Low-Temperature CO$_2$-Assisted Assembly of Cyclic Olefin Copolymer Ferroelectrets of High Piezoelectricity and Thermal Stability

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A novel supercritical carbon dioxide (CO$_2$)-assisted low-temperature assembly approach to fabricate cyclic olefin copolymer (COC) ferroelectrets is reported. The process takes advantage of the strong COC–CO$_2$ interaction and associated severe depression of both bulk and surface glass transition temperature. Using a multilayer structural design to implement a bending mechanism in the ferroelectrets, the apparent compression modulus can be greatly reduced and tailored, leading to COC ferroelectrets with excellent piezoelectric activity. The COC ferroelectrets exhibit excellent thermal stability. The study presents a viable low-cost technology to mass produce COC ferroelectrets with high piezoelectric activity that can be used in structurally and thermally demanding conditions.

1. Introduction

Piezoelectrets or ferroelectrets are space-charged porous polymers with significant piezoelectricity.$^{[1-4]}$ The cellular voids with charges of opposite signs on the upper and lower walls form macroscopic dipoles. The effective dipole moment varies under mechanical stress, which gives rise to the piezoelectricity.$^{[5-7]}$ Compared with their inorganic counterparts, polymer ferroelectrets demonstrate many advantages, such as thinner and lighter weight, more flexible, lower cost, ease of processing, and non-toxicity. To date, the most intensively studied ferroelectrets are based on the cellular polypropylene (PP) films, which exhibit high piezoelectric coefficients of several hundred to thousand pC/N. However, their low operation temperature (normally lower than 60 °C), which results from the poor charge-storage stability of PP at elevated temperatures,$^{[8]}$ restricts their application. Therefore, various strategies were explored to improve the thermal stability of the ferroelectrets. For example, Rychkov et al.$^{[9]}$ showed that by orthophosphoric acid treatment the piezoelectric-coefficient decay curves of the ferroelectrets (polyethylene based) can be shifted to higher temperatures by 40 K. Nonetheless majority of the efforts in this area are development of ferroelectrets from more thermally stable polymers. Several groups of materials with superior insulating and charge-storage properties over PP have been explored, such as fluoropolymer,$^{[10-26]}$ polyethylene terephthalate (PET),$^{[27-29]}$ polyethylene naphthalate (PEN),$^{[30-32]}$ polycarbonate (PC),$^{[33,34]}$ polyetherimide (PEI),$^{[29,34]}$ and cyclo-olefin copolymers (COCs)$^{[35-38]}$.

Currently, the most investigated thermal stable polymer ferroelectrets are mainly based on fluoropolymers. Despite their substantially higher thermal stability than PP, their low mechanical properties and severe creep behavior (continuous deformation under constant force) would constrain their use in many cases. Moreover, most fluoropolymer-based ferroelectrets contain large amount of open porosity, which is detrimental to the long-term electromechanical stability due to the potential charge de-trapping along the surface of the fibrils.$^{[31,12]}$

COCs (Figure 1a) are also promising candidate materials for thermally stable ferroelectrets. They show excellent storage stability of positive surface charges (superior to any known positively charged polymer)$^{[39,40]}$. Their

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potential is further augmented by the low water adsorption, exceptional solvent and environmental stability, low dielectric constant and dielectric losses, and excellent mechanical and thermomechanical properties.\cite{41} However, the progress on COCs ferroelectrets to date has been disappointing. There are only scant studies, achieving $d_{33}$ around only 15 pC/N.\cite{35-38}

In this work, a supercritical carbon dioxide (CO$_2$)-assisted macroscopic assembly approach was used to fabricate COC ferroelectrets with high thermal stability and significant piezoelectricity, with piezoelectric $d_{33}$ coefficient over 1000 pC/N. The fabrication takes advantage of the strong COC–CO$_2$ interactions and associated severe depression of both bulk and surface glass transition temperatures. COC ferroelectrets were successfully assembled at 120 °C (60 °C below the glass transition temperature) with excellent structural fidelity and bonding strength (>1.8 MPa by lap shear measurement). This technology thus overcomes some challenging issues in fabricating ferroelectrets by fusion bonding that is commonly used for the fabrication of high-temperature ferroelectrets such as fluoropolymers ferroelectrets.\cite{10,12-24} As the fusion bonding involves partial melting of the patterned structures, structural deformation is a concern. In addition, the high temperature required for bonding (=230–240 °C for COC 6017 used in the study) presents considerable challenges to process the material while avoiding potential oxidation that is detrimental to the charge-storage stability and increases dielectric losses.\cite{42-44}

2. Results and Discussion

The fabricated ferroelectrets are assemblies of five-layers structures (step 2, Figure 1b), consisting three COC films and two patterned COC films with rectangular arrays that were prepared by laser machining (step 1, Figure 1b). The five-layer film system was assembled via a CO$_2$ bonding (at 120 °C and 10 MPa CO$_2$ pressure) with good bonding strength (1.8 MPa).

During bonding, polymer interfaces undergo interfacial wetting, diffusion, and randomization to forge the bonded interface.\cite{45} Assembly of the ferroelectrets at the aforementioned condition is possible because the fundamental physical processes that govern the polymer bonding are greatly facilitated by CO$_2$, which can dissolve in substantial amount in COCs. This significantly enhances the polymer chain mobility and diffusion, reducing the temperature required for the polymer chain inter-diffusion and development of a bonded interface. In fact, we have calculated the glass transition temperature of the COC–CO$_2$ system (Figure 1c) to guide the selection of bonding conditions. The glass transition temperature profile was calculated by using the Sanchez–Lacombe equation of state (SL-EoS)\cite{46,47} and applying the Gibbs–DiMarzio thermodynamic criterion for glass transition, following the thermodynamic framework developed by Condo et al.\cite{48} The selected bonding temperature is slightly lower than the bulk $T_g$ of the COC–CO$_2$ solution at 10 MPa CO$_2$ pressure, so that the bulk deformation of the predefined structure is prevented since the polymer chain motions are inhibited. On the other hand, the surface
$T_g$ can be substantially lower than that of the bulk $T_g$ and the polymer chains near the surfaces possess significantly higher mobility and diffusivity. Therefore, polymer chains inter-diffusion readily proceeds to enable bonding. Similar principles were used in fabricating micro and nano-scale polymer assemblies.\[50–52\]

Previous modeling of ferroelectrets has yielded the following relationship:\[1\]

\[
d_{33} \propto K \frac{\sigma_{\text{eff}}}{E}
\]

where $d_{33}$ is the piezoelectric activity, $K$ is a structure-related constant, $\sigma_{\text{eff}}$ is the effective polarization in the ferroelectret, and $E$ is the compression modulus. It follows that the piezoelectric $d_{33}$ coefficient is inversely proportional to the compression modulus of the ferroelectrets. To improve the piezoelectric activity, many groups have attempted to reduce the compression modulus by fabricating a porous sandwich structure.\[15–24\] For example, Altafi m et al.\[18–20\] prepared single- and multilayer FEP ferroelectrets with well-controlled open-channel structures using a thermal lamination technique. Similar approach was also adopted to fabricate polyethylene (PE) ferroelectrets and their piezoelectric properties were compared with those of FEP ferroelectrets.\[21\] Zhang et al.\[24\] fabricated fluorocarbon films with regular void structure consisting of compact FEP and patterned polytetrafluoroethylene (PTFE) layer by using a metal mesh and similar fusing bonding process. Their results suggest that it is possible to enhance the resulting piezoelectricity by careful tuning of the porous structures during preparation. Nevertheless they also noted the limited extent of improvement by this approach. While the exact mechanisms deserve further investigation, it is hypothesized that that the limited extent of reduction of the compression modulus in their structure, which is mainly dictated by the overall porosity of the sandwich structure, might be responsible for the observed limitation.\[53\] Here, we achieve the reduction of the overall compression modulus of the ferroelectrets by implementing a bending mechanism in the basic structure, using a multipoint, long, clamped plate configuration in the pattern design (see details in the Experimental Section). While the concept of superimposed offset tubular channels structure has previously been explored for ferroelectrets fabrication,\[19,20\] the current study is, to our knowledge, the first systematic investigation of such configuration and associated bending mechanism in the structure design of ferroelectrets. Figure 2a shows the schematic view of this plate structure. The basic structure or “unite cell” is a long plate with a rectangular strip clamped to two rigid supports. This structure allows the compression of the overall ferroelectrets to be realized by the bending of the “unit cell.” By varying the design parameters of the “unit cell” (e.g., thickness ($h$), width ($w$), and length ($l$)), the compression modulus of

![Figure 2. a) Side view of the schematic showing the multipoint, long, clamped plate structure enabling the bending mechanism, a SEM image showing a typical fabricated structure, and detailed view of the “unit cell” structure in COC ferroelectrets. In the current study, $w_0 = 1$ mm and $h = 0.05$ mm were kept constant. b) Finite element modeling results of the overall deformation in the thickness direction of the COC ferroelectrets with different geometry. A compression load of 10 kPa was applied in the center circular region (diameter 25 mm, indicated by the dotted vertical lines) of the square-shaped ferroelectrets (width 35 mm, indicated by the solid vertical lines). This is the configuration used for the measurement of the quasi-static piezoelectric $d_{33}$ coefficient. Note the broad range of deformation realized by design, and uniformity of the deformation achieved in each design. c) Simulated deformation (in thickness direction) of COC ferroelectrets with different design under a series of pressure showing excellent linear response.](image)
the ferroelectrets can be tailored over a very broad range. Finite element analysis was conducted to verify this. Thus, several assemblies with different structural parameters were subjected to a series of applied compression loads and the deformation in the thickness direction was modeled by using COMSOL software and the results are shown in Figure 2b. A wide range of deformation can be realized by varying \( w \). Furthermore, the deformation is very uniform across the loaded area (Figure 2b), and is proportional with the applied load (Figure 2c), revealing that bending is the dominant deformation mechanism in our study.\(^{[54–56]}\) The effective compression modulus \( E \) for COC ferroelectrets was calculated by using the applied pressure and simulated deformation. They are in the range of 0.3 MPa (\( w = 3 \) mm) to 270 MPa (\( w = 1 \) mm), orders of magnitude lower than the bulk modulus of COC (3 GPa),\(^{[57]}\) demonstrating the effectiveness of this type of structure to reduce the compression modulus for potentially higher piezoelectric activity. It is envisaged that the piezoelectric \( d_{33} \) can be further tailored by the grid design and change of the effective compression modulus of the ferroelectrets.

We thus fabricated a series of ferroelectrets using the same grid design simulated in Figure 2b. Figure 3a shows their piezoelectric coefficient \( d_{33} \). They are in the range of \( 10^2–10^3 \) pC/N, 1–2 orders of magnitude higher than the 15 pC/N previously achieved.\(^{[35–38]}\) For comparison, a ferroelectret without the aforementioned offset structure was fabricated (\( w = 3 \) mm). The bending mechanism is disabled by aligning their respective geometric features (rectangular cavities and ridges) of the two patterned films in the vertical direction. The \( d_{33} \) of this ferroelectret was also measured, as shown in Figure 3a (filled square). The \( d_{33} \) is \( =10 \) pC/N. In comparison, the ferroelectrets with the same geometric design but with bending mechanism enabled (open square, Figure 3a) show \( d_{33} = 1000 \) pC/N over the entire pressure range, a powerful manifestation of the new design.

The piezoelectric coefficient \( d_{33} \) is almost independent of the applied pressure, though for a wide grid (\( w = 3 \) mm) a deviation from linear scaling occurs at higher pressures due to reduced structure stability. Thus, care needs to be taken in balancing the high piezoelectric activity and structure stability in the design of COC ferroelectrets.

Short-term thermal stability of the COC ferroelectrets was examined by measuring the \( d_{33} \) after annealing the samples at a series of temperatures. As shown in Figure 3b, the COC ferroelectrets exhibit excellent thermal stability, with \( d_{33} \) retaining 90% of the initial value even at 120 °C. Decay of \( d_{33} \), due to the thermally stimulated discharge process accelerated at temperatures higher than 120 °C, but is still relatively slow compared with other polymer ferroelectrets. Even when heated to 160 °C, the \( d_{33} \) retains over 35% of the initial value.

Figure 3. a) Quasi-static piezoelectric \( d_{33} \) coefficient of a series of COC ferroelectrets with different designs similar to those in Figure 2b. The red line (15 pC/N) indicates the performance level of the COC ferroelectrets reported in the literature.\(^{[35–38]}\) b) Normalized piezoelectric activity of the COC ferroelectrets as a function of the annealing temperature (short-term test). Measurements were conducted after sample was annealed at designated temperature for 1 h. d) Normalized piezoelectric activity of the COC ferroelectrets as a function of time when annealed at 120 °C (long-term test).
The isothermal decay of the piezoelectric $d_{33}$ coefficients of the COC ferroelectrets were studied at 110 °C (long-term thermal stability test) and are depicted in Figure 3c. The initial decay of the piezoelectric $d_{33}$ coefficients of COC ferroelectrets is probably due to the combined effect of the aging of the material elasticity and a loss of unstable charges in the films.[14] The $d_{33}$ reaches a stable value after 50 h of annealing, and remained essentially constant thereafter. After 200 h at 110 °C, the $d_{33}$ coefficient maintains 70% of the initial value, demonstrating the superiority of the COC ferroelectrets we have developed: high piezoelectric activity with excellent long-term thermal stability.

3. Conclusion

We have developed an innovative technology to fabricate COC ferroelectrets by CO$_2$-assisted assembly of patterned structures from laser machining. Using a multilayer structural design to implement a bending mechanism in the ferroelectrets, the apparent compression modulus can be greatly reduced and tailored, leading to COC ferroelectrets with excellent piezoelectric activity. The COC ferroelectrets exhibit excellent thermal stability. The study presented a viable low-cost technology to mass produce COC ferroelectrets with high piezoelectric activity in both low- and medium-pressure regimes (0.1–20 kPa) that can be used in structurally and thermally demanding conditions. Future research work will focus on better understanding and controlling the structure and charging mechanism in order to optimize the device performance.

4. Experimental Section

4.1. Materials

High-temperature grade COC film (Topas 6017, thickness 50 and 100 μm) was purchased from Topas Advanced Polymers. The polymer has a glass-transition temperature of 180 °C.

4.2. Fabrication of COC Ferroelectrets Film

The COC ferroelectrets consisted of five layers of COC films. The top and bottom layers were COC films with 100 nm-thick aluminum electrodes on one side. Two of the five layers were patterned with rectangle channel arrays generated by machining of the 100 μm-thick COC film using a CO$_2$ laser (VersaLaser, Universal Laser Systems). The two patterned COC films had the same dimensions, that is, the same length and width of the rectangles and the same spacing between the rectangular cavities. However, the two patterns were offset by the width of half of the total width of the cavity and spacing (see Figure 1b and 2a).

The five layers (35 mm × 35 mm) were then stacked in sequence (plain–patterned–plain–patterned–plain) and placed between two stainless-steel plates. The whole assembly was subsequently placed in a pressure reactor (CL-1, High Pressure Equipment Company) and a contact pressure was applied by a weight on the assembly. Carbon dioxide was injected by a high-pressure ISCO syringe pump (500 HP, Teledyne Technologies, Inc.) that also was used to maintain the constant system pressure. The system was maintained at 120 °C and 10 MPa CO$_2$ pressure for 12 h, after which the pressure was released and bonded assembly removed from the reactor. The bonded COC samples were charged at room temperature by the direct-contact charging method in air via a precision high-voltage power supply (PNC 10000–6ump, Heinzinger electronic Gmnh). The applied voltage was 5 kV and the charging time was 10 s. The charged samples were stored between aluminum foil for at least 8 h to allow for completion of fast relaxation processes.

4.3. Characterization

The bonding strength was measured by the lap-shear measurements using a video extensometer system (Shimadzu DV-201) machine in a strain rate of 0.5 mm s$^{-1}$, in accordance with ASTM 3163(01). The specimen dimension was 0.55 mm thick, 12.7 mm wide, and 50 mm long. The overlapped area was 6.4 mm × 12.7 mm. The piezoelectric $d_{33}$ coefficients were determined by means of static method using Keithley electrometer (6517A, Keithley Instruments, Inc.), from the well-known equation: $d_{33} = Q/F$. Care was taken to remove potential artifacts that may be caused by the possible air gap by a preloading of 1 N on the sample surface (contact area) before the measurements.[11] A calibrated force $F$ was first loaded on the sample for sufficient time, and then it was removed. The induced charge, $Q$, was measured and integrated over 10 s. Values averaged from five separate measurements were used for calculation. To investigate the short-term thermal stability, samples were annealed in an oven for 1 h at temperatures between 40 and 160 °C. Their $d_{33}$ were determined after cooling to room temperature. The isothermal decay of the $d_{33}$ coefficient was investigated to determine the long-term thermal stability of the ferroelectrets. Samples were heat-treated at 110 °C for a specific amount of time, and then the samples were cooled to room temperature to measure the $d_{33}$ coefficient.

4.4. Microstructures

Scanning electron microscopy (SEM) images were recorded with a JEOL scanning electron microscope (JEOL 7401F). Samples were fractured in liquid nitrogen and the fracture surface was sputter-coated with a thin layer of gold before observation.

4.5. Finite Element Simulation

A commercial finite element modeling (FEM) package, COMSOL (version 4.3), was used to simulate the deformation (deflection) of the ferroelectrets under a series of load. The model’s geometry parameters were the same as those in the static piezoelectric
measurement setup. A linear elastic stress–strain assumption was made in the simulation.

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