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Shashi Poddar

University of Nebraska-Lincoln, shashi.poddar@huskers.unl.edu

Stephen Ducharme

University of Nebraska-Lincoln, sducharme1@unl.edu

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Temperature dependence of flexoelectric response in ferroelectric and relaxor polymer thin films

Shashi Poddar^{a)} and Stephen Ducharme^{b)}

Department of Physics and Astronomy and the Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588-0299, USA

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We report the temperature dependence of the flexoelectric response in thin films of both ferroelectric and relaxor forms of vinylidene fluoride polymers. The ferroelectric samples were depoled to minimize piezoelectric response by heating them beyond their Curie temperature and then cooling in zero applied electric field. In both the relaxor ferroelectric polymer and the paraelectric state of the ferroelectric copolymer, the flexoelectric coefficient was proportional to the dielectric constant over a limited range of temperatures, in agreement with general theoretical principles. The enhancements in flexoelectric response were also observed near the Curie transition temperature for the ferroelectric polymer and near the dielectric relaxation temperature for the relaxors. The broad dielectric anomaly in these systems provides greater temperature stability for these enhancements.

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I. INTRODUCTION

The flexoelectric effect yields a change in electrical polarization proportional to an inhomogeneous strain gradient, and as such, is a more general phenomenon than the linear change in polarization due to stress, the piezoelectric effect, which requires a non-centrosymmetric crystal structure.^{1–4} The inhomogeneous strain gradient becomes appreciable at the nanoscale and behaves as an applied electric field, capable of poling,⁵ switching,⁶ and rotation of polarization.⁷ Thus, fundamentally, the flexoelectric effect can produce similar effects to the piezoelectric effect. The flexoelectric response is of practical interest, because it lifts the symmetry restrictions that limit piezoelectric response, and therefore can be found in crystalline and amorphous materials alike, allowing much greater flexibility in material and device design.⁸ The theoretical background laid down by Kogan⁹ and Tagantsev^{10,11} supposes the flexoelectric coefficient μ to be proportional to the dielectric constant of the material. The dielectric constant of a ferroelectric material shows a strong temperature dependence near the ferroelectric to paraelectric phase transition temperature as described by the Curie-Weiss law and predicted within the framework of the Landau-Ginzburg-Devonshire theory.¹² The dielectric constants can be 10 000 or higher in ferroelectric oxides near the ferroelectric to paraelectric transition and, therefore, could be exploited for increased flexoelectric efficiency. The dielectric response of relaxor ferroelectrics, on the other hand, shows relatively broad shallow peak.¹³ The predicted scalability of the flexoelectric response with dielectric constant indicates that the flexoelectric effect should also exhibit a strong enhancement near the Curie transition temperature for normal ferroelectric and near the dielectric relaxation temperature regimes for the relaxors. Ma and Cross observed similar flexoelectric enhancements in ceramic relaxor samples and perovskite

ferroelectrics.^{14–21} These enhancements of the flexoelectric effect in finite temperature regimes can be exploited for use in actuation, sensing, and electromechanical energy harvesting.

The ferroelectric polymers belonging to the vinylidene fluoride family have certain advantages over the perovskite ferroelectrics, such as low temperature processing, use of non-toxic elements, and easy integration into flexible electronics.^{22–24} The investigation of flexoelectricity has been mainly focused on inorganic materials and there has been relatively little work reported on soft materials like polymers.^{25–27} In a prior report,²⁸ we described a procedure to determine the true flexoelectric response in ferroelectric polymer thin films by minimizing and correcting for piezoelectric contributions. Most notably, the flexoelectric response in three distinct states—ferroelectric, paraelectric, and relaxor—was compared. Here, we report comprehensive studies of the temperature dependence of the flexoelectric response in all three states, and find that the response is proportional to the dielectric constant over a range of temperatures. The dielectric constants have distinct temperature dependences in the ferroelectric²² and relaxor form of the polymers.²⁹ In ferroelectrics, at temperatures above a transition temperature known as the Curie temperature (T_C), where the spontaneous polarization disappears, the dielectric constant k follows the Curie law $1/(T - T_C)$ dependence on temperature T . For these studies, we chose two ferroelectric copolymer of vinylidene fluoride and trifluoroethylene P(VDF:TrFE), with monomer ratios of 70:30 and 50:50, and a relaxor terpolymer of vinylidene fluoride, trifluoroethylene and chlorotrifluoroethylene P(VDF:TrFE:CFE) in the compositional ratio of 55.8:35:8. The dielectric constant in relaxors yields broad peaks as a function of temperature that is also frequency dependent.^{30,31}

II. METHODS

The samples consisted of thin film capacitors with structure Al/polymer/Al deposited on a glass cantilever, and were

^{a)}shashi.poddar@huskers.unl.edu

^{b)}sducharme1@unl.edu

made as follows. The cantilever substrates were glass microscope cover slides measuring $50\text{ mm} \times 10\text{ mm} \times 0.2\text{ mm}$. The top and bottom electrodes were aluminum stripes 2-mm wide and 25 nm thick deposited by thermal evaporation at right angles to each. The polymers for study were purchased in powder form from Kunshan Hisense Electronics (Shanghai) and used as received. The polymers were dissolved in dimethylsulfoxide and the terpolymer in dimethylformamide, both to concentrations of 0.05% by weight, dispersed on the water surface, compressed to a surface pressure of 5 mN/m, and transferred to the substrate by horizontal Langmuir-Blodgett (LB) deposition. The sinusoidal cantilever oscillation was driven by an offset circular cam arrangement. The details of film fabrication and the principle of cantilever flexing technique are described in greater details in earlier published reports.^{22,28,32} The frequency of cantilever oscillation was 6 Hz and the oscillation amplitude was 1 mm in all the measurements carried out in this report, resulting in a constant strain amplitude $\varepsilon = 2 \times 10^{-4}$ and strain gradient amplitude $\varepsilon' = 1\text{ m}^{-1}$. The current from the sample was measured using a lock-in amplifier (Stanford Research Systems model SR 830) referenced to the cantilever oscillation frequency f , while reflecting a He-Ne laser reflected from the sample onto a quadrant photodetector monitored the relative displacements. The temperature-dependent study was carried out by enclosing the cantilever apparatus in a homemade TeflonTM oven controlled to within $\pm 1^\circ\text{C}$ by a Band-Gauss temperature controller. The cams were machined out of UltemTM blocks. The TeflonTM oven had a small double glass window for allowing the He-Ne laser to transmit with minimal heat loss. The pyroelectric response was measured by the Chynoweth modulation method, where a He-Ne laser–chopper arrangement modulated the sample temperature at 1 kHz and the current was measured by a second SR 830 lock-in amplifier.³³ The sample capacitance was measured using a HP 4192 A LF impedance analyzer with a test signal of 0.1 V at 1 KHz and the temperature was measured with a K-type thermocouple. The film thicknesses used for calculation of the dielectric constant was 1.8 nm per nominal monolayer for the ferroelectric copolymer³⁴ and 4 nm per monolayer for the relaxor terpolymer.³⁵

In the cantilever measurement, the contributions to changes in surface polarization ΔP of the polymer films from both the piezoelectric and the flexoelectric effect is according to the expression²⁸

$$\Delta P = \Delta P_p + \Delta P_f = d\lambda\varepsilon + \mu\varepsilon' = (d\lambda b + \mu)\frac{Y}{L^2}, \quad (1)$$

where the subscripts p and f denote the piezoelectric and flexoelectric contributions, respectively, and λ is the Young's modulus of the polymer. For the cantilever geometry (shown in Fig. 1), the strain ε is along the cantilever axis and the strain gradient ε' is the strain gradient perpendicular to the film and the substrate of thickness $b = 0.2\text{ mm}$ and length $L = 3\text{ cm}$; and μ and d , without subscripts, are the effective values of the flexoelectric and piezoelectric. With the deflection Y , and therefore the strain ε and strain gradient ε' , modulated sinusoidally at frequency f , the amplitude of the induced polarization modulation is $\Delta P = J/(2\pi fA)$, where J is the amplitude of the sample output current.

III. RESULTS AND DISCUSSIONS

A. Relaxor ferroelectric terpolymer

In the case of the relaxor terpolymer P(VDF-TrFE-CFE), the bulky –CFE– groups inhibit long-range polarization correlations to produce the relaxor nature, where the sample polarization is highly nonlinear in applied field, but lacking hysteresis or a piezoelectric response in zero applied field.²⁹ Therefore, the current induced in the terpolymer film on bending the cantilever should be almost entirely flexoelectric in origin. For this study, we found that the relaxor terpolymer films exhibit a small remnant polarization of $0.18 \pm 0.01\ \mu\text{C}/\text{cm}^2$, as measured by the Sawyer-Tower method, a value that is approximately 2% of the spontaneous polarization of a ferroelectric copolymer.^{28,35} The variation of the dielectric constant of the terpolymer with temperature exhibits broad peaks just above the room temperature with the peaks shifting to higher temperature with increased frequency.³⁶ The dielectric constant of the relaxor polymer has a peak at approximately 50°C on heating (Fig. 2(a)) and a peak at approximately 47°C on cooling (Fig. 2(b)) with the heating and cooling rates being $1^\circ\text{C}/\text{min}$. The flexoelectric current was measured concurrently with the sample dielectric constant. In order to test the expected proportionality of the flexoelectric effect to the dielectric constant, the flexoelectric signal was overlaid on the dielectric constant for the same temperature range, as shown in Fig. 2. There is a definite correlation between the dielectric constant and the flexoelectric-induced polarization in the terpolymer. Both the flexoelectric signal and the dielectric constant peak at approximately the same temperature

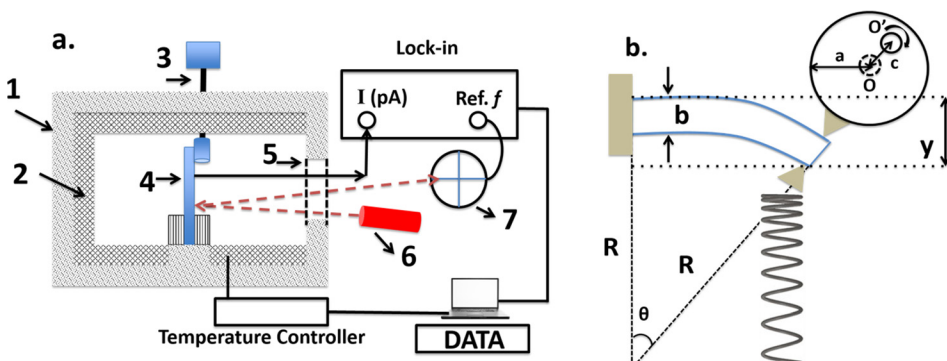


FIG. 1. (a) Experimental set up for the temperature dependent response of flexoelectricity: (1) Teflon enclosure, (2) heater elements, (3) off-center cam on the shaft of a dc motor, (4) cantilever sample, (5) double sided glass window, (6) He-Ne laser, and (7) quadrant photo detector. (b) The geometry of the cantilever oscillation and the cam arrangement.

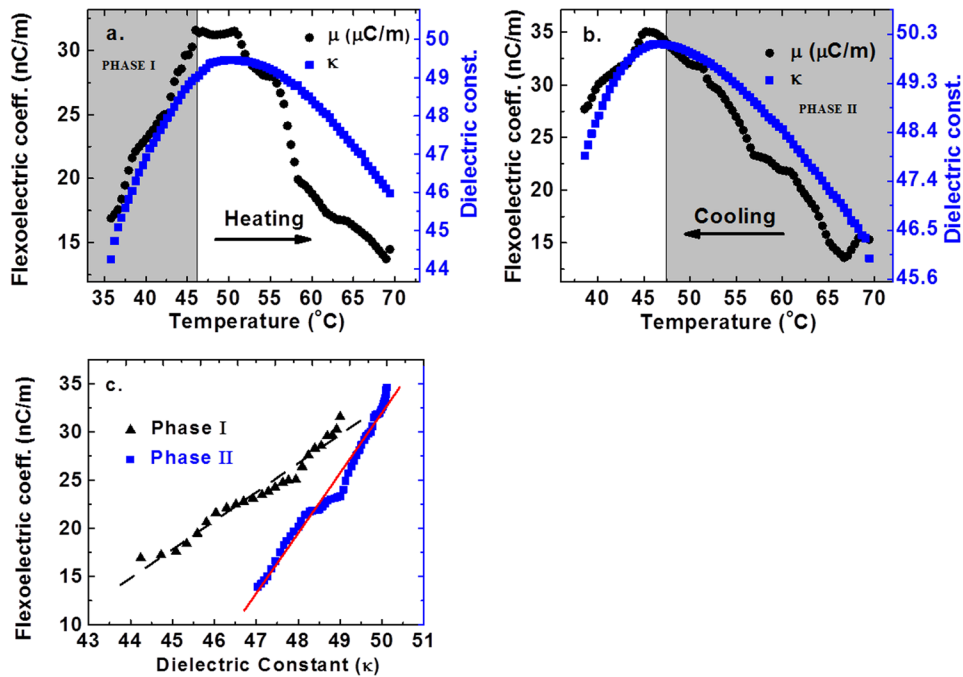


FIG. 2. The variation of the flexoelectric coefficient and dielectric constant with temperature for relaxor terpolymer (a) during the heating cycle from the low temperature Phase I, and (b) during the cooling cycle from the high temperature phase II. (c) The variation of flexoelectric coefficient with dielectric constant for temperature ranges corresponding to Phase I and Phase II. The slopes give the effective flexoelectric coupling coefficient F for each case.

region from 45 °C to 55 °C. In order to further elucidate the correlation, we extracted the value of the flexoelectric coefficient and plotted it against the dielectric constant with temperature as the common parameter. There are two distinct ranges, where the flexoelectric response is proportional to the dielectric constant, as shown in Fig. 2(c), one approaching the dielectric peak on heating and the other one approaching on cooling. These ranges are indicated by the shaded regions in Figs. 2(a) and 2(b). We can explain this behavior in the context of the nanopolar domain model of relaxor behavior.²⁰ In the low temperature state on heating, the relaxor system contains randomly oriented nanopolar domains, which are locally polarized, lacking any intrinsic average polarization. We designate this phase as phase I in this report. In the high temperature state on cooling, there are presumably no nanopolar regions, analogous to the paraelectric state. We designate this phase as phase II. The slope of the graph of the flexoelectric coefficient vs. the dielectric constant (Fig. 2(c)) gives the value of the flexoelectric coupling constant defined as $F = \mu/k\epsilon_0$. The value of the flexoelectric coupling coefficient F was 33.6 ± 1.8 V in Phase I, while for phase II was nearly double 69.8 ± 2.4 V.

B. Ferroelectric copolymer

The flexoelectric response and the pyroelectric response were both measured for as-grown and poled samples of the ferroelectric copolymer, while heating the sample from room temperature to temperatures well above its Curie transition temperature and cooling it back to the room temperature. The heating and the cooling rates were 1 °C/min. The purpose of measuring the pyroelectric current was to monitor the net sample polarization, and consequently the relative piezoelectric response, since both the pyroelectric and piezoelectric responses are proportional to the net polarization.³³ In the ferroelectric case, we studied two compositions of the

P(VDF:TrFE) copolymer, 70:30 and 50:50, which have slightly different transition temperatures.³⁷ Because the P(VDF-TrFE) copolymers exhibit a first-order ferroelectric-paraelectric phase transition, they exhibit thermal hysteresis in the dielectric constant. The transition temperature on heating appears at 110 °C for the 70:30 copolymer and at 90 °C for the 50:50 copolymer, while on cooling the transition temperatures are 75 °C and 63 °C for the 70:30 and 50:50 copolymers, respectively, as shown by dashed-dotted lines in Figs. 3(a) and 3(b). In case of the 70:30 copolymer, the flexoelectric signal was first measured with the samples as grown, and again after poling with +15 V bias for 20 min, as shown in Fig. 3(a). The pyroelectric signal was also measured for the poled samples, as represented by the dashed curves in Fig. 3(a). The sample dielectric constant measured as a function of temperature was overlaid on the flexoelectric curve for as-grown and poled samples, along with the pyroelectric signal, as shown in Fig. 3(a) for 70:30 copolymer composition. Similar curves with overlaid flexoelectric signal for as grown (solid lines) and poled samples (dashed lines), the pyroelectric signal (dotted line) and the sample dielectric constant (dashed-dotted lines) are overlaid for the 50:50 copolymer as shown in Fig. 3(b). The values of the dielectric constant for the LB deposited films are 2–3 times smaller²² than the bulk stretched films for the copolymers^{38,39} at the phase transition temperature and could be attributed to the different intrinsic nanostructures formed as a result of different modes of preparation of the film. Heating the sample well into the paraelectric phase and cooling at zero electric field should leave the sample nearly depolarized. This was verified by a drop in the pyroelectric signal by over 95% for both the compositions after the heating-cooling cycle was complete, as shown in Figs. 3(a) and 3(b). The near elimination of piezoelectric contribution, therefore, makes it possible to focus on the flexoelectric contribution. The normalized flexoelectric response along with the dielectric constant was plotted on cooling until just

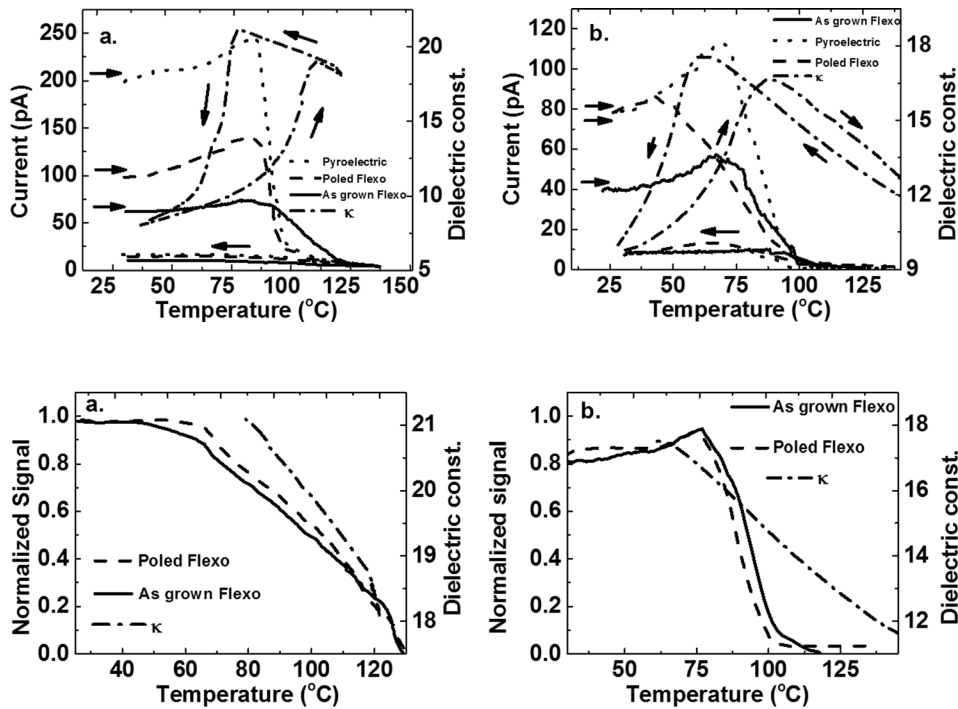


FIG. 3. The variation of the flexoelectric current and dielectric constant with temperature for ferroelectric copolymer for both heating and cooling cycle. The variation of the pyroelectric current for a poled sample as a function of temperature is also shown in the same plots for (a) P(VDF:TrFE) 70:30 and (b) P(VDF:TrFE) 50:50.

below the respective transition temperatures of the two copolymers. In these temperature regimes, the flexoelectric signal was proportional to the dielectric constant as shown in Figs. 4(a) and 4(b). The flexoelectric response thus obtained was graphed vs. the dielectric constant, with temperature as the common parametric variable, as shown in Figs. 5(a) and 5(b). Each graph has two distinct linear regions, as indicated by the arrows, one in the ferroelectric phase, and the other in the paraelectric. For each linear region, the slope of linear least squares fits of the data yields the value of the flexoelectric coupling coefficient F . In the case of the 70:30 copolymer in the paraelectric phase ($115^\circ\text{C} \leq T \leq 125^\circ\text{C}$), the ratio of the flexoelectric coefficient to the dielectric constant gives the flexoelectric coupling coefficient as $F_p = 523 \pm 22 \text{ V}$. The flexoelectric coupling coefficient in the ferroelectric phase ($\leq 95^\circ\text{C}$) of the 70:30 copolymer is $F_f = 1537 \pm 78 \text{ V}$, about three times larger. In the case of the 50:50 copolymer, the values are $F_p = 3.1 \pm 0.5 \text{ V}$ in the paraelectric phase and $F_f = 754 \pm 18 \text{ V}$ in the ferroelectric phase, a much larger change. In both these copolymers, the flexoelectric coefficient shows dramatic enhancements as it approaches the transition temperature regime. The values of the coupling coefficient F

determined by this procedure are in good agreement to the values obtained from direct measurement obtained at fixed temperatures in earlier reports.²⁸ The main source of discrepancy is the fact that the slope method used in the present study excludes the non-ferroelectric contributions to the dielectric constant, whereas the simple ratio of the flexoelectric coefficient μ to the dielectric constant includes both ferroelectric and background contributions, thus underestimating the value of the flexoelectric coupling coefficient. Another important observation is that the ratio $F = \mu/k\epsilon_0$ holds only for a narrow temperature range in a particular phase, and that comparison of the values of F among similar materials, as among ferroelectric polymers, is approximate at best and that quantitative comparison between fundamentally different materials should not be quantitatively meaningful, as with liquid crystals,⁴⁰ polymers, or ferroelectric oxides.

IV. SUMMARY

In conclusion, this study experimentally determines the temperature dependence of the flexoelectric response for two VDF-based copolymers and one terpolymer and demonstrates

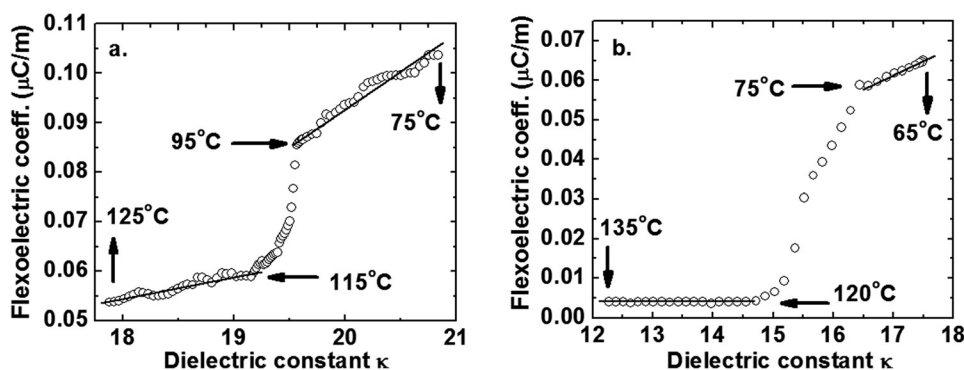


FIG. 5. The flexoelectric coefficient as a function of the dielectric constant as cooled from the paraelectric phase to just below the transition temperature region for (a) P(VDF:TrFE) 70:30 and (b) P(VDF:TrFE) 50:50.

an improved method for determining the flexoelectric coupling coefficient $F = \mu/k\epsilon_0$ for limited temperature ranges above and below the transition temperature. It also underlines the consequent enhancement of the flexoelectric response near the transition in a relaxor, as well as in a ferroelectric, as was previously reported.^{14,15,41,42} The relaxor terpolymer, in principle, has two temperature-dependent phases: a low temperature phase comprising of nanopolar regions (Phase I) and high temperature paraelectric phase (Phase II). The flexoelectric coupling coefficient F for Phase II is twice the value for Phase I. In case of the ferroelectric copolymer, the flexoelectric coefficients exhibit enhancement in the paraelectric phase near the transition temperature T_C . These organic polymer materials have a broader dielectric anomaly than the oxide ferroelectrics and relaxors and therefore exhibit enhanced flexoelectric response over a wider temperature range. Therefore, these materials stand a good chance to be incorporated in future flexoelectric-based devices, where greater temperature stability is expected.

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