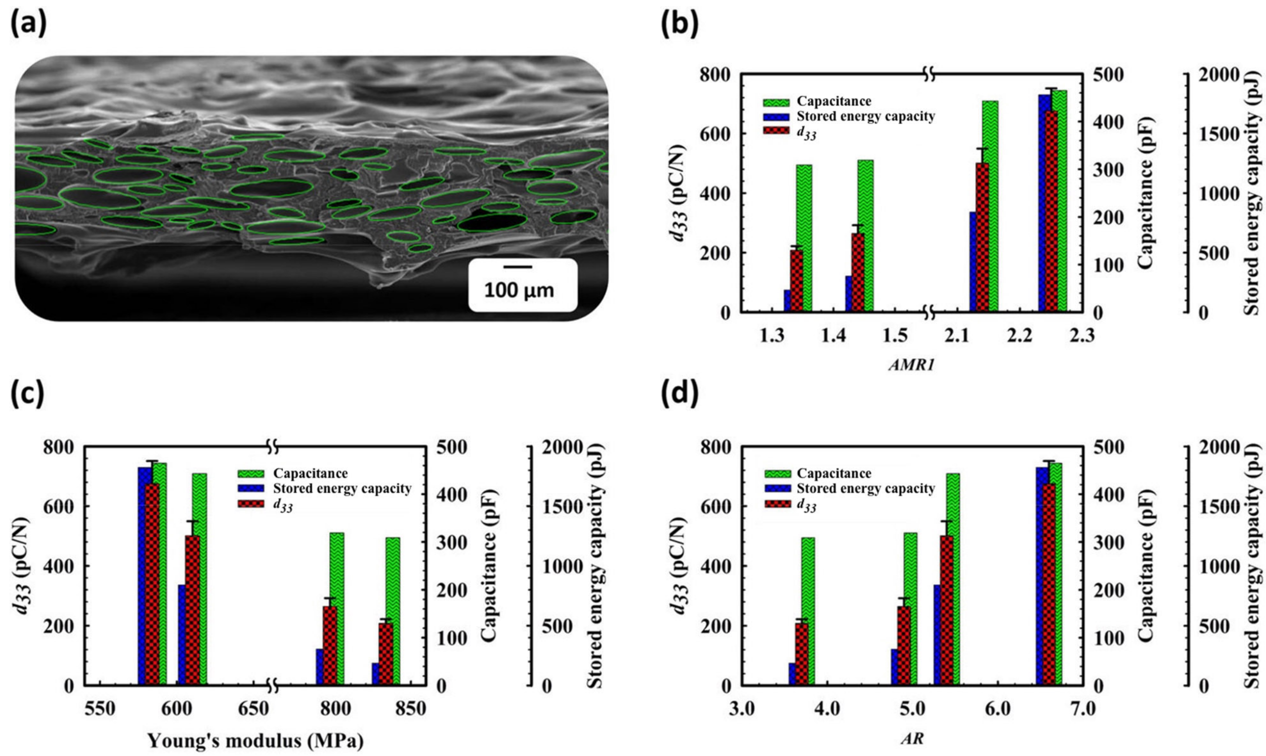

Figure 2. (a) Typical scanning electron microscope image in the machine direction of a PP film having a well-developed eye-like cellular structure, and the piezoelectric d_{33} coefficient, capacitance, and stored energy capacity of the cellular PP films as a function of (b) AMR1, (c) Young's modulus, and (d) AR value. AMR: Anisotropic modulus ratio. AR: Aspect ratio.

PP film and cut sample from the PP film for charging. The corona charging and piezoelectric measurement systems are shown in Figure 1(c) and (d), respectively.

Our previous studies investigated the piezoelectric behavior of different cellular structures in terms of cell aspect ratio (*AR*).[9–11] We also investigated the effect of the ionizing gas inside the cells on the piezoelectric behavior and stored energy capacity of the samples by replacing the air inside the cells by N_2 before charging. The results showed that, for all the samples, the d_{33} (i.e., the coefficient, pC/N, typically used to report the piezoelectric property[12]) was improved. For example, a PP cellular film having $AR = 5.4$ showed a d_{33} increase from 250 to 550pC/N after replacing air with N_2 as the ionizing gas.[9] We have suggested dynamic mechanical analysis (DMA) as a simple and fast characterization of the material's suitability. By measuring the storage (E′) and loss (E″) moduli in the longitudinal (L) and transverse (T) directions, we proposed two new parameters called *AMR* (anisotropic modulus ratio) as $AMR1 = E'(L)/E'(T)$ and $AMR2 = E''(L)/E''(T)$.[9,10]

As shown in Figure 2(b–d), the highest *AMR1* (2.25) is associated with the lowest Young's modulus (584MPa) and the highest *AR* value (6.6), whereas the lowest *AMR1* (1.34) is associated with the highest Young's modulus (833MPa) and the lowest *AR* value (3.7). Moreover, the most elongated cellular structure ($AR = 6.6$), having the highest *AMR1* (2.25), showed the highest d_{33} coefficient (800pC/N), capacitance (465pF), and stored energy capacity (1824pJ). But this sample was the best one obtained from the foaming process.[10] In contrast, the least elongated sample ($AR = 3.7$), which has the lowest *AMR1* (1.34), showed the lowest d_{33} coefficient (220pC/N), and the lowest capacitance (309pF) and stored energy capacity (187pJ). We conclude that the stored energy is much more dependent on the cellular morphology than is the capacitance. Moreover, the foam morphology has a direct effect on the mechanical and piezoelectric properties of the material. Finally, an *AMR1* above 2.0, which is associated with $AR > 5$,
is required to obtain good d_{33} values of about 450pC/N for PP cellular films. Hence, d_{33} prediction using *AMR1* can be a useful and sensitive method that is in agreement with morphological (*AR*) and mechanical (Young's moduli) parameters.

In summary, although we were able to determine some relationships

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between the cell morphology, mechanical properties, and piezoelectric behavior of cellular PP films, the effects of other parameters for further improving the piezoelectric response, such as cell density and ionizing gas, remain to be investigated. In addition, the same production process should be applied to other polymers to obtain ferroelectret materials with comparable piezoelectric properties. As a next step, we plan to improve the general properties of the films and their sensitivity using biaxial stretching and multilayer structures.

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Denis Rodrigue obtained a BSc and PhD in chemical engineering from Université de Sherbrooke (Canada). His research areas are the characterization and modeling of the morphological/mechanical/thermal/rheological properties of polymer foams and composites.

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