Bending-Electrostrictive Response of Polyurethane Films Subjected to a Reversed Electric Field

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ABSTRACT: This study dealt with the bending-electrostrictive response of a polyurethane film, which was a promising candidate for a material to be used in polymer actuators. The film bent under an electric field (2.5 MV/m). However, when the field polarity was reversed, the bending direction curiously did not change. To clarify the mechanism of this behavior, we measured the space charge distribution in the film. The measurement showed a pair of charges (induced charge on an electrode and space charge in the film) on one side of the film during the application of the field. However, when the field polarity was reversed, the location of the charges did not change. The charges were assumed to be the cause of the bending. Therefore, we concluded that the bending direction did not change despite the reversed field because the location of the charges did not change. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3644–3650, 2004

Key words: elastomers; polyurethanes; rubber

INTRODUCTION

Over the past decade, electrostrictive elastomers have attracted much attention as materials for polymer actuators and artificial muscles.[1] Polyurethane (PU) is an example of such an elastomer. Zhenyi et al. reported its large strain as an electrostrictive response in 1994.[2] After their article was published, there were several studies of the electrostrictive response of PU.[3–7] Other elastomers were also investigated by Ma and Reneker.[8] They reported the electrostrictive responses of various elastomers, including polychloroprene, nitrile rubber, and polyisoprene. A recent topic in this field was the usage of compliant electrodes made from carbon-impregnated grease. Pelrine et al. obtained huge strains by coating elastomer films with such an electrode.[9]

The field-induced strain that these studies dealt with was expansion in the plane or a contraction in the thickness of the elastomer films. However, we reported a bending deformation induced by an electric field with a PU film that was coated on either side with a thin gold electrode.[10] The film was a monolayer and was homogeneous but bent like a bimorph. Because the deformation was proportional to the square of the electric field applied, the bending phenomenon was bending electrostriction as we reported earlier.[10] However, except for our recent articles,[11,12] there have been only two articles on this phenomenon. That is, Kawai reported on the bending-electrostrictive response of some polymers in 1967 and 1970.[13,14] However, we felt the need for further investigation to reveal the details of this phenomenon.

As we reported earlier,[15] we discovered a unique feature of bending electrostriction that can be observed when one reverses the field polarity. The following is a brief description of this feature. As shown in Figure 1(a), a PU film bent to the right during the first application of an electric field. After that, another field with a reversed polarity was applied to the film as the second application. However, the film bent to the right again [Fig. 1(b)]. Although the application of the reversed field was maintained, the film gradually changed its bending direction and finally bent to the left. Thus, the film did not change its bending direction during the initial period of the second application despite the reversed polarity. This behavior seemed to be curious but was observed in most of the PUs that we examined. This curious behavior, therefore, seemed to be common to the bending-electrostrictive responses of PUs.

Therefore, we were interested in this behavior and decided to investigate its mechanism. In this study, we measured the space charge distributions in the films to reveal the mechanism because such distributions were closely related to the bending mechanism we reported earlier.[12] The measurements were performed with the pulsed electroacoustic method reported by Maeno et al.[16] Maeno and Fukunaga reported recent improvements in the apparatus in ref. 17, and Fukunaga re-

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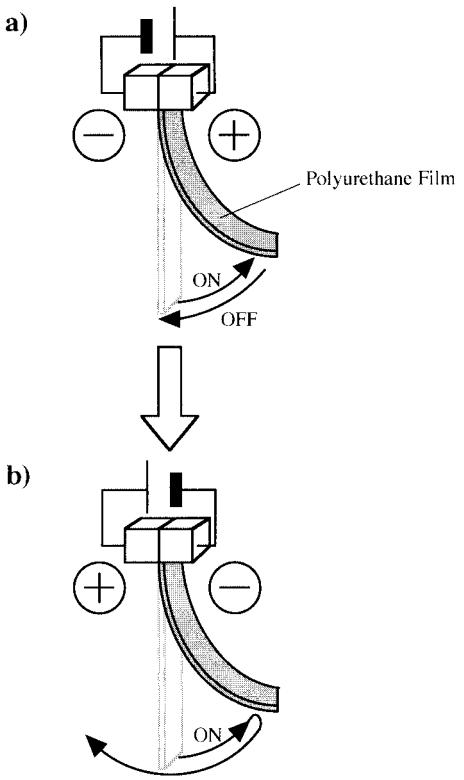

Figure 1 Bending of a PU film during (a) the first application of an electric field and (b) the second application of a reversed field.

viewed various applications of this method in ref. 18. In this method, a pulse voltage applied to the film induces an acoustic wave because of the Maxwell stress that comes from the electrostatic force between the induced charge on the electrodes and the space charge in the film. By measuring the acoustic wave, one can reveal the position and the density of the space charge.

EXPERIMENTAL

Preparation of the PU films

We prepared two kinds of PU (PU-1 and PU-2) from the raw materials summarized in Table I. The diisocyanates used for the preparation of PU-1 and PU-2 were 1,6-diisocyanatohexane and 1,4-phenylene diisocyanate, respectively. A crosslinking agent [2-ethyl-2-(hydroxymethyl)-1,3-propanediol] was also used for PU-2. The PUs were synthesized by the conventional prepolymer route.[19] A typical procedure was as follows. Poly(3-methyl-1,5-pentamethylene adipate)diol [80.0 g; number-average molecular weight (M_n) = 2930; Kuraray Co., Ltd., Tokyo, Japan; Kurapol P-3010] was placed in a glass reactor with a nitrogen inlet and outlet and was dried at 100°C *in vacuo* for 1 h before use. 1,6-Diisocyanatohexane (6.89 g; Wako Pure Chemical Industries, Ltd., Osaka Japan) was charged into the reactor and stirred at 90°C for 1 h. 1,4-Butanediol (0.79 g; Wako Pure Chemical Industries) was then added to the reaction mixture, which was then agitated for 15 min. After the mixture was degassed *in vacuo*, it was cast in a brass mold treated with a detaching agent in advance. By keeping the mold at 130°C for 18 h, we obtained the PU film (~0.28 mm in thickness).

TABLE I
Raw Materials

PU	Raw materials
PU-1	Poly(3-methyl-1,5-pentamethylene adipate) diol (M_n = 2930, 80.0 g) 1,6-Diisocyanatohexane (6.89 g) 1,4-Butanediol (0.79 g)
PU-2	Poly(3-methyl-1,5-pentamethylene adipate)diol (M_n = 5171, 80.0 g) 1,4-Phenylene diisocyanate (4.95 g) 1,4-Butanediol (0.56 g) 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (0.69 g)

Measurement of the field-induced bending deformation

The PU films obtained were coated with gold as the electrode on either surface with an Eiko Engineering IB-3 ion-sputtering coater (Hitachinaka, Japan). The films were cut into 5 × 30 mm rectangular pieces; these were used to measure the field-induced bending deformation.

The measurements were carried out with the experimental setup shown in Figure 2. The film was vertically suspended in air, and the top of the film was fixed. During application of the electric field, the displacement of the film tip was measured with a Keyence LB-62 laser displacement meter (Osaka, Japan). The application of the electric field and the measurement of the current were carried out with an Advan-

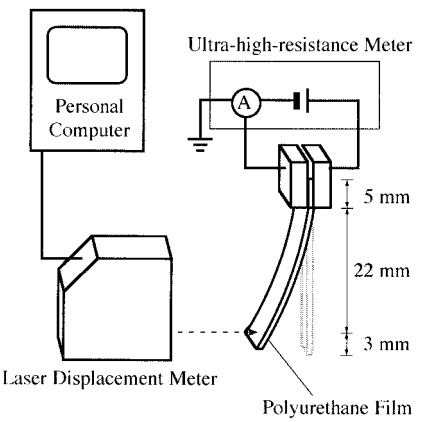

Figure 2 Experimental setup for measuring the field-induced bending deformation of PU films.

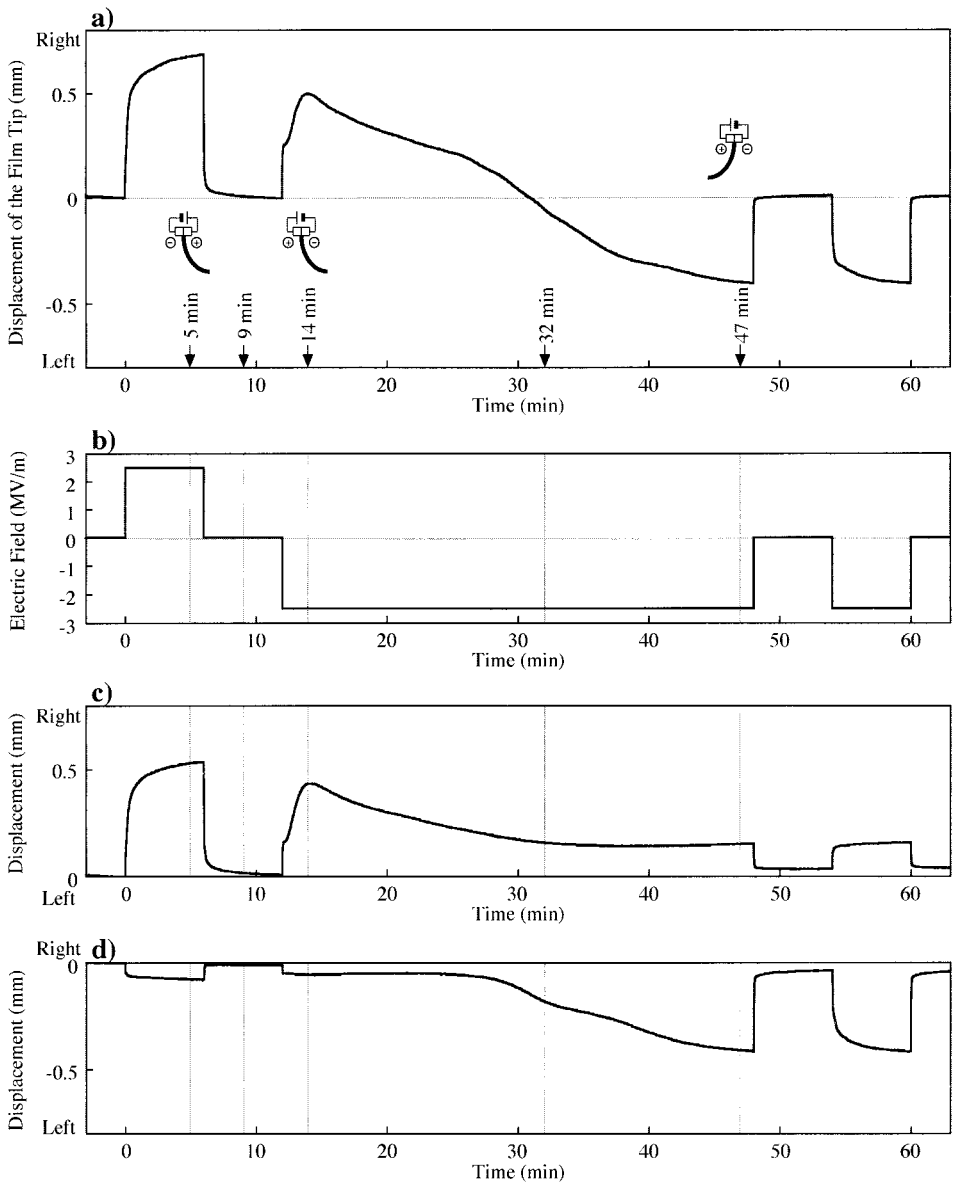

Figure 3 (a) Bending deformation of the PU-1 film, (b) application of the electric field, (c) bending observed when an adhesive tape was stuck on the right surface of the film, and (d) bending observed when the tape was stuck on the left surface. All of the measurements were carried out after the preliminary application of an electric field (+2.5 MV/m) for 18 min.

test R8340A ultra-high-resistance meter (Tokyo, Japan). We carried out all of the measurements by maintaining the air temperature at 30°C so that there was no change in temperature that could affect the measurements.

Observations of the space charge distribution

The space charge distribution in the PU films was observed with a Five Lab Co., Ltd. pulsed electroacoustic nondestructive test system (Kawasaki, Japan). The film surfaces were coated with sputtered gold electrodes to ensure good reproducibility of the measurements.

RESULTS AND DISCUSSION

Field-induced bending of the PU films

An example of the field-induced bending is shown in Figure 3(a). The PU film used was PU-1, and we applied the electric field (2.5 MV/m) following the pattern shown in Figure 3(b). During the first application, the film bent to the right, that is, to the anode side [see ~5 min in Fig. 3(a)]. When the application was interrupted, the bending deformation disappeared (see ~9 min). Subsequently, a reversed field was applied. Curiously, the film bent back to the right despite the reversed field polarity (see ~14 min). After that, the film gradually changed its

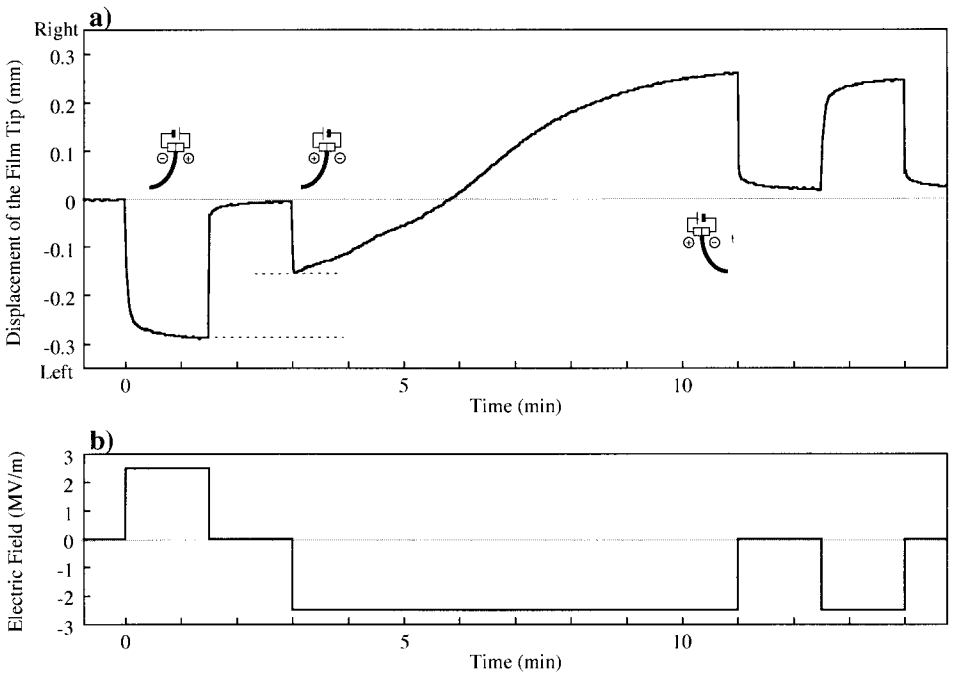

Figure 4 (a) Bending deformation of the PU-2 film and (b) application of the electric field. The measurement was carried out after the preliminary application of an electric field (+2.5 MV/m) for 3 min.

bending direction (see ~32 min) and finally bent to the left (see ~47 min).

Figure 4 shows another example of the bending behavior with the PU-2 film. The first application of the electric field (2.5 MV/m) bent the film to the left, that is, to the cathode side. (However, the PU-1 film bent to the anode side during the first application. As we reported earlier,[12] bending directions depend on the kind of PU used.) The subsequent application of the reversed field bent back the film to the left again despite the reversed field polarity. This behavior was similar to that observed with the PU-1 film, although the bending direction was totally opposite to that of PU-1, and the bending back was incomplete; that is, the film bent back by about half as indicated by the broken lines in Figure 4. After that, the film gradually changed its bending direction.

Thus, the PU films showed a unique behavior when subjected to the reversed field. We observed this behavior with most of the PUs that we examined, although the bending back was incomplete in some cases. Because this behavior seemed to be curious but common to PUs, we were interested in its mechanism. In the following section, we discuss this with the data obtained from the PU-1 film on behalf of the PUs.

Expansion of the film surfaces

As we earlier reported,[10] the field-induced bending of films results from the difference in expansion between the two film surfaces. For instance, when the left surface expands much greater than the right surface, the film bends to the right [Fig. 5(a)]. One can measure such an expansion by sticking an adhesive tape on one surface of the film. For example, one sticks the tape on the right surface to prevent its expansion or contraction [Fig. 5(b)]. If the film with the tape bends to the right during the application of the field, this indicates the expansion of the left surface.

Figure 1(c) shows the bending observed when we stuck the adhesive tape on the right surface of the PU-1 film. The electric field (2.5 MV/m) was applied in the same manner shown in Figure 3(b). During the first application of the electric field, the film bent to the right. This indicated the expansion of the left surface. The subsequent application of the reversed field bent the film to the right again and then reduced the bending deformation.

Alternatively, Figure 3(d) shows the bend observed when we stuck the tape on the left surface. During the first application, the film only slightly bent to the left. During the next application of the reversed field, the film slightly bent for the first half of the period, then significantly bent to the left for the second half. This bending direction indicated the expansion of the right surface.

These results are summarized in Table II. The main expanding surfaces shown in the table were determined by the comparison of Figures 3(c) and 3(d). Also shown in Table II is the bending direction of the free film (i.e., the film without the tape), based on the

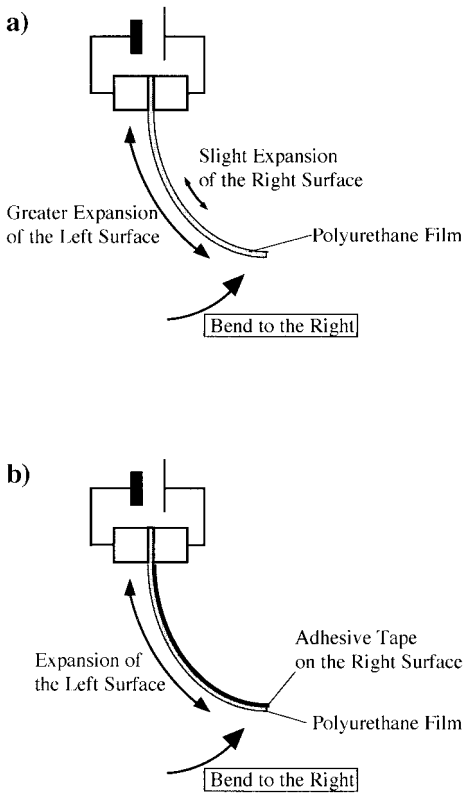

Figure 5 Schematic diagram of the relation between the bending direction and the surface expansion for (a) a free film and (b) a film with adhesive tape on the right surface.

data shown in Figure 3(a). As explained with Figure 5(a), when the main expanding surface was the left surface, the bending direction of the free film should have been to the right. However, when it was the right surface, the direction should have been to the left. The data shown in the table are surely consistent with this relationship. The table also shows the location of the pair charges; we explain this in the next section.

Space charge distribution

We measured the space charge distribution in the PU-1 film with the pulsed electroacoustic method. The measurements were carried out while an electric field (2.5 MV/m) was applied to the film according to the pattern shown in Figure 3(b); it was the same as the pattern that we used in the measurement of the bending deformation.

Figure 6(a) shows the charge distribution during the first application of the electric field. There was a pair of charges: a negative induced charge on the left electrode (i.e., the cathode) and a positive space charge inside it. As we reported earlier,[12] such a distribution can result from electrode-limited conduction. Details of this conduction were already reported by Yoshino and Inuishi as a type of conduction through polymer dielectrics.[20] They described two types of conduction, that is, electrode-limited and space-charge-limited conduction. In these types of conduction, space charges are generated in the dielectrics as a result of a balance between the charge injection from the electrode and the bulk conduction. Although the distribution of the space charge depends on the type of the conduction, in our case, it was similar to the distribution during the electrode-limited conduction. Therefore, we concluded that the observed space charge distribution was due to this type of conduction.

Figure 6(b) was measured while the application of the field was interrupted. There was no charge detected.

Figure 6(c–e) shows the charge distribution during the second application of the field, which had the reversed polarity. The charge distribution was measured at 14, 32, and 47 min, which represented the initial, middle, and final periods of the application [see Fig. 3(a,b)]. For the initial period, there was a pair of charges on the left electrode [Fig. 6(c)]. That is, the positive induced-charge was on the left electrode (i.e., the anode), and the negative space charge was inside it. Although Figure 6(a) also shows the pair charges on the left electrode, the polarity was opposite to that shown in Figure 6(c). For the middle period, there were two pairs of charges on both electrodes [Fig. 6(d)]. However, for the final period, the pair charges were only on the right electrode [Fig. 6(e)].

In Table II, these results are summarized with the addition of the location of the pair charges. At 5 min, the main expanding surface was the left one, and the location of the pair charges was also the left side. The same relation was also seen at 14 min. However, at 47 min, the expanding surface was the right one, and the location of the charges was also the right side. Thus, the expanding surface always agreed with the location

TABLE II
Relationships Among the Bending Direction, Surface Expansion, and Location of the Charges

Time (min)	Main expanding surface	Bending direction of the free film	Location of the pair charges
5	Left surface	Right	Left side
9	No expansion	No bend	No charge
14	Left surface	Right	Left side
32	Right ≈ left	No bend	Right and left sides
47	Right surface	Left	Right side

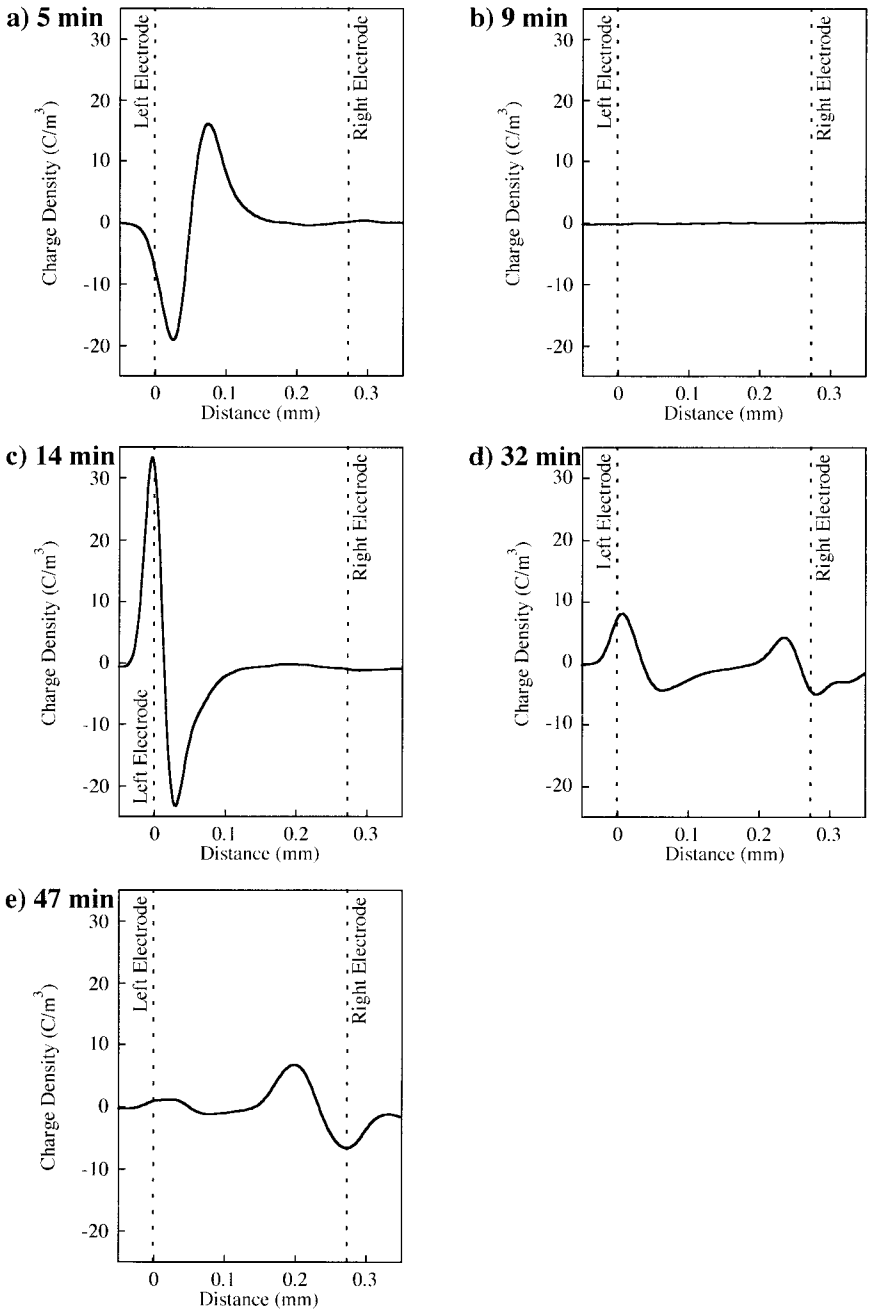

Figure 6 Charge distribution in/on the PU-1 film under an electric field that was applied according to the pattern shown in Figure 3(b). The measurement was carried out after the preliminary application of an electric field (+2.5 MV/m) for 18 min.

of the charges. This suggests that the charges might have been the cause of the surface expansion. The same suggestion was also obtained from other experiments that we reported earlier.[12]

As described in the Introduction, the objective of this study was to clarify why the PU film did not change its bending direction for the initial period when subjected to the reversed field. From these results, we can explain it as follows: The location of the charges did not change when the field polarity was reversed, although the polarity of the charges changed. The charges were assumed to be the cause of the surface expansion, which led to the bending deformation. Therefore, the unchanged location of the charges resulted in the unchanged bending direction.

A remaining question is why the location of the charges did not change despite the reversal of the field polarity. To answer this question, we need to investigate further, but the reason might be related to the increase in resistance on the interface between the electrode and the PU. Such an increase could result from the electrochemical deposition of impurities contained in the film. In

addition, the increase could be unequal on each side of the film. Therefore, we speculated that the location of the charges did not change because the resistance increased only on one side of the film.

CONCLUSIONS

A PU film bent under an electric field because of bending electrostriction. However, the bending direction did not change when the polarity of the field was reversed. The pulsed electroacoustic method revealed the distribution of the induced charge and space charge; they were located on one side of the film. However, the location did not change when the field was reversed. Because the charges were assumed to be the cause of the bending, we concluded that the unchanged location of the charges resulted in the unchanged direction of the bending.

The authors used an apparatus on consignment from Five Lab Co., Ltd., to measure the space charge distribution.

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