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Large effective piezoelectric response from the spontaneously polarized surface layer in P(VDF-TrFE) arch films

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In this work, we show that a d_{33}~150 pC/N can be obtained in nonpoled poly(vinylidene fluoride trifluoroethylene) (P(VDF-TrFE)) copolymer films with an arch structure. The copolymer films, which are often thought to be homogeneous, are in fact inhomogeneous in microstructure and physical properties after film fabrication. Although a large proportion of the copolymer film is nonpolar, as expected in a nonpoled ferroelectric film, the surface regions of the film are spontaneously polarized. We propose that inhomogeneous stress in the surface regions, which is either from the constraint of the substrate or skin layer effect formed during the film fabrication, generates a flexoelectric response and orients the spontaneous polarization of the ferroelectric film. As a result of the polar surface regions, the nonpoled films exhibit a piezoelectric response. The piezoelectric response is further amplified by the special arch structure of the films, leading to the observed large effective piezoelectric response. This study not only discovers the polar surface effect in ferroelectric polymer films, but also proposes an approach to design polymer materials with a strong piezoelectric response.

Keywords: Ferroelectric films; dielectric polarization; piezoelectricity; surfaces.

1. Introduction

Polyvinylidene fluoride (PVDF)-based polymers have been widely investigated as piezoelectric materials for flexible sensors, actuators and energy harvesting devices.[1–4] Among various PVDF-based polymers, copolymers of vinylidene fluoride and trifluoroethylene (P(VDF-TrFE)) possess the best piezoelectric property.[1–3] Although the piezoelectric property of the copolymers can be improved by optimizing the VDF/TrFE ratio, the property of the polymers is much lower than that of many inorganic piezoelectric ceramics and single crystals.[5] The piezoelectric response of piezoelectric polymers can also be enhanced by designing a special mechanical structure.[6] For example, the P(VDF-TrFE) films with an arch structure exhibit a high effective piezoelectric response ~2000 pC/N, which is enhanced by ~100 times compared with the films without the structure. The enhancement is caused by the stress concentration effect of the special arch structure of the films.[6]

Piezoelectric materials can be designed by exploiting the flexoelectric effect.[7–10] Flexoelectricity is a gradient electromechanical effect in solid dielectrics, by which dielectric polarization is generated by a strain gradient in the materials.[11–14] In the so-called flexoelectric piezoelectric materials

(or metamaterials), at least one component has a special geometry or structure to generate a strain gradient under stress, and a piezoelectric-like response can be generated by the flexoelectric effect.[7–10] A strong apparent piezoelectric response (d_{33} > 4000 pC/N) has been achieved in flexoelectric piezoelectric materials fabricated by ferroelectric ceramics because of the large flexoelectric response of the ceramics.[9] Polymer-based flexoelectric piezoelectric materials have also been studied.[10] Compared with ceramics, polymers are flexible and more mechanically reliable. However, because the flexoelectric effect of polymers is generally weak compared with inorganic materials, the resultant apparent piezoelectric response is low.[15–18] An apparent d_{33} of approximately 11 pC/N was reported in PVDF-based flexoelectric piezoelectric materials in which the flexoelectric response was generated by the bending of PVDF-based polymer circular plates.[10] One favorable feature of flexoelectric piezoelectric materials is that the poling process required to obtain the piezoelectric effect in ferroelectric materials is not necessary.

In this study, a design of a flexoelectric piezoelectric material is presented. We show that after unpoled P(VDF-TrFE) films are molded into an arch shape, a relatively high apparent piezoelectric response (d_{33} > 150 pC/N), which is

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superior to that of poled PVDF-based piezoelectric polymers (typically much smaller than 70 pC/N), can be achieved.[5] We found that the polymer films prepared by the solution casting method, which are often thought to be uniform, are inhomogeneous in microstructure and properties, especially in the regions close to the surfaces. The inhomogeneity may generate a flexoelectric effect, causing a preferred orientation of the crystallites and a piezoelectric response in the nonpoled films. The piezoelectric response is further amplified by the arch structure of the films, resulting in a large apparent piezoelectric response.[6] Because the polarity of the films originates from the flexoelectric effect, the materials can be deemed a new design of flexoelectric piezoelectric materials.

2. Experimental

P(VDF-TrFE) (VDF content of 70 mol% (70/30) and 55 mol% (55/45)) copolymers were purchased from Piezotech Arkema. To prepare the polymer films, P(VDF-TrFE) powders and N, N-dimethylformamide (DMF) were mixed for 24 h. The P(VDF-TrFE) (70/30) solution was dried on a silicon substrate at 90°C and the P(VDF-TrFE) (55/45) solution was dried at 75°C. Some dried polymer films were further annealed at 140°C for 5 h to improve the crystallinity. Plastic molds with a spherical structure of different sizes were fabricated by the three-dimensional (3D) printing method, and the mold is schematically shown in Fig. 1(a). Circular flat P(VDF-TrFE) films with a radius of 5 mm and varying thicknesses (t) were pressed into arch structures with different radii of curvature (R) and arch heights (h) at 60°C for 5 min using molds under a pressure of approximately 150 N/cm^2. After the films were cooled to room temperature without pressure, the arch structure remained. For electrical testing, gold electrodes were applied to the surfaces of the films using an EMS150T sputter coater (Electron Microscopy Sciences, Hatfield, PA, USA). The dielectric property of the materials

was determined using a system consisting of a furnace and an E4980 LCR meter (Agilent Technologies, Santa Clara, CA, USA). The apparent piezoelectric response d_{33} of the films was measured using a quasi-static d_{33} meter (ZJ-6A, Institute of Acoustics, CAS, Beijing, China). The high-temperature piezoelectric response was measured on a system consisting of a quasi-static d_{33} meter (ZJ-3AN, Institute of Acoustics, CAS, Beijing, China), a furnace, and a test fixture in the furnace. The d_{33} of piezoelectric materials is usually measured by clamping the materials between two point probes of a d_{33} meter (the point–point method).[6] In this work, the apparent d_{33} of the nonpoled P(VDF-TrFE) films with an arch structure was measured by clamping the films between two metal hard plates (the plane–plane method). As discussed in our prior study, under compression, the arch film becomes buckled due to its high flexibility (schematically shown in Fig. 1(b)).[6] The stress is concentrated in a certain part of the film, leading to an amplified effective piezoelectric d_{33} relative to the d$_{33}$ measured by the point–point method.

To study the inhomogeneity of the copolymer films, we removed the surface regions of the films step by step using an ion milling machine (EM TIC3X, Leica, Germany). To determine the etching thickness, part of a P(VDF-TrFE) (55/45) film was first coated with aluminum (Al) by the sputtering method, and the thickness of Al was ~100 nm. This part of the film was masked by the Al metal during the etching process. The part without Al was removed by etching. After the film was etched for 10 min, the etched thickness of the film was measured by atomic force microscopy (AFM) (Dimension Icon, Bruker, Germany). Figures 2(a) and 2(b) show the AFM image of the etched film and the depth of the etched part relative to the masked part. From Fig. 2(b), we can see that after 10 min of etching, a thickness of 3.55 μm was removed. If we assume that the etched thickness is proportional to the etching time, the etched thickness can be estimated based on the etching time.

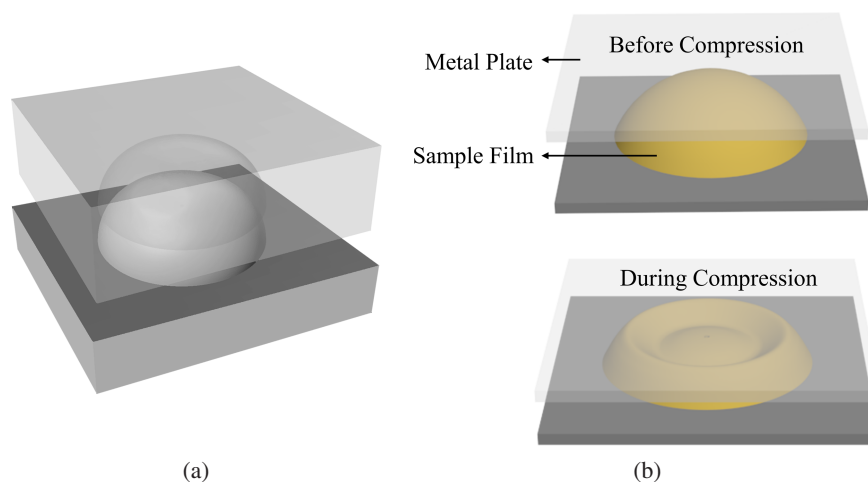(a)   (b)

Fig. 1. (a) Schematic drawing of the mold used to fabricate P(VDF-TrFE) films with an arch structure. The mold is composed of a concave part and a convex part. (b) Schematic of the film with an arch structure before and during the force is applied using two hard plates. The film becomes buckled after compression.
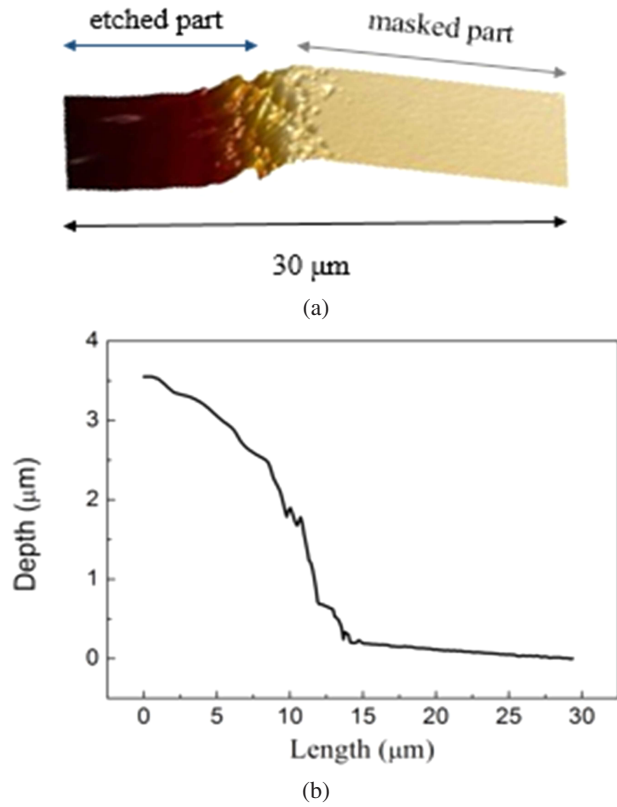
(a)

(b)

Fig. 2. (a) The AFM image of the etched P(VDF-TrFE) (55/45) film. (b) The depth of the etched part of the film relative to the masked part.

3. Results and Discussion

Figure 3(a) shows the apparent d_{33} of P(VDF-TrFE) (70/30) copolymer films with an arch structure measured using the plane–plane method. The radius of the curvature (R) of the arch structure is 10 mm, and the arch height (h) is 1.3 mm. The thickness (t) of the films varies from 10 μm to 73 μm. As shown in Fig. 3(a), the arch films exhibit a strong apparent

piezoelectric response. The highest d_{33} was approximately 25.0 pC/N in the film with a thickness of 14 μm. The apparent d_{33} was strongly dependent on the thicknesses of the films. When the thickness was increased from 23 μm to 73 μm, the apparent d_{33} decreased from 15.6 pC/N to 0.5 pC/N. However, a decrease in the thickness of the film also led to a reduction in d_{33}. The d_{33} of the films with a thickness of 9 μm was approximately 7.8 pC/N. Similar to observations in conventional piezoelectric materials, the piezoelectric-like response of the arch films exhibits a polarity. When the arch films were turned upside down, an apparent d_{33} with almost the same magnitude but an opposite sign was determined (Fig. 3(a)). The d_{33} of the film without an arch structure (flat film) was measured using the plane–plane method and d_{33} was zero (Fig. 3(a)), as expected in an unpoled film. These results suggest that compressed between two hard plates, nonpoled P(VDF-TrFE) films with an arch structure can exhibit a large piezoelectric-like response similar to that of a real piezoelectric material. However, unlike that of conventional piezoelectric materials, the piezoelectric-like response is dependent on the dimensions of the films.

To further evaluate the size effect of the piezoelectric-like response, P(VDF-TrFE) (70/30) films with arch structures were fabricated with $R = 1.9$ mm and varying arch heights ($h = 0.5, 0.7, 0.8$ and 0.9 mm). The arch structure was fabricated into 2×2 arrays. The apparent d_{33} of the films with different arch heights and thicknesses is shown in Fig. 3(b). For $h = 0.5$ mm, a d_{33} of approximately 18 pC/N can be measured at $t = 8$ μm. When h is increased to 0.7 mm, the maximum apparent d_{33} can increase to 23.5 pC/N at $t = 8$ μm. When $h = 0.8$ mm, the maximum d_{33} can be further increased to 28.2 pC/N when t is 13.5 μm. Typically, a larger piezoelectric-like response can be obtained by increasing the arch height if the R value is fixed. However, if h is increased to 0.9 mm, the apparent d_{33} is reduced, and the maximum d_{33} is limited to 12.4 pC/N, which was observed in the films with a thickness of 14 μm. We also fabricated an arch structure with
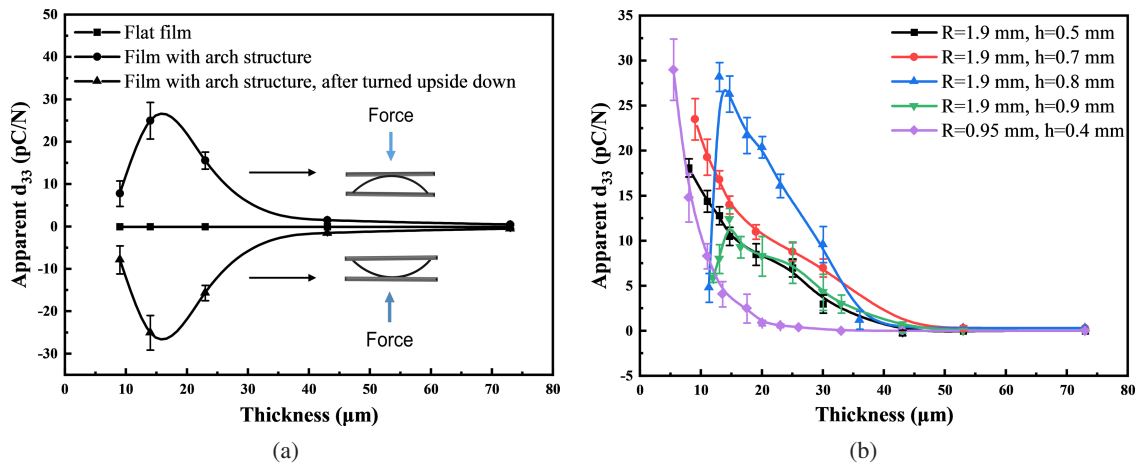

(a)

(b)

Fig. 3. (a) Thickness dependence of the apparent d_{33} of arch and flat P(VDF-TrFE) films ($R = 10$ mm, $h = 1.3$ mm). (b) Thickness dependence of apparent d_{33} responses on arch P(VDF-TrFE) films with different radii of curvature and heights.

$R = 0.95$ mm and $h = 0.4$ mm, and the maximum d_{33} obtained was ~29 pC/N when $t = 5.5$ μm (Fig. 3(b)). The large piezoelectric-like response from the arch P(VDF-TrFE) (70/30) films is comparable to that from poled PVDF-based polymers.[2,5]

To elucidate the origin of the piezoelectric response, we also measured the apparent piezoelectric response of the P(VDF-TrFE) (55/45) arch film ($R = 1.9$ mm, $h = 0.8$ mm, and $t = 13.5$ μm) and the apparent d_{33} at different temperatures is presented in Fig. 4. The curvature and thickness of the P(VDF-TrFE) (55/45) film were chosen according to the results measured in the P(VDF-TrFE) (70/30) film, with which a strong d_{33} was obtained. Strikingly, a much stronger apparent d_{33} of ~150 pC/N, which is higher than the response achievable in the existing piezoelectric polymers, was measured in the nonpoled P(VDF-TrFE) (55/45) arch film.[1,2,5] The d_{33} slightly increases to a maximum value at ~70°C and becomes zero at ~80°C. As a comparison, the d_{33} of the unpoled P(VDF-TrFE) (70/30) arch film at different temperatures is also shown in Fig. 4. The d_{33} of the P(VDF-TrFE) (55/45) arch film is more than three times that measured in the P(VDF-TrFE) (70/30) film below 60°C.

We also measured the piezoelectric response of a flat P(VDF-TrFE) (55/45) copolymer film. Unlike the P(VDF-TrFE) (70/30) copolymer film, a weak piezoelectric response (~2 pC/N) could be measured, as shown in Fig. 4. This implies that P(VDF-TrFE) (55/45) copolymer films are spontaneously polarized during the film fabrication process even though the films are not subjected to an electric field.

Our recent work indicated that the applied stress in poled copolymer films with an arch structure was concentrated in certain parts of the films, leading to an amplification of the piezoelectric response.[6] The amplification ratio can be more
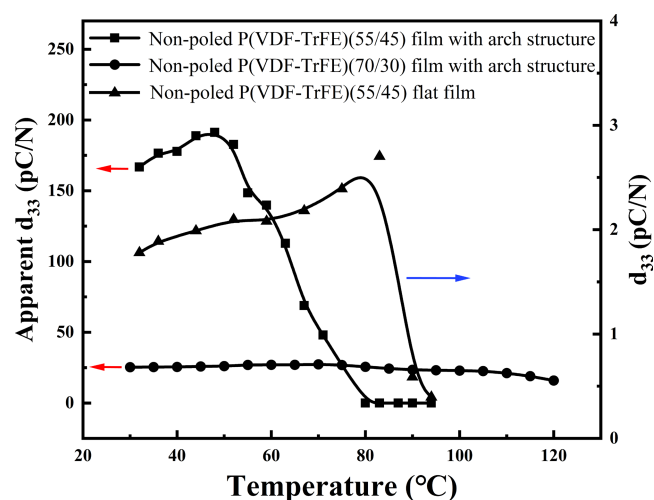

Fig. 4. Temperature dependence of apparent d_{33} of nonpoled P(VDF-TrFE) films with and without arch structure. Note that the scales of Y-axis on the left and right are different. The apparent d_{33} of the arch film was measured by the plane–plane method and the d_{33} of the flat film was measured by the point–point method.

than 80 times. In the nonpoled P(VDF-TrFE) (55/45) arch film, the piezoelectric response generated during the fabrication process can be amplified by the arch structure, which can explain the measured large apparent d_{33}. The same mechanism can also be applied to P(VDF-TrFE) (70/30) arch films. For P(VDF-TrFE) (70/30) films, the apparent d_{33} is much lower than that measured in P(VDF-TrFE) (55/45) film. This means that the piezoelectric response generated in P(VDF-TrFE) (70/30) films during film processing is weaker than that in P(VDF-TrFE) (55/45) films and cannot be accurately measured by the d_{33} meter. Because the effect of the dimensions of the arch films on the effective piezoelectric response has been investigated in the prior study, we will not discuss this issue in this work.[6]

It is interesting to observe a piezoelectric response in the unpoled copolymer films. P(VDF-TrFE) copolymers are semicrystalline polymers, but the polymer films should not possess macroscopic polarity without being subjected to a poling electric field, although each crystallite has a polarity.[1,2] The appearance of macroscopic piezoelectricity implies that the crystallites in the films have a preferred orientation after film fabrication.

Our results further reveal that the copolymer films are inhomogeneous in physical properties and microstructure, and the observed piezoelectric response in unpoled films is a combined effect from different regions of the films. Furthermore, the polarity is mainly from the surface regions of the thin films. The conclusions are supported by the measurement of the piezoelectric response after the two surfaces of a copolymer film are removed step by step. The change in the piezoelectric response with the removed thicknesses from the upper surface (the surface facing air during film fabrication) and the lower surface (the surface grown on the substrate during film fabrication) is shown in Fig. 5(a). The unpoled P(VDF-TrFE) (55/45) copolymer film has a piezoelectric response ~–1.7 pC/N measured by the point–point method. The sign was determined by the d_{33} meter with the upper surface facing upward during the measurement. After a thickness of ~0.9 μm was removed from the upper surface, the piezoelectric response was changed to –0.5 pC/N. The magnitude of the piezoelectric response was further reduced to 0.2 pC/N with a positive sign when a thickness of ~1.75 μm was removed. After that, the piezoelectric response almost did not change if the surface layer was further removed. This result suggests that there exists a surface layer with a negative piezoelectric response close to the upper surface, and its thickness is ~1.75 μm. The rest of the film has a positive but weak piezoelectric response (~0.2 pC/N) after the surface layer is removed. The thickness of the upper surface layer is estimated to be ~1.75 μm (Fig. 5(a)). Based on these results we can estimate the d_{33} of the upper surface assuming that the film can be treated as a composite with a two-layer structure: the upper surface layer and the remaining film (including the middle part and the lower surface layer). The piezoelectric response $\bar{d}_{33}$ of the whole films can be estimated by

$$\bar{d}_{33} = \frac{v_1 \varepsilon_2 \bar{d}_{33}^1 + v_2 \varepsilon_1 \bar{d}_{33}^2}{v_1 \varepsilon_2 + v_2 \varepsilon_1},$$

where v_1 and v_2 are the volume fractions of the upper surface layer and the remaining film; ε_1 and ε_2 are the dielectric constants of the upper surface layer and the remaining film; $\bar{d}_{33}^1$ and $\bar{d}_{33}^2$ are the piezoelectric responses of the upper surface layer and the remaining film. The total thickness of the surface layer is ~15 μm. v_1 can be estimated to be 1.75/15, and v_2 is $1 - v_1$. We assume $\varepsilon_1 = \varepsilon_2$ and substitute $\bar{d}_{33} = -1.7$ pC/N and $\bar{d}_{33}^2 = 0.2$ pC/N into the above equation. The obtained piezoelectric response $\bar{d}_{33}^1$ of the upper surface layer is ~ -16 pC/N. This result suggests that the upper surface layer is almost fully polarized after the film fabrication process.[1,2]

If we remove the lower part of the films layer by layer, as shown in Fig. 5(a), the piezoelectric response exhibits a different variation trend with the removed thicknesses. After one layer of ~0.9 μm was removed from the lower surface, the piezoelectric response sharply changed from the original -1.7 pC/N to $+0.4$ pC/N. It should be noted that the piezoelectric response after one layer of ~0.9 μm is removed from the lower surface is larger than that measured after the upper surface layer is completely removed (~$+0.2$ pC/N). This result implies that there must be a layer with a negative piezoelectric response adjacent to the lower surface. The thickness of this layer is thinner than 0.9 μm. After this surface layer is removed, the middle part of the films has a positive piezoelectric response larger than the total response from the middle part and lower surface layer. Due to the relatively large positive piezoelectric response from the middle part of the films, after the lower surface is removed and the negative

piezoelectric response from the upper surface layer is neutralized, a positive piezoelectric response can still be measured, as we observed experimentally. If the film was further etched from the lower surface, the piezoelectric response was reduced, and the sign of the response was changed. When a thickness of ~3.5 μm is removed from the lower surface, a piezoelectric response of ~-0.8 pC/N is obtained and the negative response is mainly from the upper surface layer. From these results, it can be concluded that the piezoelectric response in the middle part of the films is also nonuniform. The region close to the lower surface has a stronger positive piezoelectric response, and the response diminishes away from the lower surface. When the removed thickness is larger than ~2.6 μm, the piezoelectric response from the middle part cannot offset the negative response from the upper surface layer, resulting in a negative piezoelectric response. From Fig. 5(a), we can also see that, after a layer of ~3.5 μm is removed from both surfaces, the piezoelectric response from the remaining film is ~0 pC/N. Therefore, the large proportion of the middle part of the film (total thickness ~15 μm) is nonpolar.

From the above analysis, we can see that although the unpoled P(VDF-TrFE) (55/45) copolymer films exhibit an overall negative piezoelectric response, the piezoelectric response is not uniform throughout the films. The distribution of the piezoelectric response in the films is schematically illustrated in Fig. 5(b). There are two surface layers with a negative piezoelectric response. The thickness of the surface layer adjacent to the upper surface is in the range of 0.9–1.8 μm. The thickness of the lower surface layer is much thinner (< 0.9 μm). The inner part of the thin films has a
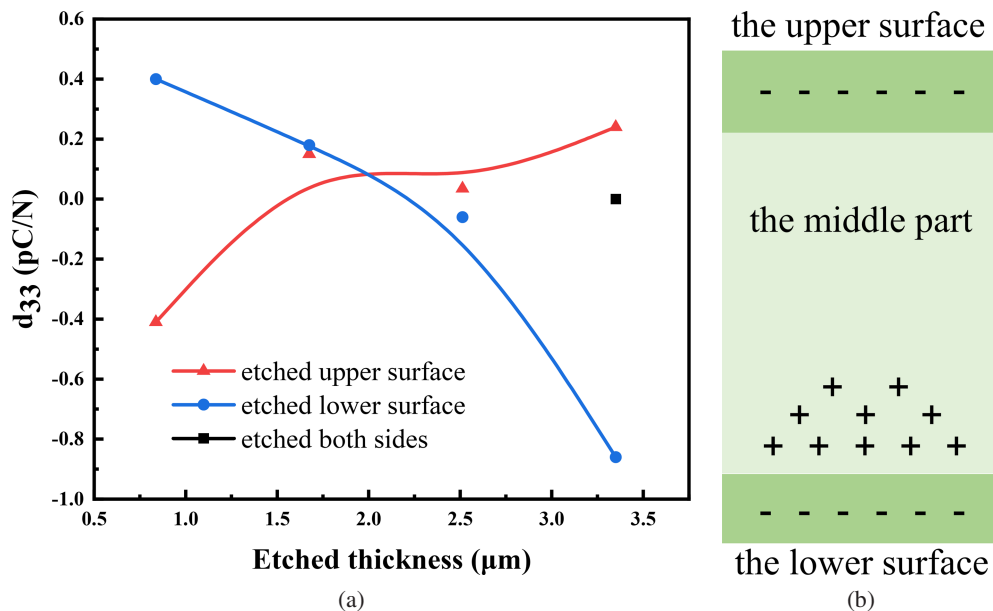

Fig. 5. The inhomogeneous piezoelectric response in P(VDF-TrFE) (55/45) copolymer film. (a) Change of the piezoelectric response after the surface layers are removed step by step. (b) A schematic of the distribution of the local piezoelectric response in the film. The plus and minus signs indicate the polarity of different regions. d_{33} was measured by the point–point method.

positive response, but the response is mainly concentrated in the region close to the lower surface layer. The large proportion of the middle part of the films is nearly nonpolar, as expected in an unpoled ferroelectric material.

The piezoelectric response of ferroelectric materials is often obtained by applying an electric field (the poling process). The polymer films investigated in this work were not subjected to an electric field, and there must be other mechanisms causing the observed locally polarized regions. One possible mechanism is the flexoelectric effect. Studies have shown that the flexoelectric effect, either from the internal inhomogeneity in a material or from externally applied inhomogeneous stress, is equivalent to an electric field.[19,20] The field can orient the polarization of ferroelectric materials. This orientation effect from flexoelectricity is more remarkable on a smaller scale because the strain gradient becomes more intense by reducing the dimensions of the materials. From the discussion of Figs. 5(a) and 5(b), we can see that the local polarity of the thin films is limited to a thickness of several μm. If there is inhomogeneous residual strain in the thin films, the strain gradient (defined by inhomogeneous strain/thickness) could be strong because of the thin thickness, and the resulting flexoelectric response may be strong enough to polarize the film locally.

It is difficult to directly measure the distribution of local strain or stress in the copolymers. However, we indeed observed the existence of an inhomogeneous microstructure in the copolymer films. Figure 6 shows the surface and cross-sectional SEM images of a P(VDF-TrFE) (55/45) copolymer film. As shown in Fig. 6(a), compared with the region close to the lower surface, the middle and upper parts of the film exhibit a looser microstructure. The difference in microstructure between the lower and upper parts of the thin film can be more clearly observed in Figs. 6(b)–6(d), in which the SEM images with a higher magnification are shown. In Figs. 6(e) and 6(f), the SEM images from the upper and lower surfaces are shown. The crystalline phase of the copolymer films has a feather-like microstructure. It is obvious that the crystallites on the upper surface are larger than those on the lower surface. These results indicate that the copolymer film has an inhomogeneous microstructure. The inhomogeneity could be one source of the inhomogeneous stress in the films, leading to the flexoelectric field required for the poling of the copolymer.

The fabrication of polymer films by drying polymer solutions involves complex physical processes such as solvent evaporation, solvent diffusion and solidification.[21] There are different mechanisms causing inhomogeneity in polymer films, which often results in residual stress in the films. The constraint from substrates on which polymer films are fabricated is an important origin of the residual stress in the film.[22] The stress can be relaxed when the thickness is thicker
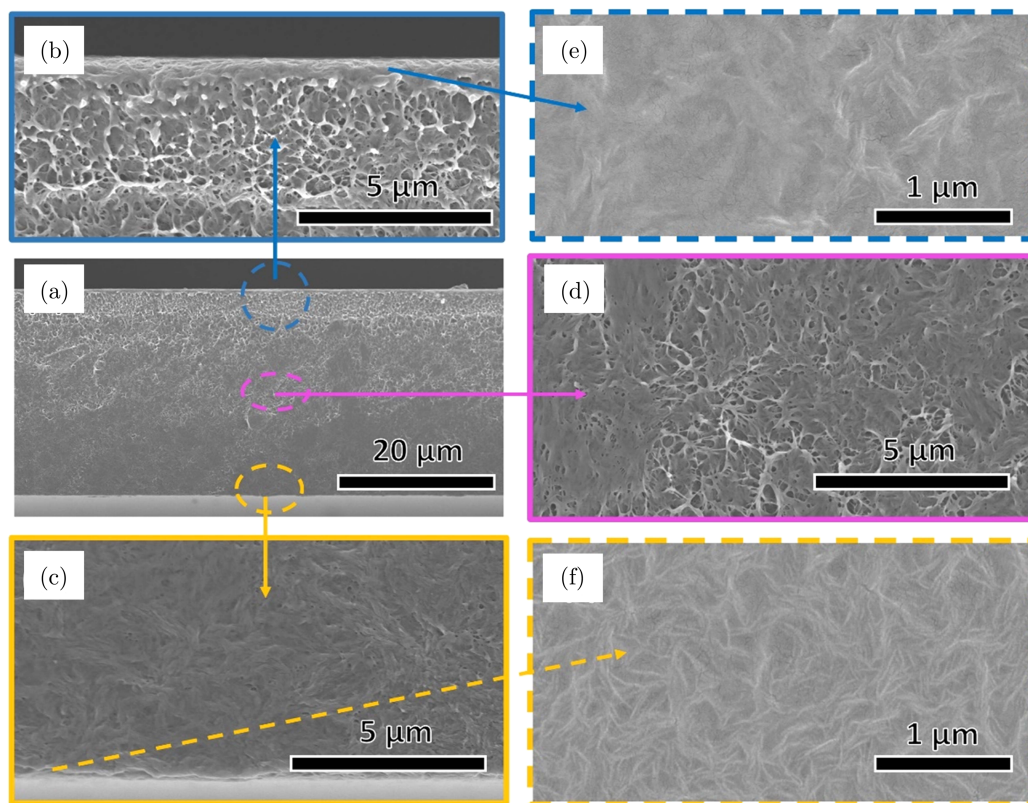

Fig. 6.   The SEM images of P(VDF-TrFE) (55/45) copolymer films. (a) The cross-sectional image from the whole film. (b)–(d) The cross-sectional images from the regions indicated in (a). (e), (f) The surface images from the upper and lower surfaces.

than a threshold thickness, generating a strain gradient. The polarity measured in the lower part of the copolymer films may be related to the constraint from the substrate. However, we observe a negative piezoelectric response adjacent to the lower surface and a positive response in a much thicker region above the region with a negative response. One possible reason for the two regions with the piezoelectric response of opposite signs is the complex distribution of the inhomogeneous residual stress, which generates a strain gradient of different signs. Another possibility is that the negative polarity close to the lower surface is caused by the orientation effect of the substrate.[23] Considering that positive polarity exists in a wider region, the polarity may be caused by the strain gradient from the relaxation of the constraint of the substrate.

Regarding the upper surface region, studies have shown that a skin layer can be formed during the evaporation of the solvent in the polymer solution and the internal stress in the skin layer is sometimes large enough to cause the cracking of the films.[21] Considering that the negative piezoelectric response measured in the region close to the upper region is limited to a thickness less than 2 μm, we propose that the negative piezoelectric response may originate from the skin layer formed during the drying of the films. The stress in the skin layer could be inhomogeneous and the upper region of the films was polarized by the flexoelectric effect caused by the stress.

Drying can cause a relatively large strain in the surface region of polymers, and in the extreme case, the surface layer cracks, indicating that the strain level can be more than several percent. If we assume that the strain in the surface layer in our study is ~1%, the relaxation of the strain in the upper surface layer may lead to a strain gradient on the order of 10^4 1/m (the thickness of the surface layer is in the range of 1–2 μm). Similarly, for the lower surface, the thermal expansion of the Si substrate is lower than 5×10^{-6}/K and that of the PVDF-based polymer is larger than 100×10^{-6}/K. The difference in thermal expansion between the two materials is ~10^{-4}/K.

This means that even when the temperature is reduced by 1 K, the difference in the strain between the substrate and the polymer is ~0.01. Because the thickness of the lower surface layer is < 1 μm, the strain gradient should be much larger than 10^4 1/m. The flexoelectric coefficient of the PVDF-based copolymers is several nC/m.[18] For P(VDF-TrFE) (55/45), which has a large effective piezoelectric response, the dielectric constant close to the Curie temperature is ~70 (Fig. 7(a)), and the equivalent electric field caused by the flexoelectric effect can be estimated to be 2×10^4 V/m. Because P(VDF-TrFE) (55/45) films were dried at 75°C, and the temperature is higher than the Curie temperature (~73°C) of the copolymer, as shown in Fig. 7(a), a small field may polarize the films even though the field is much lower than the coercive field of the polymers at room temperature (Fig. 7(b)). For the P(VDF-TrFE) (70/30) copolymer, because the drying temperature (~90°C) is below the Curie temperature (~108°C), as shown Fig. 7(a), the field may not be enough to fully polarize the surface layer. As a result, the copolymer exhibits a much lower effective piezoelectric response (Fig. 4).

This study has important implications for understanding the physical properties of ferroelectric polymer films. Thick ferroelectric polymer films are often treated as homogeneous materials. However, our results reveal that the polymer films are inhomogeneous in both microstructure and physical properties. The stress field is an important factor affecting the properties of ferroelectrics and there are various sources of stress in ferroelectric materials.[24,25] The effect of constraint from the substrate on the physical properties of ferroelectric films has been frequently investigated, but the complex consequence of the constraint has not been fully understood. Our results indicate that near the interface constrained by the substrate, at least two regions with opposite polarities exist, implying the complexity of the stress field near the interface. What is more interesting is that we observe a polarized upper surface layer, which may originate from the skin layer produced during the drying of the films. Furthermore, the
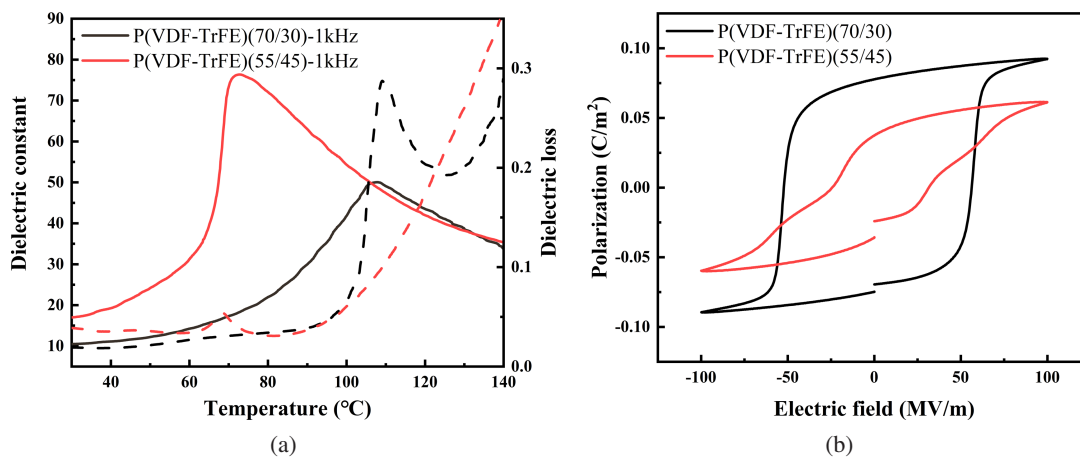

Fig. 7.   (a) The temperature dependence of the dielectric properties of P(VDF-TrFE) (55/45 and 70/30) copolymers. (b) The P–E loops of P(VDF-TrFE) (70/30) copolymer and P(VDF-TrFE) (55/45) copolymer at room temperature.

flexoelectricity of ferroelectric polymers has attracted considerable interest in recent years.[15,18] Because of the existence of an inhomogeneous piezoelectric response in polymers, the piezoelectric response may generate a flexoelectric-like response and contribute to the measured flexoelectric coefficient. Therefore, caution should be taken to explain the experimental data of the flexoelectric measurement.

4. Conclusions

In summary, we found that unpoled P(VDF-TrFE) copolymer films with an arch structure exhibit a strong apparent piezoelectric response. The highest piezoelectric response is larger than 150 pC/N, which is superior to the piezoelectric property reported in piezoelectric polymers, and materials with an arch structure are promising for sensor applications. We show that there exists a polarity in the unpoled copolymer films and the piezoelectric response is amplified by the special arch structure of the films, leading to the observed large apparent piezoelectric response. We also found that the films are inhomogeneous in microstructure and physical properties. The films can be divided into at least four regions with different local polarities. We propose that the local polarity in the films originates from the flexoelectric effect, which is caused by the inhomogeneous strain or stress due to the constraint of the films by the substrate or the formation of a skin layer during the film drying process.

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