

LETTER

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## Apparent piezoelectric response from the bending of non-poled PVDF

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By exploiting the flexoelectric effect, piezoelectric composites, in which none of the individual components is piezoelectric, can be designed. Here, the flexoelectric piezoelectric composite was designed and fabricated using polyvinylidene fluoride (PVDF). Although the flexoelectric response of PVDF is much lower than that of ferroelectric ceramics, which are normally utilized to fabricate the piezoelectric composites because of their high flexoelectric response, a relatively high apparent piezoelectric response ( $>11 \text{ pC N}^{-1}$ ), is obtained in the polymer-based composite because of its low elastic modulus. Our results demonstrate that polymers can be used to fabricate composites with good piezoelectric response and mechanical reliability. © 2019 The Japan Society of Applied Physics

Piezoelectric materials are an important class of functional materials with wide applications in sensors, actuators, transducers and energy harvesting devices.<sup>1,2)</sup> For a material to be piezoelectric, the crystal structure of the material should not have a center of symmetry. When piezoelectric composites are designed, at least one component in the composite is required to be piezoelectric. However, by exploiting the flexoelectric effect, a gradient electrochemical coupling effect in dielectrics, a material can exhibit apparent piezoelectric response even when the material has the center symmetry in its crystal structure or does not have a piezoelectric component if the material is a composite.<sup>3–9)</sup> In the material, at least one component has a special geometric design or structure, which converts the applied mechanical input into a strain gradient to generate a flexoelectric response, and as a result, an apparent piezoelectric response can be measured from the system.<sup>3,4)</sup> The concept of this type of material, which has been called flexoelectric piezoelectric composites or piezoelectric metamaterials, was first proposed by Fusek and Cross in 1999.<sup>3)</sup> Since, unlike piezoelectricity, a flexoelectric response exists in dielectric materials with any structure, the concept of flexoelectric piezoelectric composite allows more material options for the design of piezoelectric systems.<sup>3,10,11)</sup>

The concept of flexoelectric piezoelectric composites or piezoelectric metamaterials with different designs have been realized experimentally.<sup>5–9)</sup> The (Ba,Sr)TiO<sub>3</sub> ceramics with an asymmetric truncated pyramid-like structure (in the dimension of several millimeters) exhibit an apparent piezoelectric response  $d_{33}$  of  $6 \text{ pC N}^{-1}$ .<sup>5)</sup> Another design of composites is based on the bending deformation of rectangular or circular plates, and the composites can have a much higher apparent  $d_{33}$  ( $>1000 \text{ pC N}^{-1}$ ) because a stronger strain gradient can be generated by the bending deformation.<sup>6–9)</sup> In those studies, ferroelectric ceramic disks or plates with rectangular or circular shapes were exclusively used to fabricate the flexoelectric piezoelectric composites or metamaterials. Those materials show promising apparent piezoelectric response because of the high flexoelectric response of ferroelectric ceramics. However, since ceramics are brittle, the mechanical reliability is of concern in many applications of these composites.

Polymers are often flexible, tough, and resistant to catastrophic failure under external mechanical loads. They

can therefore be mechanically more reliable than ceramics. One drawback for polymers is that their flexoelectric response is much weaker than that of ferroelectric ceramics, and polymer-based flexoelectric piezoelectric composites have rarely been studied. In this work, we show that a relatively large apparent piezoelectric response can be achieved in composites fabricated by creating a bicomponent assembly of a non-poled polyvinylidene fluoride (PVDF) ferroelectric polymer disk and a metal ring. PVDF is selected because the polymer is a ferroelectric material and has a relatively large flexoelectric coefficient compared with other polymers. We show that although the flexoelectric coefficient of PVDF is several orders of magnitude lower than those measured in ferroelectric ceramics, the adverse effect of low flexoelectric response can be partially counteracted by the low elastic modulus of polymers, leading to a substantial apparent piezoelectric response in polymer-based flexoelectric piezoelectric composites. Our study suggests that polymers can be used to fabricate flexoelectric piezoelectric composites with substantial piezoelectric response and high mechanical reliability.

PVDF homopolymer plates were purchased directly from GEHR GmbH (Mannheim, Germany). The original thickness of the plates was about 3 mm. The plates were hot-pressed and then ground to different thicknesses in the range of 0.4–0.6 mm. The hot-press was performed at 200 °C for 10 min and, after that, the plates were cooled naturally to room temperature. Following the hot-press process, the plates were cut into a circular shape with a diameter of approximately 30 mm. The circular plates were annealed at 140 °C for 5 h to further increase the crystallinity of the polymer. The crystal structure of the polymer plates was determined by X-ray diffraction (XRD) using a SmartLab TM9kw diffractometer (Rigaku, Tokyo, Japan). Attenuated total reflection Fourier transform infrared spectra (ATR-FTIR) were collected using a Thermo Fisher–Nicolet 6700 instrument (Nicolet, Madison, WI, USA). The mechanical properties were measured by a dynamic mechanical analyzer (DMA 8000, Perkin-Elmer, Waltham, MA, USA).

For the dielectric, piezoelectric, and flexoelectric measurements, gold electrodes were coated on the surfaces of the polymer plates by a sputter coater (EMS150T, Electron Microscopy Sciences, Hatfield, PA, USA). The temperature dependence of the weak-field dielectric properties of the

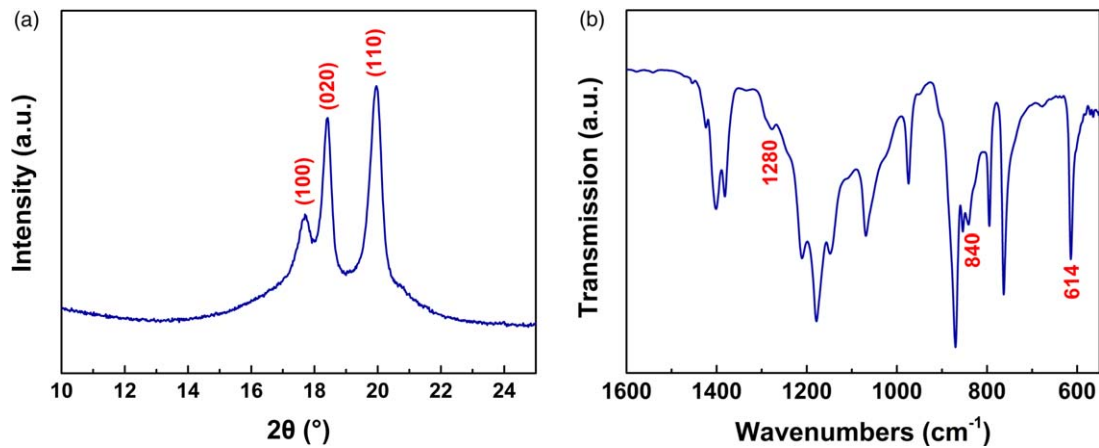


Fig. 1. (Color online) (a) The XRD pattern and (b) The ATR-FTIR spectrum of the PVDF polymer plates.

polymer was measured by a system composed of an E4980 LCR meter (Agilent Technology, Santa Clara, CA, USA) and a furnace. The temperature dependence of the piezoelectric response  $d_{33}$  of the poled PVDF or the apparent  $d_{33}$  of the flexoelectric piezoelectric composites was measured in a system composed of a quasi-static  $d_{33}$  meter (ZJ-3AN, Institute of Acoustics, CAS, Beijing, China) and a furnace.<sup>8)</sup> To measure the apparent  $d_{33}$  of the flexoelectric piezoelectric composites, the one point probe of the  $d_{33}$  meter was modified into a metal ring with a diameter of approximately 20 mm. During the measurement, the PVDF plate was supported by the metal ring and a mechanical vibration was applied to the center of the opposite surface of the plate by a point probe. The PVDF was not subjected to any electric field in this experiment. In this context, it is clear that the term “composite” does not refer to a structure with which it is more commonly associated in the field of polymer composites, where one or more functional constituent material is dispersed in the polymer matrix (which can also be advantageously designed for flexoelectric applications),<sup>12)</sup> but to a bicomponent assembly in which the final properties do not derive simply from the material properties of the base components, but from their combined geometric structure. This is also consistent with the definition of a metamaterial.

PVDF is a semicrystalline polymer and the crystalline phase has at least three polymorphs ( $\alpha$ ,  $\beta$  and  $\gamma$  phases) depending on the processing conditions of the polymer.<sup>13,14)</sup> The crystal structure of the polymer plates used in this study was investigated by XRD and FTIR. Figure 1(a) shows the XRD pattern of the PVDF polymer plates and the three peaks at 17.7°, 18.4° and 19.9° can be assigned to (100), (020) and (011) planes of the  $\alpha$  phase, respectively.<sup>14)</sup> Figure 1(b) shows the FTIR spectrum of the polymer. The peak at 614  $\text{cm}^{-1}$  is assigned to the chain conformation typically observed in  $\alpha$ -phase PVDF (TG $\overline{\text{T}}\text{G}'$  conformation), and it is very strong in the hot-pressed polymer plates.<sup>15–17)</sup> The peaks from  $T_{m>4}$  and  $T_3\text{G}$  chain conformations at 840 and 1279  $\text{cm}^{-1}$ , which are typically observed in PVDF with  $\beta$  phase or  $\gamma$  phase, are weak. The XRD and FTIR results indicate that the crystalline phase of the PVDF plates has a predominantly  $\alpha$  crystal structure.

Figure 2 shows the temperature dependence of the weak-field dielectric properties of the PVDF plates at different frequencies. The polymer exhibits both frequency and

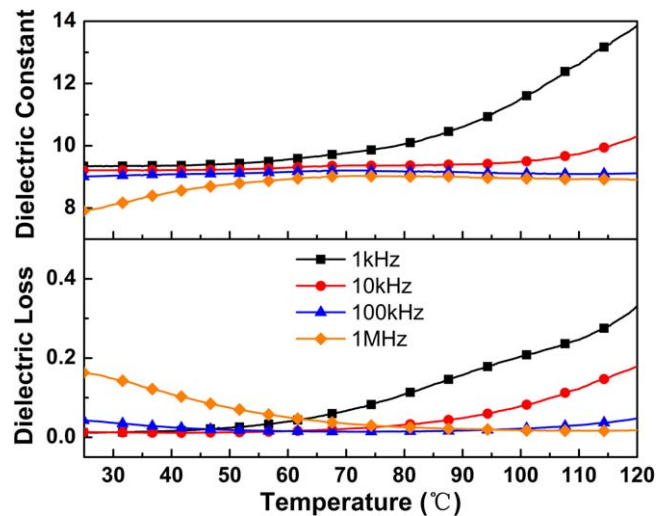


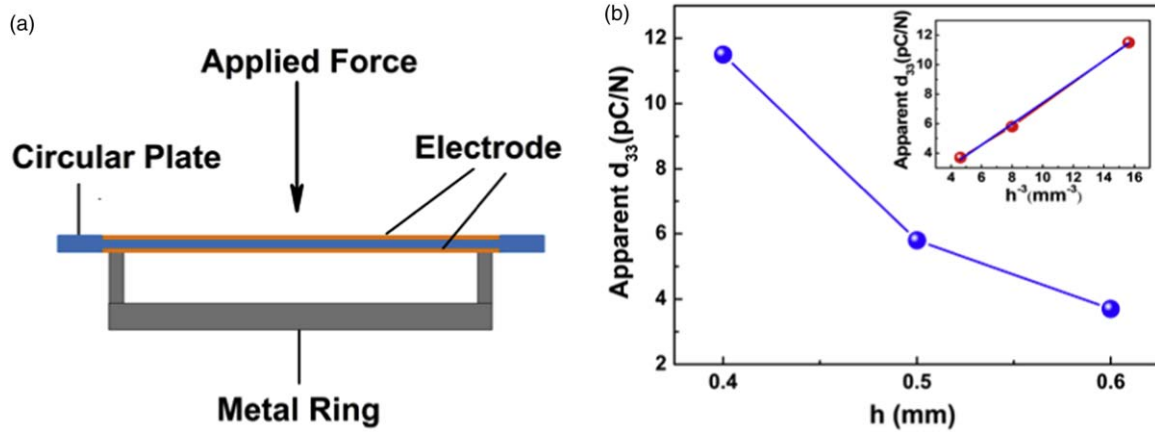
Fig. 2. (Color online) The temperature dependence of dielectric constant and dielectric loss of the PVDF polymer plates under different frequencies.

temperature dependent dielectric properties. At room temperature, the dielectric constant is approximately 9 (at 1 kHz). The dielectric constant almost does not change with temperature before the polymer is heated to around 60 °C. The increase of the dielectric constant above 60 °C can be attributed to a relaxation process related to the molecular motion in the crystalline phase.<sup>17)</sup> Accordingly, above 70 °C, the dielectric loss increases due to the relaxation process.

The polymer-based flexoelectric piezoelectric composite was designed by supporting a circular PVDF plate on a metal ring, as schematically shown in Fig. 3(a). The plate was not fixed on the ring and the radial deformation of the plate was not constrained. Under an applied stress, an apparent piezoelectric response  $d_{33}$  can be generated due to the bending of the plate. The relationship between the apparent  $d_{33}$  and the flexoelectric coefficient  $\mu_\rho$  of the plate can be expressed by:<sup>8)</sup>

$$d_{33} = \frac{3\mu_\rho R^2(1-\nu)^2}{2Eh^3}, \quad (1)$$

where  $R$  is the radius,  $h$  is the thickness of the circular plate,  $E$  is elastic modulus, and  $\nu$  is the Poisson's ratio. From the equation, we can see that the apparent  $d_{33}$  is proportional to  $\mu_\rho$  and inversely proportional to  $E$  of the materials used to fabricate the composites. Although the flexoelectric



**Fig. 3.** (Color online) (a) A schematic plot of the configuration of the PVDF plate and the metal ring for the apparent  $d_{33}$  measurement (b) The apparent  $d_{33}$  of the PVDF circular plates with different thicknesses. The inset shows the linear fitting of the experimental data according to Eq. (1).

coefficient of PVDF ( $\sim$ several  $\text{nC m}^{-1}$ ) is several orders of magnitude lower than that of ferroelectric ceramics (typically  $>1 \mu\text{C m}^{-1}$ ), the elastic modulus of the PVDF ( $<2 \text{ GPa}$ ) is about two orders of magnitude lower than that of ferroelectric ceramics ( $\sim 100 \text{ GPa}$ ).<sup>4,6,18–25</sup> Consequently, a substantial apparent  $d_{33}$  can still be expected in the composites fabricated with the PVDF because of its low elastic modulus. From the above equation, we can see that unlike conventional piezoelectric materials, the apparent  $d_{33}$  can also be adjusted by changing the dimensions (thickness or radius) of materials.

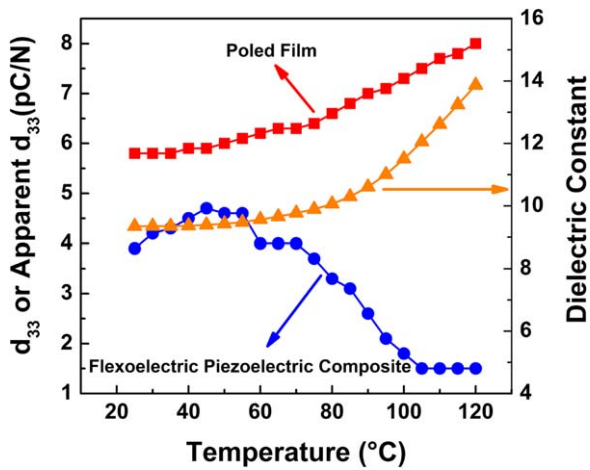
Figure 3(b) shows the apparent  $d_{33}$  measured in the flexoelectric piezoelectric composites fabricated by the PVDF circular plates of different thicknesses (0.4, 0.5 and 0.6 mm) and metal ring assembly, based on the design shown in Fig. 3(a). A  $d_{33}$  of approximately  $3.5 \text{ pC N}^{-1}$  can be measured in the PVDF plates with a thickness of 0.6 mm. When the thickness is reduced to 0.4 mm, the  $d_{33}$  increases to more than  $11 \text{ pC N}^{-1}$ . Although the measured apparent  $d_{33}$  of the PVDF-based flexoelectric piezoelectric composites is typically lower than that of the ferroelectric ceramic-based composites (which can be as high as  $1000 \text{ pC N}^{-1}$ ), the  $d_{33}$  is comparable or even better than that of many conventional piezoelectric polymers.<sup>6–9,14</sup> In the inset of Fig. 3(b), the relationship between  $d_{33}$  and  $h^{-3}$  is shown. Consistent with Eq. (1),  $d_{33}$  is inversely proportional to  $h^3$ . Using Eq. (1), the flexoelectric coefficient  $\mu_{\rho}$  of the PVDF is calculated to be approximately  $5.8 \text{ nC m}^{-1}$ , the order of which is consistent with the measurement results of  $\mu_{\rho}$  in our prior study.<sup>18–20</sup> We also tested the polymer plates with thickness of 0.2 and 0.8 mm. For the plate with 0.8 mm thickness, the apparent  $d_{33}$  is lower than  $2 \text{ pC N}^{-1}$ , which cannot be accurately measured by the  $d_{33}$  meter (the meter can accurately measure a  $d_{33}$  in the range of  $2\text{--}2000 \text{ pC N}^{-1}$ ). For the 0.2 mm thick plate, a larger  $d_{33}$  than that measured in the 0.4 mm thick plate is expected, but the reading of the  $d_{33}$  meter is close to zero. When the  $d_{33}$  is measured by the  $d_{33}$  meter, an alternating force of 0.25 N and a static clamping force are applied to the tested materials. For the 0.2 mm thick plate, after the  $d_{33}$  measurement, a noticeable plastic deformation, caused by the applied static and dynamic forces, was observed. We think the reason that no apparent  $d_{33}$  can be measured in a thin plate is because the applied force is large enough to induce

plastic deformation and the vibration of the plate cannot follow the dynamic force due to this plastic deformation.

The linear fitting of apparent  $d_{33}$  and  $h^{-3}$  [Fig. 3(b)] is consistent with our expectations that the  $d_{33}$  is from the flexoelectric effect of PVDF. However, it is possible that there is some level of polarization in non-poled PVDF materials resulting from the details of the processing history, which may contribute a piezoelectric contribution to the flexoelectric-like response.<sup>21,22</sup> By measuring and comparing the temperature dependent behavior of the apparent  $d_{33}$  of the bent PVDF plates and the piezoelectric response of the poled PVDF, we are able to exclude the piezoelectric contribution as a significant mechanism for the measured apparent  $d_{33}$  of the bent plates. The temperature dependence of the apparent  $d_{33}$  of PVDF-based flexoelectric piezoelectric composites (with plate thickness of 0.6 mm) is shown in Fig. 4. The  $d_{33}$  increases slightly with temperature below  $50 \text{ }^{\circ}\text{C}$ ; above  $50 \text{ }^{\circ}\text{C}$ , the  $d_{33}$  decreases. As a comparison, the temperature dependence of the piezoelectric response  $d_{33}$  of PVDF film which was poled at  $150 \text{ MV m}^{-1}$ , is also shown in Fig. 4. From the figure, we can see that the apparent  $d_{33}$  of the flexoelectric piezoelectric composite exhibits a different temperature dependent behavior from that of the poled PVDF, indicating the different microscopic mechanisms for the measured piezoelectric response between the two types of materials. In Fig. 4, the temperature dependence of the dielectric constant (at 1 kHz) of PVDF is also shown. The  $d_{33}$  of the poled PVDF and the dielectric constant of the polymer exhibit a similar temperature dependence. This is understandable because the piezoelectric response of the poled PVDF originates from the spontaneous polarization  $P_s$ , and the piezoelectric coefficient  $d_{33}$  correlates with the dielectric properties via the following equation:<sup>26)</sup>

$$d_{33} = 2\varepsilon_0\varepsilon_3 Q_{33} P_s, \quad (2)$$

where  $\varepsilon_0$  and  $\varepsilon_3$  are the vacuum dielectric constant and the relative dielectric constant of PVDF, and  $Q_{33}$  is the electrostrictive coefficient. Because the parameters  $Q_{33}$  and  $P_s$  are normally less temperature dependent, it is not surprising that  $d_{33}$  exhibits a similar temperature dependent behavior to that of the dielectric constant. It should be pointed out that the absolute values of  $d_{33}$  were reported in Fig. 4 (also other plots). For poled PVDF film, it is known that the  $d_{33}$  is



**Fig. 4.** (Color online) The temperature dependence of the apparent  $d_{33}$  of the PVDF-based flexoelectric piezoelectric composite and the piezoelectric response  $d_{33}$  of poled PVDF polymer film. In the figure, the temperature dependence of the dielectric constant (at 1 kHz) of the PVDF polymer plates was also shown for comparison.

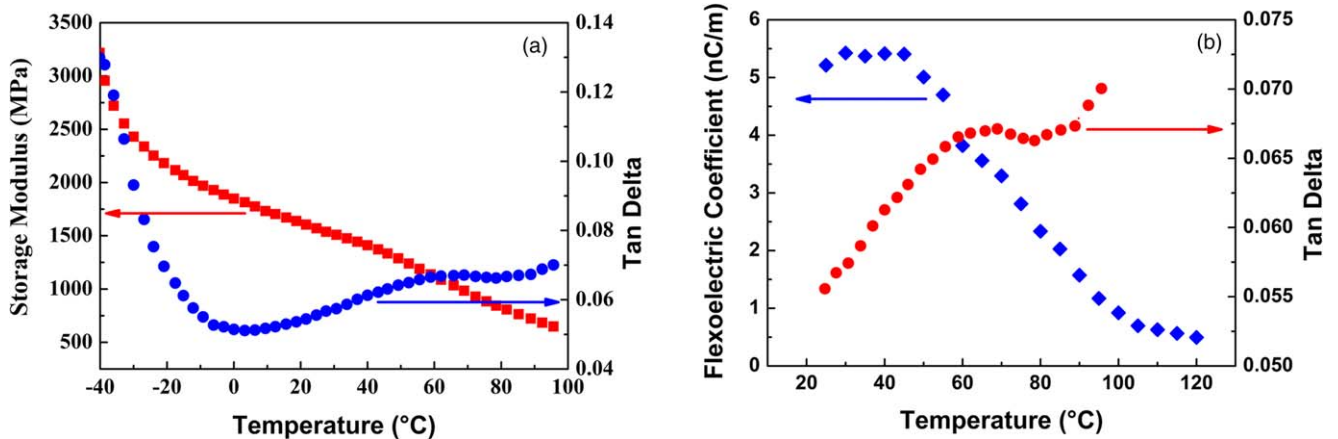
negative (relative to the poling direction).<sup>27,28)</sup> However, for the flexoelectric piezoelectric composites, the PVDF plates were not poled, and the sign of the apparent  $d_{33}$  cannot be defined in the same way as that of poled PVDF. The sign for the composites is related to the bending deformation of the plate. With the configuration of the bicomponent assembly shown in Fig. 3(a), the sign of the reading was positive when the composite was measured using a  $d_{33}$  meter. After the whole assembly was flipped over, the sign became negative, as expected.

For the flexoelectric piezoelectric composites, using the measured  $d_{33}$  and the temperature dependence of the mechanical properties of PVDF, which is shown in Fig. 5(a), the flexoelectric coefficient  $\mu_p$  of PVDF at different temperatures can be calculated by Eq. (1). The temperature dependence of the  $\mu_p$  of PVDF is shown in Fig. 5(b). For ionic crystals, it was proposed that the flexoelectric coefficient is proportional to the dielectric susceptibility (approximately equal to the dielectric constant for ferroelectrics) of the materials.<sup>29)</sup> As shown by comparing Figs. 2 and 5(b),  $\mu_p$  exhibits a different temperature dependent behavior from the dielectric constant

of PVDF when the temperature exceeds about 55 °C, and it is evident that the flexoelectric coefficient of PVDF is not proportional to the dielectric constant of the polymer in that temperature region.

The  $\mu_p$  of PVDF exhibits a weak, or negligible, temperature dependence below 50 °C and starts to decrease dramatically when the temperature is increased above 55 °C. This temperature is close to the mechanical loss peak [also shown in Fig. 5(b)] which is caused by the molecular relaxation process in the crystalline phase.<sup>17)</sup> This observation is consistent with what we observed in other PVDF-based polymers.<sup>20)</sup> The flexoelectric response of PVDF-based polymers is typically reduced near a temperature where a relaxation process occurs. Near that temperature, the polymers often exhibit a maximum in mechanical loss. The flexoelectric response of the polymer can be attributed to the redistribution or orientation of the polar functional group under an inhomogeneous deformation.<sup>30)</sup> The high mechanical loss implies a high internal friction for the redistribution or orientation of those function groups, resulting in a reduction of the flexoelectric response. At a high temperature after this relaxation process occurs, the flexoelectric coefficient reduces continuously because of the increasing mechanical loss, as shown in Fig. 5(b).

In summary, polymer-based flexoelectric piezoelectric composites, using a PVDF-disk/metal ring assembly, were fabricated. We show that the materials exhibit a substantial apparent piezoelectric response because of the low elastic modulus of the PVDF, which compensates for its weak flexoelectric response compared with that of ferroelectric ceramics. An increase in apparent piezoelectric response with reduced thickness of the circular PVDF plate was also demonstrated. For a composite fabricated by a PVDF circular plate with a thickness of 0.4 mm (and diameter of approximately 20 mm), the apparent  $d_{33}$  is approximately 11 pC N<sup>-1</sup>, which is comparable to the piezoelectric response measured in poled PVDF. The temperature dependence of the apparent piezoelectric response of the composites was also measured and it was found that the response decreases near the temperature where a molecular relaxation process in the crystalline phase occurs. The mechanism for the measured apparent piezoelectric response of polymer-based composites



**Fig. 5.** (Color online) (a) The temperature dependence of the storage modulus and mechanical loss of PVDF (b) The temperature dependence of the flexoelectric coefficient of PVDF calculated from the measured apparent piezoelectric response of the flexoelectric piezoelectric composites. For comparison, the temperature dependence of the mechanical loss is also shown in (b).

was also discussed and it was demonstrated that the response should mainly come from the flexoelectric effect of the polymer.

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