

Chapter 15

Piezoelectric Polymers

Yoshiro Tajitsu

Abstract The study of the piezoelectric polymers has advanced in the last few decades, and their practical application to sensor and actuator devices has progressed. The piezoelectric polymers in practical use are divided into the following classes with different piezoelectric characteristics: chiral polymers (optically active polymers), ferroelectric polymers, and cellular electrets. The piezoelectricity of a chiral polymer is in response to shear strain, that of a ferroelectric polymer is in response to tensile strain, and that of cellular electrets is in response to strain perpendicular to film surface. In this chapter, the fundamental properties and applications of these different types of polymers are systematically discussed.

Keywords Chirality • Electrets • Ferroelectricity • Optically active polymers • Piezoelectricity • Poly-L-lactic acid • Polypeptide • Polyvinylidene fluoride

15.1 Introduction

The development of new human-machine interface (HMI) for mobile devices such as smartphones etc., has been actively progressed. As a key material of such HMIs, the piezoelectric element has attracted attention. Organic piezoelectric materials such as piezoelectric polymers, are transparent, light and flexible, and the fabrication of thin films is easy, resulting in high expectations of their application as actuators and sensors for many years [1–9]. However, the large resonance essential to drive an actuator cannot be induced. This is because the mechanical loss of piezoelectric polymers is almost the same as that of general polymeric materials. Moreover, the piezoelectric constant of piezoelectric polymers is no more than one-tenth that of practical piezoelectric ceramics [4–6]. On the other hand, elucidation of the crystal growth and higher-order structure of the crystalline polymers has progressed significantly [3, 7–9]. Following the progress in the research, various novel control technologies for higher-order structures have been established. To achieve this, the properties of piezoelectric polymers have also

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been significantly improved. Concrete examples of organic piezoelectric materials in current use are poly-L-lactic acid (PLLA) as a chiral piezoelectric polymer, porous polypropylene (cellular PP) as a cellular electret, and polyvinylidene fluoride (PVDF) as a ferroelectric polymer [3, 6, 8, 10]. First, the history of piezoelectric polymers is reviewed. The first research report on piezoelectric polymers was published in 1955. Its theme was the piezoelectricity of wood [3] and the author was Dr. Eiichi Fukada, who is known as “father of piezoelectric polymers” worldwide. The existence of piezoelectricity in silk, hemp, and wool was subsequently proved. Collagen, which is a protein, is a type of polypeptide having a molecular structure in which amino acids are linked by a peptide bond (CONH) [3, 4, 7, 8]. Research on piezoelectricity in many types of polypeptides and their compounds has been carried out. The shear piezoelectricity of biological materials such as silk, wool, skin, horns, blood vessel walls, muscles, teeth, and shells has been demonstrated. Typical synthetic polymers in which many amino acids are bonded through a covalent bond whose piezoelectricity has been investigated are poly-L-alanine (PA), poly- γ -methyl-L-glutamate (PMLG), and poly- γ -benzyl-L-glutamate (PBLG) [3, 4, 7, 8].

Lead zirconate titanate (PZT) ceramic, in which lead zirconate is occluded in lead titanate crystals, is the most popular one of actual piezoelectric material in actual use [5]. PZT crystal has a unique ordered structure in which the ionized atoms are arranged. Therefore, when an electric field is applied to PZT, large internal displacement of the ions is induced. As a result, PZT was a high dielectric constant and also exhibits ferroelectricity. In contrast, the main chain molecules of polymers are formed by covalent bonds. Thus, until the end of the 1970s, it was considered that polymer materials do not exhibit ferroelectricity or have a large dielectric constant [2, 3]. This established theory was overturned by the discovery of ferroelectricity in PVDF. It is now widely accepted that ferroelectric polymers exist [2, 3].

Furthermore, electrets are among the most important piezoelectric organic materials [10]. Traditional electrets were insulating materials such as carnauba wax. The fabrication process of traditional electrets was apply a high voltage to an insulating material at a high temperature. In traditional electrets, the positive charges and negative charges are separately trapped on opposite sides of a film surface. In general, the piezoelectric constant of an electret is lower than that of piezoelectric organic materials such as PVDF. However, it was recently reported that cellular electrets have large piezoelectric constants that are almost as high as that of PZT ceramic.

15.2 Macroscopic Piezoelectricity of Polymers

Piezoelectricity is the ability of dielectrics to generate an electric charge in response to mechanical stress. The opposite effect also occurs: the application of an electric voltage produces mechanical strain in piezoelectric materials. Both these

effects can be measured, making piezoelectric materials effective in sensors and transducers. In considering the piezoelectricity of a polymer film, the strain s_m (extension: $m = 1-3$, shear strain: $m = 4-6$) induced by an electric field E_i ($i = 1-3$) is represented by the equations below. The electric displacement D_i ($i = 1-3$) induced by stress T_m (tensile stress: $m = 1-3$, shear stress: $m = 4-6$) is also give [1-11].

$$D_i = d_{im}T_m \quad (15.1)$$

$$s_m = d_{im}E_i \quad (\text{opposite effect}) \quad (15.2)$$

Here, d_{im} ($i = 1-3, m = 1-6$) is a piezoelectric tensor.

In general, amorphous components are always present in complex high-order structures in polymer films with piezoelectricity, including electret type piezoelectric films. Therefore, the macroscopic symmetry of a piezoelectric polymer film must be considered on the basis of point group theory. For a right-handed system ($x_1-x_2-x_3$), asymmetry is imparted to a film by conventional methods such as drawing and poling [4, 7]. The directions of the coordinate axes are different in each type of piezoelectric polymer material [3, 4, 7, 8, 11]. In particular, it is necessary to ensure that the directions of the coordinate axes do not become mixed, as shown in Fig. 15.1. The purpose of drawing is to macroscopically arrange the chain molecules in a polymer film along the same direction in the entire film [3, 4, 7, 8, 11]. In contrast, the purpose of poling is to macroscopically arrange the dipole moments of the molecules along the same direction in the entire film,. Actually, the macroscopic piezoelectricity of an isotropic film does not occur even when piezoelectricity exists in the crystal state. The point group of drawn and poled films of ferroelectric polymers such as PVDF is C_{2v} , as shown in Fig. 15.1. The symmetry is the same as that of the PVDF crystal. In the poling process a high voltage is applied perpendicular to the film surface. However, drawn and poled PVDF films exhibit high macroscopic tensile piezoelectricity. In this case, the direction of the x_1 -axis is taken along the fiber orientation axis, and the direction of the x_3 -axis is parallel to the poling direction. Five independent piezoelectric tensors, $d_{31}, d_{32}, d_{33}, d_{15}$, and d_{24} , exist as shown in Fig. 15.1.

Next, we consider the case of a chiral polymer film. The point group of a drawn polymer film without chirality is $D_{\infty v}$ [3, 4, 7, 8, 11], as shown in Fig. 15.1. In this case, it is important that a mirror plane perpendicular to the film surface exists. Furthermore, in this case, no piezoelectricity arises. However, the molecule of a chiral polymer such as PLLA has chirality, as shown in Fig. 15.1. Its point group is $D_{\infty v}$. As a result, two independent piezoelectric tensors, d_{14} and $d_{25} (= -d_{14})$, exist.

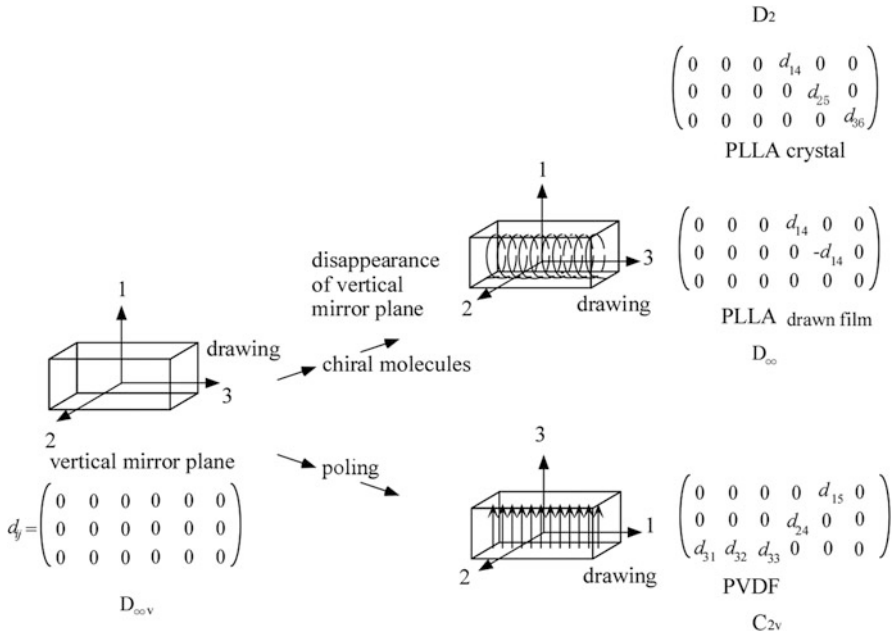


Fig. 15.1 Macro symmetry of polymer film

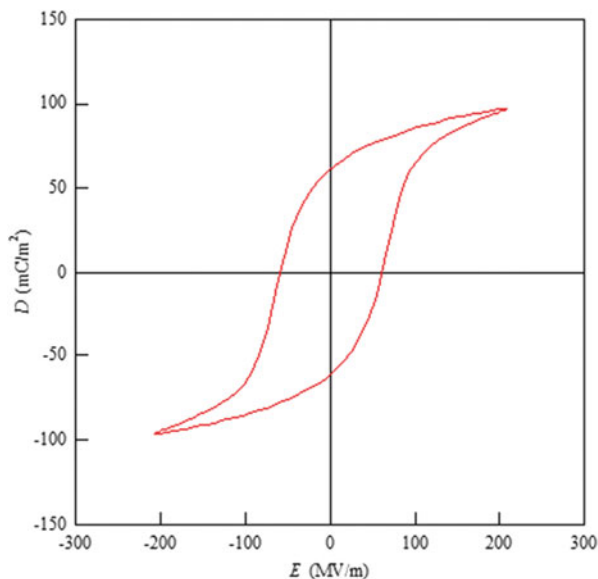
15.3 Typical Piezoelectric Polymers in Practical Use

In this section, typical piezoelectric polymers are surveyed and their characteristic features enabling their use as sensors and actuators are introduced.

15.3.1 Polyvinylidene Fluoride (PVDF)

The most well-known piezoelectric macromolecule is the ferroelectric polymer PVDF. Its large residual polarization was discovered found when a strong electric field was applied to a stretched PVDF film. It was reported by Kawai [2, 3] in 1969 that PVDF has a high piezoelectric constant of 5 pC/N. Both the poling process and the drawing process are essential for piezoelectricity to occur in a PVDF film. This discovery was the starting point of the study of ferroelectricity in polymers. As shown in Fig. 15.2, PVDF exhibits a *D-E* hysteresis loop [2, 3]. In other words, the macroscopic piezoelectricity of PVDF is not observed if spontaneous polarization does not arise in this *D-E* hysteresis loop. That is, the same poling process as that for piezoelectric PZT ceramic, is required to induce the piezoelectricity in a PVDF film. In the poling process, a DC voltage is applied to the sample to generate residual polarization. In the case of PVDF, an electric field of 50 MV/m or more

Fig. 15.2 Hysteresis loop of PVDF film drawn along one axis



must be applied at room temperature. This is difficult for a PVDF film with a thickness of 100 μm or more because we must apply a large voltage of over 5 kV without inducing breakdown or discharge phenomena. Therefore, in practice, thermal poling by the application of a dc voltage of several kV to a PVDF film at a temperature higher than room temperature is carried out. To induce piezoelectricity more effectively in a PVDF film, a uniaxial stretching process to orient the chain molecules is necessary in advance. When these treatments are applied to a PVDF film, its point group becomes C_{2v} , as shown in Fig. 15.1. The point group of a PVDF crystal is also C_{2v} . Thus, the point group of an entire PVDF film is the same as that of a PVDF crystal. The piezoelectric tensor in this case is summarized in Fig. 15.1. Here, we consider this result in detail. The point groups were should not be the same since a PVDF film is a single crystal. It is coincidental that the point group of a poled PVDF film with single-axis orientation is the same as that of a single crystal. That is, a PVDF film has a complicated higher-order structure; therefore, it does not show translational symmetry. This is a very important point in clarifying the macroscale piezoelectricity of PVDF films.

Many applications of piezoelectric PVDF films have been commercially realized in the U.S. and Europe [2–6]. In the acoustic field, these include the pickup of a loudspeaker, a guitar, and a violin. Also, microphones, and sonar (underwater microphones) used by a submarine or ship are included. In the field of security, piezoelectric PVDF films with a large area placed under a carpet have been used to detect intruders. In the field of traffic control, piezoelectric cables is embedded in roads have been used to detect the speed of vehicles, and vehicles ignoring traffic lights, and to obtain information on the occupancy of parking lots. They have also been used in switches, sensors in water meters, for nondestructive detection, and in

keyboards. They have also been employed as oscillating sensors for the vibratory control of washing machines and in eyeball sensors, sphygmomanometers, stethoscopes, and over 250,000 pacemakers as medical sensors. Moreover, ultrasonic image sensors and sensors that measure the pressure of the soles to feet have been developed that use PVDF films. Thus, PVDF films have a proven track record in many fields. PVDF sensors are also used as ultrasonic elements. Since the acoustic impedance of a PVDF film is closer to that of a living body or water than that of conventional electrostrictive ceramics, the propagation loss in the case of ultrasonic transmission and reception is small. As a result, PVDF devices are highly sensitive. Also, the separation of transmission and reception in a short pulse is possible. Therefore, high-resolution and broadband characteristics are acquired. Since PVDF films are soft, they are easy to process into the shapes of concave and convex lenses. Another use of PVDF devices is to converge an ultrasonic beam without an acoustic lens. Also the focus and depth of focus in the design of PVDF devices can be adjusted as required. Moreover, since elements with a large area are obtained easily, large transducers are realized easily. Also, since thin film elements are obtained easily, high-frequency transducers can be obtained. Thus, PVDF films have many attractive features. Taking advantage of these features, they are practically used in probes for hydrophones, ultrasonic diagnostic equipment, ultrasonic nondestructive-testing equipment, and acoustic microscopes.

15.3.2 *Poly-L-Lactic Acid (PLLA)*

First, the PLLA crystal structure is introduced to clarify the origin of the macroscopic piezoelectricity of PLLA films. The crystal structure is based on a base-centered orthorhombic unit cell [12, 13], as shown in Fig. 15.3. Here, a , b , and c are the lengths of the unit cell, which contains two $10/3$ helical chains arranged along the c -axis. Thus, PLLA is a chiral polymer, and in the crystal the chain molecules form a helical structure. The crystal structure of PLLA is characterized by this helical structure. That is, the piezoelectric characteristics of the PLLA crystal are governed by this helical structure. The point group of the PLLA crystal is D_2 . When the c -axis corresponds to the x_3 -axis, the a -axis corresponds to the x_1 -axis, and the b -axis corresponds to the x_2 -axis, three independent piezoelectric tensors, d_{14} , d_{25} , and d_{36} , are present, as shown in Fig. 15.1. After close investigation, the origin of the observed macroscopic piezoelectricity, where charges are induced on the film surface as shear stress is applied to a PLLA film, is understood as follows [7, 9]. At the microscopic scale, some carboxyl bonds (C=O) rotate, as shown in Fig. 15.3. Shear stress is applied to the chain molecules in PLLA with a $10/3$ helical structure through its side chain. All the atoms in the chain molecules are displaced. In particular, the plane on which the CO bond and carboxyl bond (C=O) exist is rotated. As a result, the C=O bond, which has a larger dipole moment than the other bond, is displaced. The rotation of the C=O bond changes the polarization of the entire long-chain molecule, resulting in the shear piezoelectricity of PLLA.

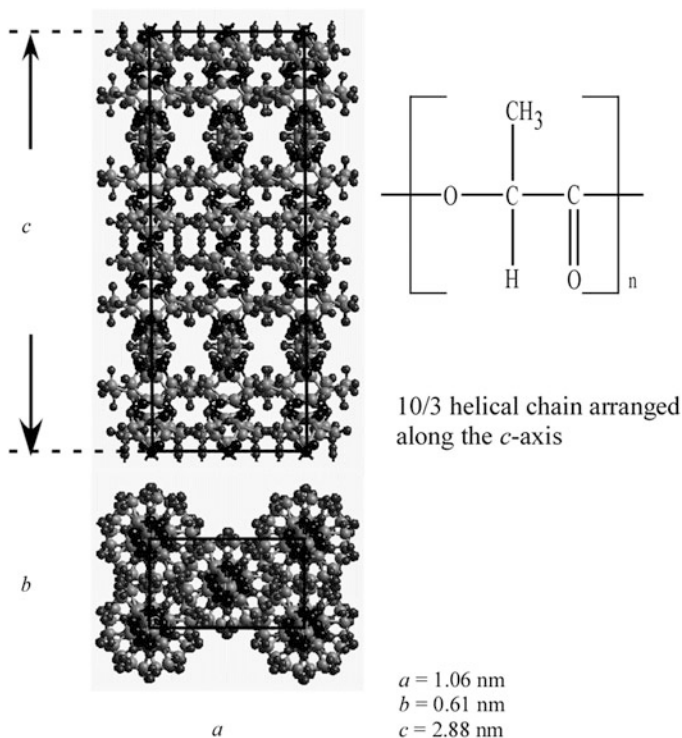


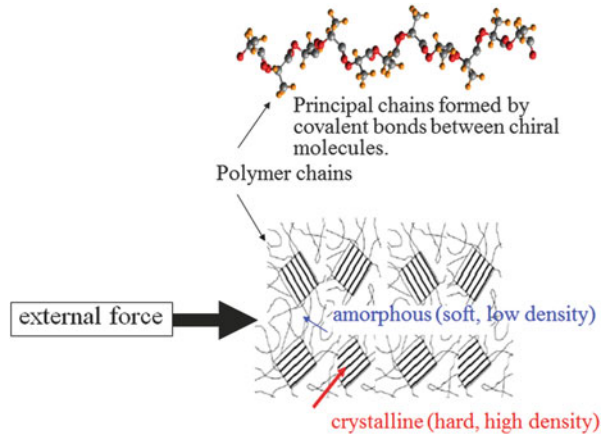
Fig. 15.3 Crystal structure of PLLA

We must change the notation to distinguish the new d_{14}^m , d_{25}^m , and d_{36}^m from the macroscopic piezoelectric tensors d_{14} and d_{36} in the entire PLLA film, as shown in Fig. 15.1. On the other hand, we must point out the difference between the point group in the crystal state, D_2 , and that in the entire film, D_∞ . The point group of an oriented PLLA film corresponds to the orientation distribution of the c -axis of each PLLA crystal around the x_3 -axis (drawing axis) in the entire PLLA film.

15.3.2.1 Improving the Piezoelectricity of PLLA Films

The piezoelectricity of PLLA is expressed when the atoms of the chain molecules move under the application of an external force. The atoms of a chain molecule are not easily displaced by an external force because the binding force of a covalent bond in PLLA is larger than that of an ionic bond in ceramics. On the other hand, an external force does not propagate through the amorphous region of PLLA. The power (force) is not sufficient to displace atoms in the chain molecules in the crystalline polymer film, as shown in Fig. 15.4. As a result, the piezoelectric constant is small. Improvement of the material properties, such as piezoelectricity and mechanical strength, and the development of processing technology for PLLA

Fig. 15.4 Higher-order structure of PLLA



films are key factors that will enable the increased use of PLLA films as flexible piezoelectric sensors. To improve the properties of PLLA films, it is necessary for the mechanical properties of the amorphous region to approach those of the crystallites. We have reported that changing the higher-order structure of PLLA by applying a high-pressure forging process [14] and supercritical CO_2 ($s\text{-CO}_2$) treatment [15] is an effective means of improving its piezoelectricity. However, these processes are difficult to apply to industrial production because their productivity is low. In the previous section, it was explained that PLLA films with 100 % crystallinity cannot be obtained through conventional methods. Thus, a one-to-one correspondence has not been found between the macroscale piezoelectric properties and the crystal characteristics. It has been observed that a PLLA film contains complex higher-order structures with various scales [16] in increasing order of size from single-chain molecules to a macroscopic film, including crystalline and amorphous regions and PLLA crystals. The existence of these complex higher-order structures in the PLLA film is the reason why the piezoelectric constant of PLLA is lower than those of conventional piezoelectric ceramics. Advanced technical skills are required to manufacture PLLA films with high piezoelectricity. To improve the piezoelectricity of PLLA films, we have employed a triblock copolymer with hard and soft parts to establish a new force propagation path between the crystallites while maintaining the application of stress to the crystallites [16]. The triblock copolymer is a pure acrylic symmetric block copolymer consisting of a center block of poly(butyl acrylate) (PBA), corresponding to its soft part, and two side blocks of poly(methyl methacrylate) (PMMA), corresponding to its hard part (hereafter denoted as PMMA-*b*-PBA-*b*-PMMA). The piezoelectric constant of most samples was more than 10 pC/N, more than twice that of conventional uniaxially drawn PLLA films. Also, the Young's modulus of most samples was from 1 to 2 GN/m². Also, we found that the glass transition temperature increases with increasing PMMA-*b*-PBA-*b*-PMMA content. It was found from atomic force microscope (AFM) images that, upon the addition of PMMA-*b*-PBA-*b*-PMMA, the

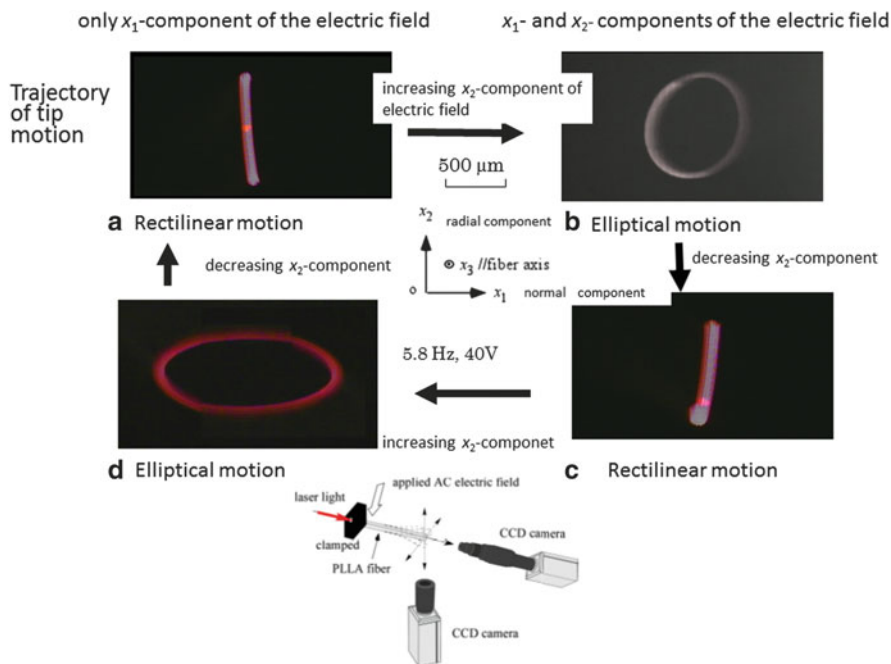


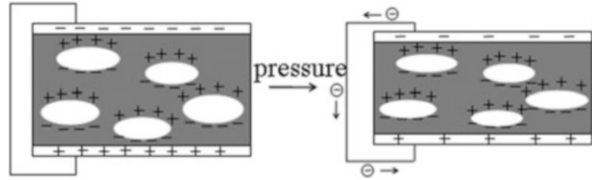
Fig. 15.5 Demonstration of PLLA fiber actuator

grain structure in the PLLA/[PMMA/PBA/PMMA] film became more homogenous than that in the reference PLLA film. Thus, to realize PLLA films with high piezoelectricity, it is important that a homogeneous higher-order structure is formed [16].

15.3.2.2 PLLA Fiber Actuator

We have investigated the application of chiral polymers to actuators with flexibility (soft actuators). However, before we can apply the shear piezoelectricity of a chiral polymer to a soft actuator, some difficult problems must be solved. For example, using shear strain, it is more difficult to include stretching and contraction than with tensile strain. Also, the chiral polymer membrane has a very small piezoelectric constant of at least two orders of magnitude less than that of inorganic ferroelectrics. However, we found that the PLLA fibers have the largest shear piezoelectricity (over 10 pC/N) among chiral polymers. Thus, we attempted to realize the electrically controlled complex motion of a PLLA fiber induced by its shear piezoelectricity such as that observed in an actuator. The results obtained were as follows [17–19]. The control of the bending motion of a PLLA fiber induced by its shear piezoelectricity upon applying an electric field was successfully demonstrated using the experimental apparatus shown in Fig. 15.5. We propagated laser light into

Fig. 15.6 Cellular PP electret



a PLLA fiber because of its similar transparency to polymeric optical fibers such as PMMA fibers. The high-speed charge-coupled device (CCD) camera used to record the motion faced the incident laser light. The CCD camera was focused on the tip of the PLLA fiber. Here, to measure the piezoelectric motion under the application of a controlled electric field, one end of the PLLA fiber was clamped, as shown in Fig. 15.5 [17]. In the experiments, a controlled sinusoidal voltage was applied to the PLLA fiber, and the direction of the transmitted laser light varied with the bending of PLLA fiber owing to its shear piezoelectric motion. The complex motion of the tip of the PLLA fiber could be controlled by applying an electric field with various directions and strengths. On the basis of these experimental results, we believe that there is a strong possibility of realizing a chiral polymeric fiber actuator using piezoelectric PLLA [17–19].

15.3.3 Cellular and Porous Electrets

Electrets, which retain residual polarization semi-permanently, are dielectrics. Usually, a polymer film with high insulation performance is used as an electret. A European research group [10, 20] has realized a large piezoelectric constant of 100 pC/N in an electret with a two-layer structure consisting of a hard film placed on a soft porous film. The piezoelectric mechanism in this electret is as follows. In this electret, the electric charge accumulates at the interface between the soft and hard layers. If pressure is applied to this film, electric charges are induced on both electrodes since the strains of the two layers are markedly different. As a result, high piezoelectricity in the electret is observed. The same research group also reported a soft electret using cellular PP with a large piezoelectric constant of up to 500 pC/N. A schematic diagram (sectional view) of the cellular PP electret is shown in Fig. 15.6 [10, 20]. Many long and slender holes exist in the film. Positive and negative electric charges were trapped on the upper and lower sides of each hole, respectively, when corona discharge was applied. Since the thickness of each hole markedly changes when pressure is applied in the thickness direction of the film, a large amount of electric charge is induced on both electrodes. Because of this unique structure, cellular PP has a large piezoelectric constant. Also, Fig. 15.6 shows the mechanism of the ferroelectric behavior of cellular PP [10, 20]. With increasing applied electric field, the sign of the trapped electric charges is reversed because of the plasma discharge induced within each hole. Therefore, the induced

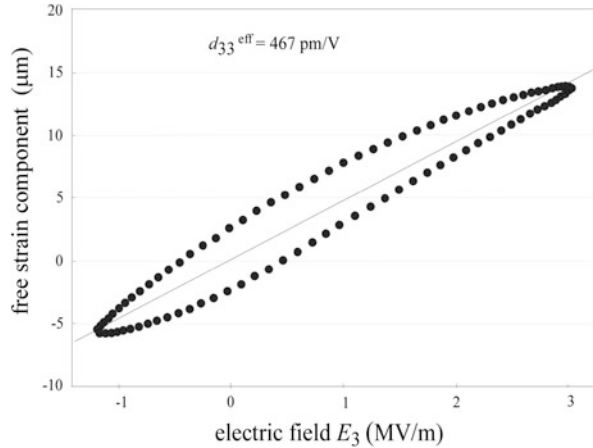
electric charge on the electrode exhibits hysteresis. In general, electrets have not exhibited ferroelectric hysteresis, and the ferroelectric hysteresis observed in cellular PP was the first case of its observation in an electret. Thus, cellular PP is as a ferroelectret. In ferroelectrets such as cellular PP, positive charges exist on one side of each hole and negative charges exist on the opposite side. The pairs of positive and negative charges result in a huge dipole moment. When a strong electric field is applied to cellular PP, ferroelectric hysteresis is observed because the positive and negative charges replace each other in each hole. Moreover, since the thickness of each hole markedly changes with the external force, the piezoelectric constant is very large [10, 20].

Many applications using the softness and high piezoelectricity of cellular PP have already been developed, for example, noncontact ultrasonic imaging, ultrasonic receivers, legless chair sensors, floor sensors for a wide area, musical instrument pickups, and broadband microphones. A new sensing device with flexibility and a large area has been developed that comprises cellular PP and an amorphous silicon field-effect transistor (FET) [20]. In this device, a 70- μm -thick cellular PP layer was bonded on a substrate fabricated from 50- μm -thick polyimide film using epoxy resin. The thickness of the bonding layer was 1–5 μm . This device is directly applicable as a piezoelectric film switch, a pressure sensor, and a microphone.

15.4 Polymeric Composite Systems

There has been considerable research on piezoelectric composite systems consisting of ceramics and polymer materials with high power and flexibility to realize novel actuators. In this section, the interesting topic of polymeric composite systems is introduced. A piezoelectric actuator called a macro-fiber composite (MFC), which was developed by Langley Laboratory of National Aeronautics and Space Administration (NASA), is a new device with unique performance [21–23]. The piezoelectric constant of the MFC, which is a plate with a thickness about 0.3 mm, is about ten times that of PVDF, and the MFC exhibits reasonable flexibility. The fabrication process of the MFC is as follows. First, after spinning PZT ceramic, bundles of PZT fibers are bonded by epoxy resin. Then, a large dc voltage is applied parallel to the fiber axis of the bundled PZT fibers to obtain the MFC [21–23]. Therefore, upon applying strain to the MFC, a voltage can be induced owing to the nonzero piezoelectric constant d_{33} . The piezoelectric strain of the MFC is dependent on the electric field, as shown in Fig. 15.7 [21–23]. The MFC can be used as an actuator and as a sensor [21–23], and it has been applied to systems in airplanes and space rockets. Typical examples of such applications are as follows. The MFC has been attached to the wings of a helicopter, and the vibration of the wings was controlled by the MFC acting as an actuator. As an advanced example, some MFCs has been installed in the tail unit of an airplane, and the vibration of the airplane was controlled by active control using the MFCs. Moreover, the MFC was successfully used to attenuate the vibration of the prop

Fig. 15.7 Induced strain of MCC under application of voltage



stick of a space shuttle. MFC sensors are used in space shuttles to inspect the bolt joints in sealed chambers and the pedestal of the rocket booster. Also, the MFC can be inserted in the washer of a bolt to control the torque at the time of bolting.

15.5 Summary

Piezoelectric polymers have now been studied for over half a century. The study of piezoelectric polymers has reached a stage where the piezoelectricity of a polymer film can be arbitrarily tailored. We believe that there is a strong possibility of realizing novel piezoelectric polymer actuators and sensors with flexibility, softness, transparency, and lightness.

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