Hysteresis in Bending Electrostriction of Polyurethane Films

MASASHI WATANABE,[1] MAKOTO SUZUKI,[2] YOSHIYUKI HIRAKO,[2] HIROFUSA SHIRAI,[1] TOSHIHIRO HIRAI[1]

[1] Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8567, Japan

[2] Narayama Laboratory, Nitta Industries Corporation, 6-5-6 Sakyo, Nara 631-0801, Japan

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ABSTRACT: This report presents the mechanism and unique features of hysteresis in bending electrostriction of polyurethane films. The films were made of segmented polyester–polyurethanes and coated with a thin gold electrode on both surfaces. The application of a 2-MV/m electric field to the 0.2-mm-thick film caused a bending deformation, which showed hysteresis. The hysteresis was closely related to the absorption current, suggesting that its origin is ionic polarization attributed to ionic impurities in the polyurethane. The existence of ionic polarization after the removal of the electric field was shown by measuring a thermally stimulated discharge current. In addition, a couple of unique features of the hysteresis in the bending deformation are described. One of the features is that the prior application of an electric field significantly improves the bending speed in the successive application. The other is that the prior application also controls the bending direction in the subsequent application of an electric field of opposite polarity. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1121–1126, 2001

Key words: bending electrostriction; hysteresis; polyurethane; actuator; ionic polarization

INTRODUCTION

Polymers as electromechanical materials have various advantages such as flexibility, low density, and ease in molding as compared with conventional electromechanical ceramics.[1–3] In particular, polyurethanes have drawn much attention as a new class of electromechanical polymers since a large electric-field-induced contraction was reported.[4–13] Although polyurethane films have been known to contract in the direction parallel to the applied electric field, we recently found that the films were also bent by applying an electric field.[14–16] This phenomenon is called bending electrostriction because the degree of the bending deformation is proportional to the square of the applied electric field.[14,15] However, to our knowledge, studies on bending electrostriction by other groups have been restricted to the articles reported by Kawai,[17,18] and the details remain uncertain. As reported in our previous article,[14] the bending electrostriction shows hysteresis, but there are no reports describing the details of the hysteresis in bending electrostriction.

The purpose of this study was to understand the mechanism and the characteristics of the hysteresis in bending electrostriction. This is necessary in order to utilize the bending electrostrictive polymer as a practical actuator. In this study, we investigated the mechanism of the hysteresis through measuring of the current during the

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Table I Raw Materials for the Preparation of the Polyurethanes

Sample Code	Raw Materials and Molar Ratio	Film Thickness
PU-1	MDI/PMPA/1,4-BD/TMP = 2/1/0.4/0.333	0.2 mm
PU-2	HDI/PMPA/1,4-BD = 2/1.3/0.7	0.5 mm

MDI: 4,4′-methylenebis(phenyl isocyanate) (Nippon Polyurethane Industries Co., Ltd., Millionate MT); HDI: 1,6-diisocyanatohexane (Wako Pure Chemical Industries, Ltd.); PMPA: poly(3-methyl-1,5-pentane adipate)diol (Kuraray Co., Ltd., Kurapol P-3010, M_n = 2945); 1,4-BD: 1,4-butanediol (Wako); TMP: trimethylolpropane (Wako).

bending deformation and a thermally stimulated discharge current (TSDC). In addition, we present the unique features of the hysteresis in bending electrostriction using two examples.

EXPERIMENTAL

The polyurethanes were prepared through the prepolymer route. The raw materials used are listed in Table I. A typical procedure is described as follows: The polyesterdiol (Kuraray Co., Ltd., Tokyo, Japan, Kurapol P-3010, M_n = 2945) (0.3 mol) was placed in a glass reactor that had a nitrogen inlet and outlet and was dried at 100°C *in vacuo* for 1 h before use. 4,4′-Methylenebis-(phenylisocyanate) (Nippon Polyurethane Industries Co., Ltd., Tokyo, Japan, Millionate MT) (0.6 mol) was charged into the reactor at 70°C. The reaction mixture was then warmed to 80°C with vigorous stirring. The reaction time was approximately 2 h, and the reaction was followed by determining the residual amount of isocyanate (NCO) groups using the conventional method of dibutylamine back titration.[19] After the theoretical NCO value was obtained, which indicates the completion of the NCO-terminated prepolymer preparation, the reaction mixture was degassed under a vacuum. 1,4-Butanediol (Wako Pure Chemical Industries, Ltd., Osaka, Japan) (0.12 mol) and trimethylolpropane (Wako) (0.1 mol) were then added to the prepolymer with slow agitation. The obtained reaction mixture was cast into a stainless-steel mold that was treated in advance with a detaching agent. After curing at 110°C for 10 h, a 0.2-mm-thick film was obtained. Using an ion-sputtering method, the prepared polyurethane film was coated with a thin gold layer on each surface as an electrode. The film was then cut into rectangular pieces of 5-mm width and 30-mm length, which were used for the following measurements:

The experimental setup for measuring the bending deformation and current is shown in Figure 1. The film was vertically suspended in air, and the top of the film was fixed. During the application of an electric field, the displacement of the free end of the film was measured using a laser displacement meter (Keyence Corp., LB-62). The current was measured using an ampere meter (Advantest Corp., Ultra High Resistance Meter R8340A).

RESULTS AND DISCUSSION

Mechanism of the Hysteresis

Figure 2 shows a typical example of the hysteresis in bending deformation when the application of an electric field (2 MV/m) was repeated. The first application for 50 s made the film gradually bend, but the second application, which was repeated at an interval of 10 s, made the film quickly bend. In addition, after 1 day, the third application was carried out, and the film led to a gradual bending at a similar speed observed during the first application.

On the other hand, the measurement of a current during these applications showed an absorption current, which also showed hysteresis (Fig. 3). The absorption current observed during the

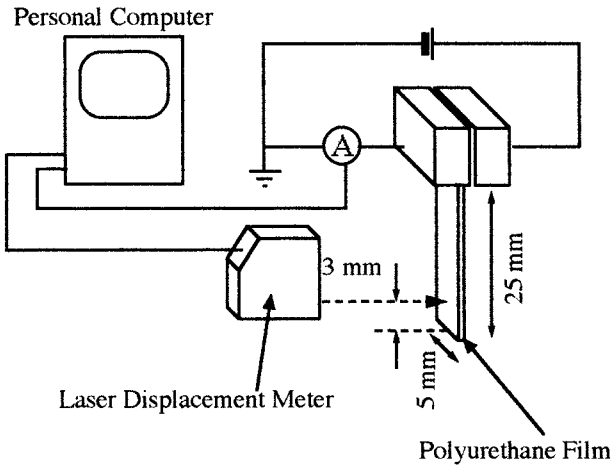

Figure 1 Schematic diagram of the apparatus used to measure bending deformation and current.

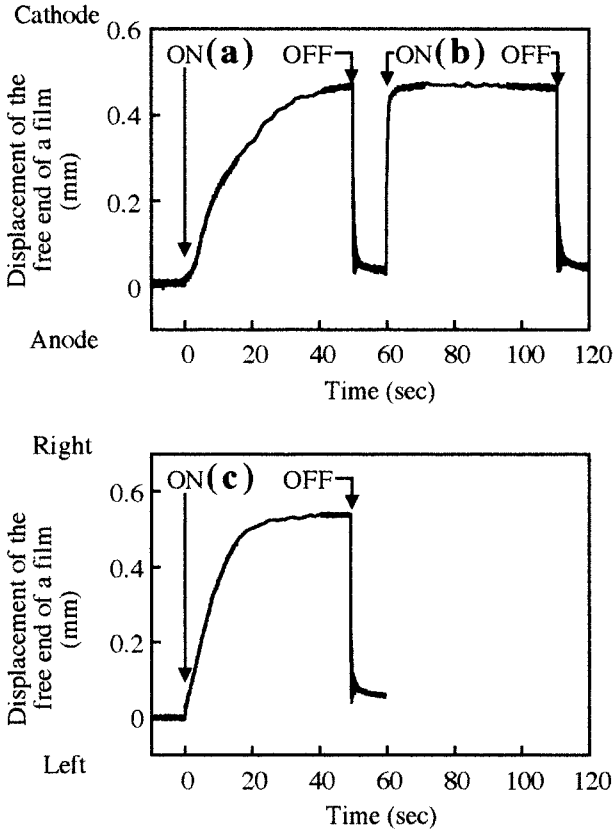

Figure 2 Bending deformation measured when the application of an electric field (2 MV/m) was repeated: (a) the first application; (b) the second application at an interval of 10 s; (c) the third application at an interval of 1 day. Sample code was PU-1.

first application was much larger than was the current observed during the second application. In addition, after 1 day, the third application was carried out, and the absorption current was almost as large as was the current observed during the first application.

As can be seen from the foregoing results, the behavior of the hysteresis in the bending deformation is similar to that of the hysteresis in the absorption current, that is, both the bending deformation and absorption current showed hysteresis when the application of the electric field was repeated at an interval of 10 s, although the hysteresis in both the deformation and current disappeared when the duration of the interval is long enough, such as 1 day. Thus, the mechanism of the hysteresis in the bending deformation can be considered to be related to the absorption current.

The causes usually considered for an absorption current are dipole orientation and ionic conduction.[20–23] In our experiments, the main cause is ionic conduction attributed to ionic impurities contained in the film. This is because removal of the ionic impurities by electrodialysis significantly reduces the absorption current as reported in our previous article.[16]

In general, the ionic conduction can change the space charge distribution in a dielectric film,[20,22,23] that is, ionic polarization and irreversible electrochemical reactions of the ionic impurities are possible causes of the change in the distribution. In our experiment, the electric-field application at an interval of 1 day caused an absorption current that was almost the same as was the current observed during the first application. This suggests that the current due to the irreversible electrochemical reactions contributed only a small part of the entire current observed. Therefore, the main change in the space charge distribution is limited to be the formation of ionic polarization.

To show that ionic polarization is certainly the cause of the hysteresis in the bending deformation, we examined the ionic polarization remaining after the removal of the electric field. This

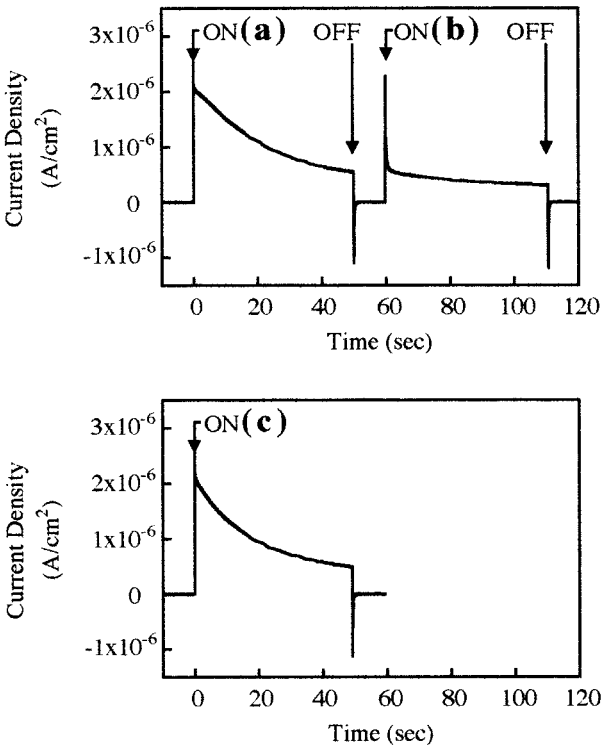

Figure 3 Current density measured when the application of an electric field (2 MV/m) was repeated: (a) the first application; (b) the second application at an interval of 10 s; (c) the third application at an interval of 1 day. Sample code was PU-1.

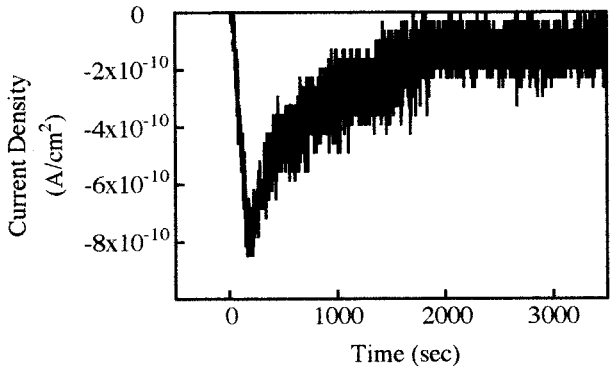

Figure 4 Thermally stimulated discharge current. Sample code was PU-1.

examination was carried out by measuring a thermally stimulated discharge current (TSDC). The TSDC measurement is a technique widely used to study residual electric charges.[13,24,25] Figure 4 shows the TSDC data measured using a simple method analogous to the usual TSDC measurement. In the method used in our experiment, a sample was first subjected to a high *dc* electric field (E = 2 MV/m) at 30°C for 15 min. After a 30-s interval, the sample was placed in a 140°C drying oven without an external bias field and the measurement of the current was started. As a result, a TSDC was observed, indicating that the ionic polarization remained at least for 30 s after the removal of the electric field. In addition, the sample was cooled to 30°C after the TSDC measurement and then the electric field was applied to the sample again. Consequently, the observed current was as large as that observed during the first application of the electric field (Fig. 5). This indicates that the space charge distribution was restored to the initial state by discharging at 140°C.

The observed TSDC (Fig. 4) was much smaller than was the corresponding absorption current (Fig. 5). Because the observable discharge in a condenser is attributed mainly to the charge induced on the electrodes, this difference suggests that the amount of the induced charge will be much less than that expected from the ionic polarization. Although the reason is still unclear, our speculation is as follows: As reported in our previous article,[15] charge injection from the electrode into the polyurethane occurs during the application of the electric field. The injected charge will cancel most of the ionic polarization, resulting in a small amount of the induced charge on the electrodes. Therefore, a smaller current flows in the external circuit during the discharging process.

Thus, the observed hysteresis and TSDC suggest that the ionic polarization of ionic impurities is the main origin of the hysteresis in bending electrostriction. As reported in our previous article,[15] we consider that the repulsion among the space charges injected from the electrode causes the bending deformation. Therefore, it is suggested that the ionic polarization formed by the first application of an electric field affects the charge injection in the second application and thus modifies the bending electrostrictive response.

Unique Features of the Hysteresis in Bending Electrostriction

Improvement of Response Speed and Shape Memory by a Prior Application of an Electric Field

As shown in Figure 2, the response speed during the second application of the electric field was much faster than that during the first application. To explain in detail, it took 30 s for the displacement to reach 0.42 mm during the first application (Fig. 6). On the other hand, it took only 0.76 s to reach the same displacement during the second application. Thus, the response speed during the second application was improved by about 40 times than that during the first application.

Another way to look at the result shown in Figure 2 is that the second application recovered the displacement with as much magnitude as that at the end of the first application in a short time, that is, the film memorized the deformation while

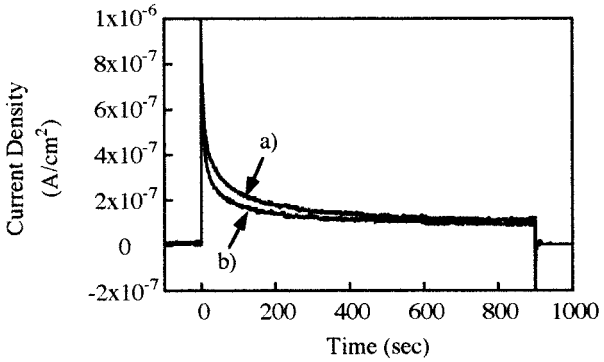

Figure 5 Current density measured during (a) the first application of an electric field (2 MV/m) at 30°C, and (b) the second application at 30°C after the discharge at 140°C. Sample code was PU-1.

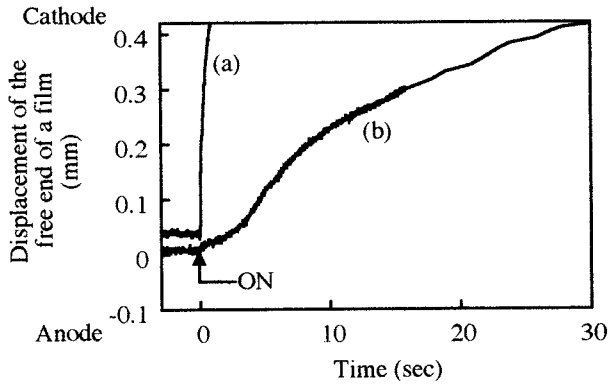

Figure 6 Bending deformation measured when the application of an electric field (2 MV/m) was repeated: (a) the first application; (b) the second application. Sample code was PU-1.

the electric field was removed, then remembered it instantly at the beginning of the next application. In this sense, this phenomenon is considered as a kind of shape memory in which an electric field can remind the sample of the electrically memorized strain.

Bending Direction and the Polarity of the Applied Electric Field

Reversion of the polarity of an electric field results in a unique bending behavior. The application of an electric field was repeated six times following the pattern shown in Figure 7(a). Although the polarities of the second and the third applications were opposite to each other, the bending directions were the same [Fig. 7(b)]. A similar relationship was observed during the fifth and sixth applications, but the measured displacements were larger than were those during the second and third applications.

The reason the bending direction was not changed by reversing the polarity of an applied electric field can be explained as follows, although the details of the mechanism are still under investigation, that is, the bending electrostriction causes the bending deformation. According to the definition of bending electrostriction, the deformation D follows eq. (1):

$$D = ME^2 \tag{1}$$

where E is the applied electric field and M is a bending electrostrictive constant. Because $(-E)^2$ is equal to E^2, the bending direction does not change with a reverse of the electric-field polarity.

Although Kawai treats M as a constant in his article,[18] we consider that, in the case of our experiment, M is changeable according to the history of the applied electric field, that is, M during the second application is smaller than is M during the fifth application. Therefore, the displacement during the second application is smaller than that during the fifth application while E was the same for both applications. On the other hand, under the condition that M can be considered constant, D follows eq. (1) for various E as reported in our previous article.[14]

CONCLUSIONS

The hysteresis in the bending electrostriction of polyurethane films is closely related to the ionic polarization of the ionic impurities contained in the polyurethane. The ionic polarization formed by a prior electric-field application influences the next bending electrostriction. For example, the prior application of the electric field significantly improves the response speed and controls the bending direction.

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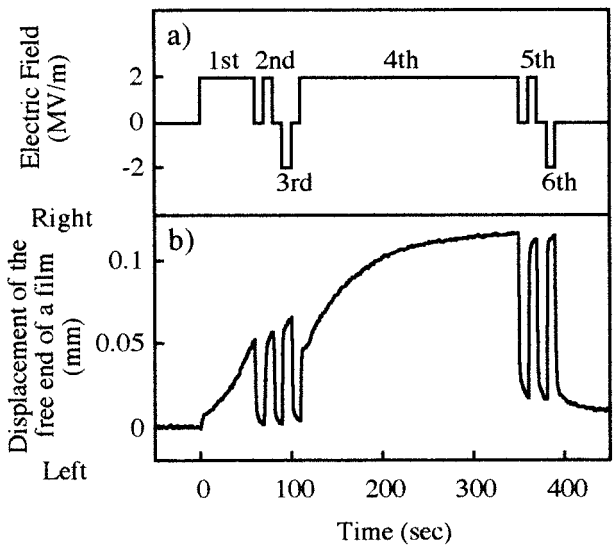

Figure 7 Application pattern of (a) an electric field (2 MV/m) and (b) bending deformation. Sample code was PU-2.

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