

Thermal Switching of the Actuation Ability of an Electroactive Polymer Actuator

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ABSTRACT: Electroactive polymer actuators have the simple ability to be actuated by a voltage. In this study, we added a new function: the ability to be actuated by temperature. We used a bending-electrostrictive actuator made of a polyurethane film. The polyurethane was designed to be rigid at room temperature but to be flexible at temperatures greater than 40°C because of the melting of the soft segment in the polyurethane. Therefore, the actuator showed slight

bending in response to a voltage at room temperature. However, it showed significant bending at 61°C. The degree of bending at 61°C was 29 times greater than that at 13°C. Thus, the actuation ability was switched on at 61°C but switched off at 13°C. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1566–1570, 2005

Key words: elastomers; polyurethanes; rubber

INTRODUCTION

Since the early 1990s, there have been many studies of electroactive polymer actuators.¹ Examples of the materials used for these actuators include conducting polymers,^{2–7} ionic polymer–metal composites,^{8–10} electrostrictive polymers,^{11–14} and carbon nanotubes.¹⁵ We have also developed actuators made of polyurethane.^{16–18} All these materials have the ability to be actuated by a voltage.

In this study, we intended to add a new function: the ability to be actuated by temperature. That is, the actuator can respond to a voltage at a certain temperature, but it cannot respond at another temperature. This new function would make it possible to control actuators in a more complicated fashion than previously possible.

We used a polyurethane actuator^{16–18} to which we intended to add the switching function. This actuator, made of a polyurethane film, can be bent by an applied voltage, as we earlier reported.^{16,17} This bending phenomenon is called *bending electrostriction*. The mechanism is related to the space charge in the film.¹⁸

In the following section, we first explain the basic structure of polyurethane as an elastic body. After that, we describe our strategy for realizing the switching function mentioned previously. A typical polyurethane is composed of hard and soft segments, as shown in Figure 1.¹⁹ The hard segment contains urethane groups, which are bonded together by hydrogen bonds. The soft segment has a polyester or polyether structure. It forms the amorphous region in the polyurethane. One of the raw materials of polyurethane is polyester or polyether diol, of which the soft segment is composed. These diols are normally liquids or low-melting-point solids. However, when the melting point of the diol is high, the polyurethane tends to harden at a low temperature. This hardening is due to the crystallization of the soft segment and is recognized as a problem in the practical use of polyurethane as an elastic body.

However, we thought of making good use of this hardening for the switching of the actuation ability. If the hardening occurs at room temperature, the polyurethane actuator will not respond to a voltage because it is too hard. However, it may be soft enough to respond at a higher temperature. This is the switching mechanism that we intended. Therefore, our strategy was as follows. The polyurethane was designed so that its soft segment had a melting point higher than room temperature.

EXPERIMENTAL

Preparation of the polyurethane film

The raw materials of the polyurethane are shown on Table I. The polycaprolactone polyester diol was sup-

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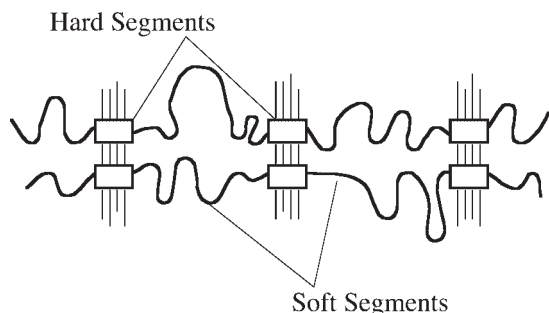


Figure 1 Hard and soft segments in a typical polyurethane.

posed to be the soft segment in the prepared polyurethane. We selected this diol because it had a melting point (48–58°C) higher than room temperature.

The polyurethane film was prepared with a two-step method (the prepolymer route).¹⁹ Before the first step, the polycaprolactone polyester diol (40.00 g) was dried in a glass reactor at 120°C *in vacuo* for 2 h. As the first step, 1,6-diisocyanatohexane (3.36 g) was charged into the reactor. The reaction mixture was stirred at 90°C for 1 h. As the second step, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (0.81 g) was added to the mixture, which was then agitated for 1 min. After the mixture was degassed *in vacuo*, it was cast into a stainless steel mold previously treated with a release agent. The polyurethane film was obtained by the mold being kept at 110°C for 18 h. The thickness of the film was about 0.18 mm.

The polyurethane film was doped with sodium acetate. This dopant was effective for improving actuation, as we earlier reported.¹⁷ The doping was carried out as follows. The film was immersed in an acetone/methanol (80/20 w/w) solution of sodium acetate (1.0×10^{-3} mol/kg) at room temperature for 12 h. After the film was dried *in vacuo*, it was coated with gold on either surface by ion sputtering with an Eiko Engineering (Hitachinaka, Japan) IB-3 ion coater. This gold coating was used as the electrode in the following experiments.

Measurements of the bending deformation caused by an applied voltage

The polyurethane film was cut into a 5 mm × 30 mm rectangle. This rectangle was used for measuring the

TABLE I
Raw Materials

Polycaprolactone polyester diol (Daicel Chemical Industries, Osaka, Japan; Placel 240, number-average molecular weight = 4000)
1,6-Diisocyanatohexane (Wako Pure Chemical Industries, Osaka, Japan)
2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (Wako Pure Chemical Industries)

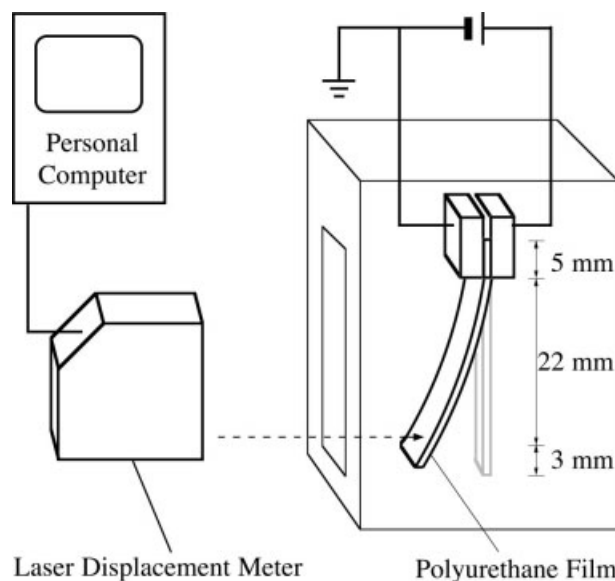


Figure 2 Experimental setup for measuring the bending deformation of the polyurethane film.

bending deformation caused by an applied voltage. The measurements were carried out with the experimental setup shown in Figure 2. The film was vertically suspended in a handmade box equipped with a heater that controlled the air temperature. Before the measurements, a direct-current electric field (4 MV/m) was applied to the film at 60°C for 30 min to improve the reproducibility of the measurements. The bending deformation of the film was measured with a Keyence LB-62 (Osaka, Japan) laser displacement meter. It measured the displacement of the film tip during the application of a voltage. The voltage source was an Advantest R8340A (Tokyo, Japan).

Differential scanning calorimetry (DSC)

The DSC curves were recorded in the ambient air with a Shimadzu DSC-60 (Kyoto, Japan) calorimeter. The temperature range was about 20–100°C at a heating rate of 10°C/min. Each sample weighed about 1.8 mg.

Dynamic mechanical analysis

The dynamic mechanical data were collected with a MAC Science TMA-4000 (Tsukuba, Japan) apparatus. The temperature range was about 20–100°C at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Thermal analyses of the polyurethane film

A DSC curve of the polyurethane is shown in Figure 3(a). It showed an endothermic peak at 51°C. Figure

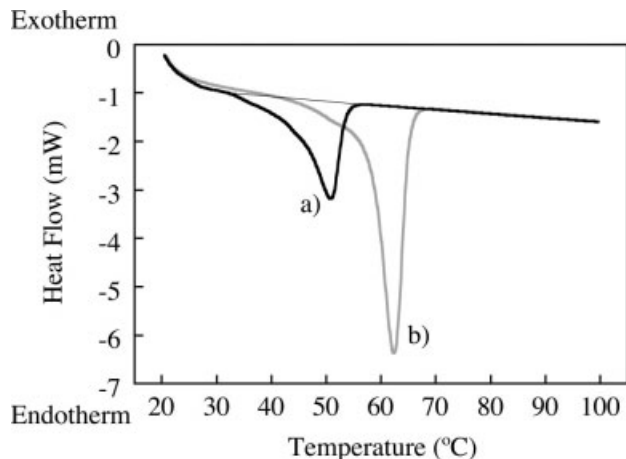


Figure 3 DSC curves for (a) polyurethane and (b) polycaprolactone polyester diol.

3(b) is a DSC curve of the polycaprolactone polyester diol, which was a raw material of the polyurethane. This curve also showed an endotherm in a similar temperature range. We attributed this endotherm to the melting of the diol on the basis of the product information from Daicel Chemical Industries (Osaka, Japan). Because the soft segment of the polyurethane was composed of the diol, the endothermic peak in Figure 3(a) was assigned the melting of the soft segment.

Dynamic mechanical analyses were also carried out. The storage modulus of the polyurethane film sharply decreased around 36°C [Fig. 4(a)]. This transition temperature was determined on the basis of the maximum of the loss tangent curve [Fig. 4(b)]. The DSC curve [Fig. 3(a)] also showed an endothermic peak, which was attributed to the melting of the soft segment, as mentioned previously. Because this endotherm started around 32°C, we assigned the transition in the modulus to the melting of the soft segment.

Actuation of the polyurethane film at various temperatures

We applied a voltage (704 V) to the polyurethane film (0.176 mm thick) at temperatures ranging from 13.0 to 60.8°C. The film was bent by the voltage. The bending responses [Fig. 5(a–f)] are shown as the displacement of the film tip. The film slightly responded to the voltage at 13.0°C [Fig. 5(a)], but it significantly responded at 60.8°C [Fig. 5(f)]. The values of the displacement were 0.02 and 0.58 mm, respectively. Thus, the response significantly depended on the temperature, although the displacement was moderate in comparison with that of other bending-electrostrictive polyurethanes.²⁰ Figure 6 presents a plot of the displacement as a function of temperature and clearly

shows a transition in the response around 40°C. Thus, the ability to respond to the voltage was switched on at temperatures greater than 40°C but was switched off below 40°C.

The mechanism of this switching could be explained as follows. The DSC measurement revealed that the soft segment of the polyurethane started to melt around 32°C [Fig. 3(a)]. The modulus was significantly reduced because of this melting [Fig. 4(a)]. That is, the rigid polyurethane film became flexible. Therefore, it was easily bent in response to the voltage.

CONCLUSIONS

Polyurethane can be designed so that its soft segment melts at temperatures greater than room temperature. An actuator made of such a polyurethane film is rigid at room temperature but is flexible at higher temperatures. As a result, the actuator does not have the ability to be actuated by a voltage at room tempera-

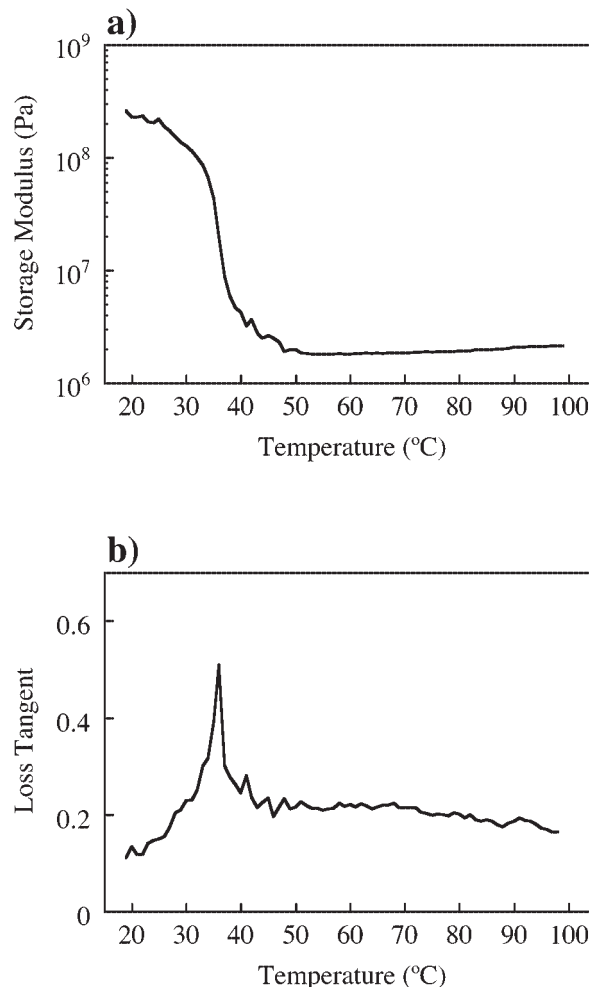


Figure 4 Dynamic mechanical analyses of the polyurethane film: (a) storage modulus and (b) loss tangent.

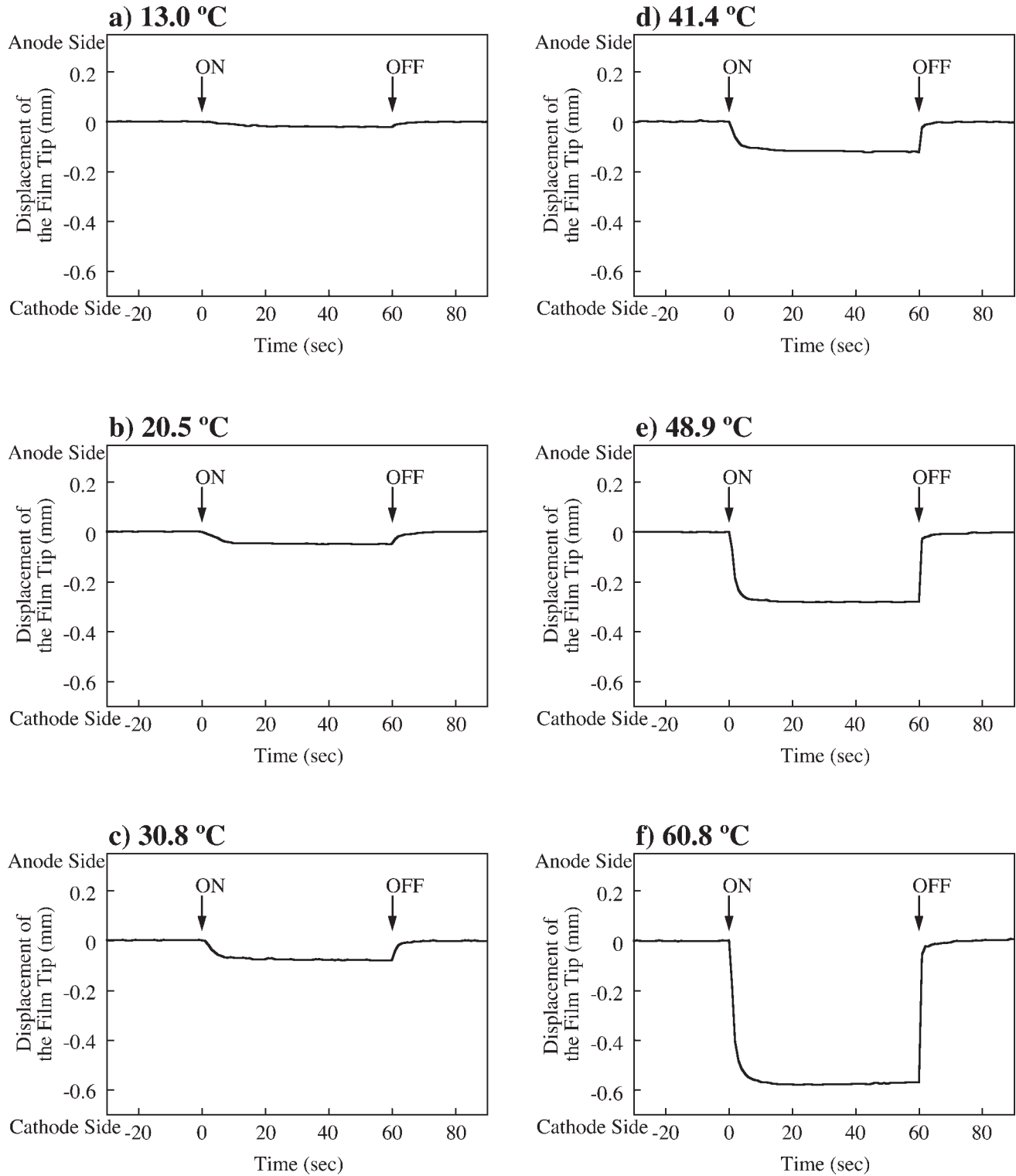


Figure 5 Bending responses of the polyurethane film at various temperatures. The applied voltage was 704 V. The thickness of the film was 176 μm . Each measurement was carried out after a preliminary application of the voltage (704 V) for 20 min at each temperature.

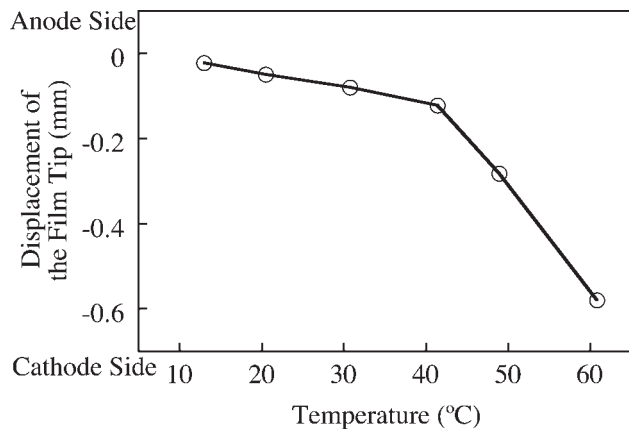


Figure 6 Bending response as a function of temperature.

ture. However, it does have this ability at higher temperatures. Thus, the actuation ability can be switched on or off by temperature. Such a switching function may be realized in another type of polymer actuator with a strategy similar to that mentioned previously.

References

1. Electroactive Polymer Actuators as Artificial Muscles; Bar-Cohen, Y., Ed.; SPIE: Bellingham, WA, 2001.
2. Baughman, R. H. *Makromol Chem Macromol Symp* 1991, 51, 193.
3. Otero, T. F.; Angulo, E.; Rodriguez, J.; Santamaria, C. *J Electroanal Chem* 1992, 341, 369.
4. Kaneto, K.; Kaneko, M.; Min, Y.; MacDiarmid, A. G. *Synth Met* 1995, 71, 2211.
5. Smela, E.; Ingnas, O.; Lundstrom, I. *Science* 1995, 268, 1735.
6. Jager, E. W. H.; Ingnas, O.; Lundstrom, I. *Science* 2000, 288, 2335.
7. Hara, S.; Zama, T.; Sewa, S.; Takashima, W.; Kaneto, K. *Chem Lett* 2003, 32, 576.
8. Oguro, K.; Kawami, Y.; Takenaka, H. *J Micromachine Soc* 1992, 5, 27.
9. Shahinpoor, M. *Smart Mater Struct* 1992, 1, 91.
10. Sadeghipour, K.; Salomon, R.; Neogi, S. *Smart Mater Struct* 1992, 1, 172.
11. Zhenyi, M.; Scheinbeim, J. I.; Lee, J. W.; Newman, B. A. *J Polym Sci Part B: Polym Phys* 1994, 32, 2721.
12. Zhang, Q. M.; Bharti, V.; Zhao, X. *Science* 1998, 280, 2101.
13. Zhang, Q. M.; Li, H.; Poh, M.; Xia, F.; Cheng, Z.-Y.; Xu, H.; Huang, C. *Nature* 2002, 419, 284.
14. Pelrine, R.; Kornbluh, R.; Pei, Q.; Joseph, J. *Science* 2000, 287, 836.
15. Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* 1999, 284, 1340.
16. Watanabe, M.; Hirai, T.; Suzuki, M.; Amaike, Y. *Appl Phys Lett* 1999, 74, 2717.
17. Watanabe, M.; Shirai, H.; Hirai, T. *J Appl Phys* 2002, 92, 4631.
18. Watanabe, M.; Wakimoto, N.; Shirai, H.; Hirai, T. *J Appl Phys* 2003, 94, 2494.
19. Hepburn, C. *Polyurethane Elastomers*, 2nd ed.; Elsevier: London, 1992; Chapter 1.
20. Watanabe, M.; Hirai, T. *J Polym Sci Part B: Polym Phys* 2004, 42, 523.