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Piezoelectric effect and Actuator Mechanism of Fullereneol doped Polyurethane Elastomer (PUE)

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Introduction

Polymer gels have been actively studied for the application to functional materials and moving devices [1,2]. There are many methods on the moving mechanisms of polymer gels. In these methods, the volume change of gels are large, but their response is slow and the control is difficult for the substitution of ionic solvent. Then, we synthesized the polyurethane elastomer films like a polymer gel. PUE films are composed by molecular structure having the hard segments and the soft segments, by replacing a role of ionic solvents with a polymer chain itself, both segments are similar to the relation of micro crystals and solvents in polymer gel [3]. Since these films were found to show the electrostriction effect, they are expected to work as the moving devices without solvent which respond to high speed under an electric field [4].

We have proposed the application to actuators fabricated by PUE films and two kinds of metal electrodes which were evaporated on the both surfaces of films by thermal or ion implantation deposition method. It tried to control the structure of films by doping C_{60} derivatives (fullereneol) into PUE so that the actuators could operate at a low voltage [6,7].

It also cleared that the fullereneol doped PUE films take place a piezoelectric properties by press on the film surfaces or pull at the films. We found the first time about the piezoelectric effect of the fullereneol doped PUE films.

Experimental

PUEs were synthesized by conventional pre-polymer method and were polymerized in the form of films with thickness from 100 μm to 400 μm by casting method [3]. The PUE actuators are monomorph type which were formed by aluminum or gold electrodes on the both surfaces of films using PVD technique such as thermal or ion implantation methods after corona discharge treatment.

The morphology of film controlled by doping the sulfurated C_{60} derivatives into PUE. The reaction from the C_{60} to the sulfurated C_{60} derivative carried out by adding oleum to destroy double bonds of fullerene. That C_{60} derivative is obtained having hydroxyl groups. The reaction until sulfurated fullerene derivative (fullereneol) was analyzed to measure the functional groups using the Furrie Trans-formation Infrared (FT-IR) absorption spectrum. The number of the hydroxyl groups is not measured, but it is assumed that the C_{60} contains 10 to 12 hydroxyl groups [5].

Detail measurement methods for the electrical and the dielectric properties of both PUE films and actuators have been reported [3,4].

Results and Discussion

PUE films of polyester type with 1mm thickness which applied to the voltage of 1 KV appear the large strain and indicate the stable response with respect to the voltage "on" and "off". The strain of PUE films increased with increasing an applied electric field, and these films showed a typical

electrostriction effect. Since this film stretches by electro-striction effect due to an electric field, PUE film itself is to bend by putting a metal electrode of different thickness on both surfaces of films. Figure 1 shows the PUE actuator of monomorph type.

The bends of PUE actuators varied in proportion to the squared of an electric field as shown in Fig.2. First, it was considered that the bending mechanism take places by different thickness of metal electrode based on stretch of the PUE films. But, when the thickness of metal electrodes thinned until 200 nm and were same, all of actuators were found to bend in the direction of negative electrode by an applied voltage. Bend of PUE actuator didn't depend on the thickness of metal electrode and its materials. Because the PUE films have many polar groups in the soft segment, it is considers that the bend of actuator occurs by stretching of molecular chains due to an orientation of the polar groups under an electric field.

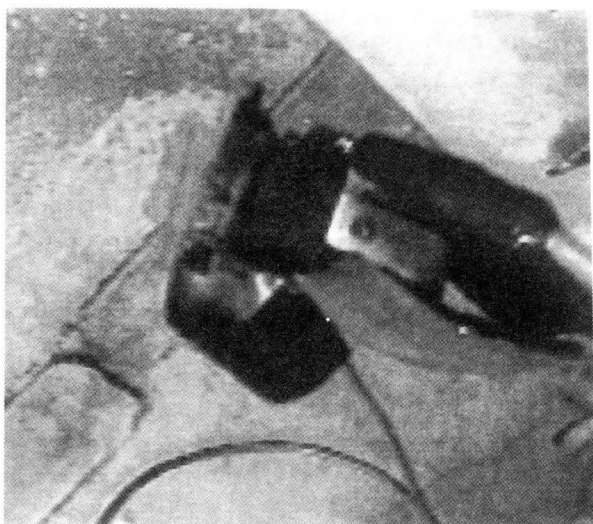


Fig.1 Monomorph type PUE actuator.

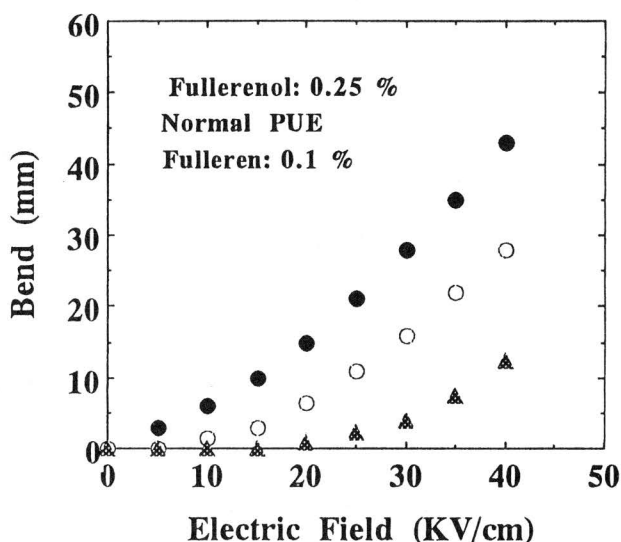


Fig.2 Dependence of the bends of several kinds of actuators on the electric field.

Working voltage of PUE actuator using the film thickness of 200 μm are more than 1 KV and these voltages are so high. It is very difficult to use commercial devices. We tried, therefore, to dope the C_{60} derivative into PUE so that monomorph actuators could obtain the large bends at a low voltage. Figure 2 also shows the bends of actuators using the non-doped PUE film, the film doped fullereneol concentration of 0.05%, and the film doped only C_{60} of 0.1%. The bends of fullereneol doped PUE actuators increase with increasing the concentration of fullereneol in PUE. In the case of fullereneol concentration of 0.25% showed maximum bend, and also fullereneol doped actuator were found to bend about three times larger than that normal films at 300V as shown in Fig.2. On the contrary, the bends of PUE actuator dispersed C_{60} became small compare with normal PUE actuator. This actuator was clear to bend at low voltage by doping fullereneol.

The large bend of the fullereneol doped actuators is considered that the crosslinking density increased in the PUE films by combining the hydroxyl groups of the star shaped fullerenols which were doped into hard segments. That is, by progressing the crosslinking density of PUE films, the apparent polar groups in soft segment increase. This effect is understood that the bends of PUE actuator doped C_{60} is smaller than non-doped actuator. All of PUE actuators indicated a polarity effect as a result of the orientation of polar groups. If the many polar groups are formed in molecular chains by crosslinking as mentioned above, the bending direction of actuator can be explained.

Then the relative dielectric constants were measured to clear the role of polar groups in PUE films. Figure 3 shows the dependence of the relative dielectric constant for the non-doped films, the fullereneol (0.25%) doped films and C₆₀ doped films under the applied voltage. The relative dielectric constant increase with increasing the applied voltages for the various kinds of PUE samples as shown in Fig.3. Especially, the apparent dielectric constant of the fullereneol doped film

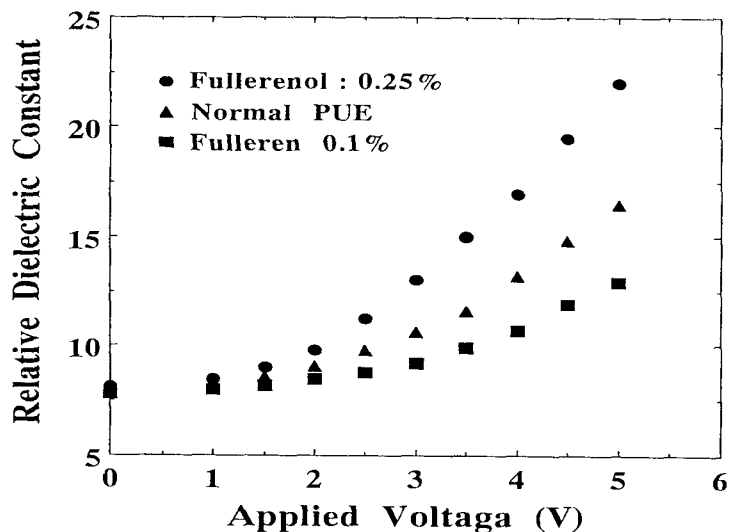


Fig.3 Dependence of the apparent dielectric constant of PUE films on applied voltage.

remarkably increased compare with another PUE films. This is explained that the apparent polar groups per a molecular chain increased to progress the crosslinking reaction of the star shaped fullereneol in the hard segments. Their results is supported the polarity effect of bends for the PUE actuators. The dipole moments originated from polar groups in the soft segments were cleared to play important role for bend of the PUE actuators in the case of thin electrode.

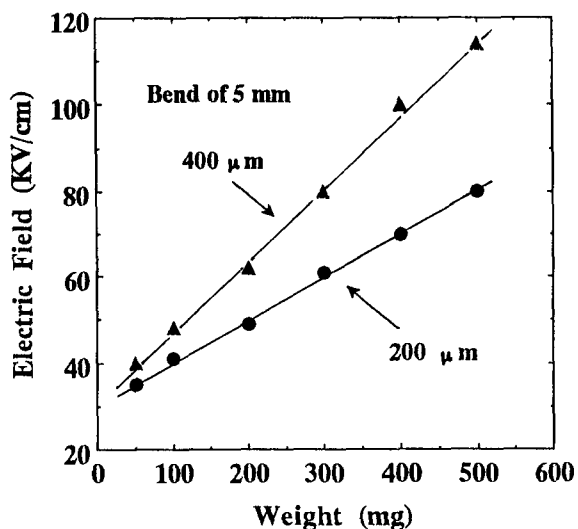


Fig.4 Induced forces, viz. the relation of electric field to weight of the PUE actuators.

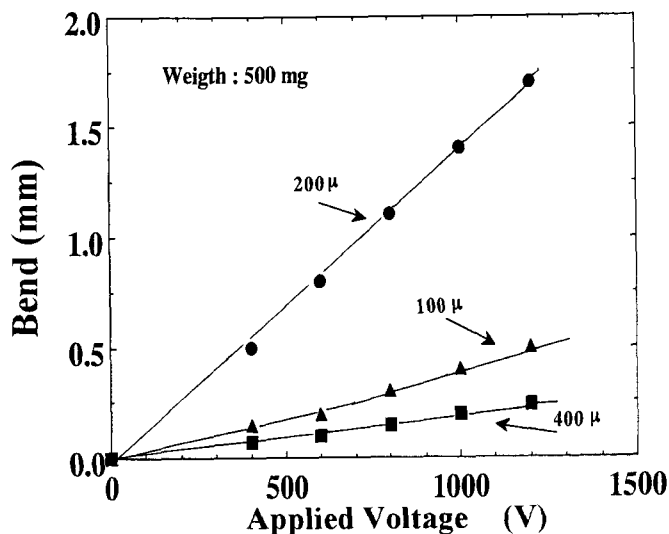


Fig.5 Dependence of the induced forces for different film thickness on applied voltage.

To obtain the induced force of actuators, it measured to put a weight to the PUE films. This force were proportional to the applied electric field with both 200 μm film and 400 μm film as

shown in Fig.4. Induced force also increased with increasing the concentration of fullerene and remarkably depended on the film thickness. In these actuators of different film thickness, 200 μm films induced the largest force under same applied voltage as shown in Fig. 5.

Furthermore, we measured a piezoelectric effect in order to clear the bending mechanism of fullerene doped PUE films. These films cleared to show a piezoelectric properties by press on the film surface or pull at the film. We found the first time about the piezoelectric effect of the fullerene doped PUE films. This phenomena could not obtain for non doped PUE films. Figure 6 indicate an induced voltage appearing on the surface of fullerene doped PUE films. The induced voltages depend on a pulling force and its maximum voltage reached at 7mV. The response of an induced voltage was very stability.

This interesting study about piezoelectric effect is in progress.

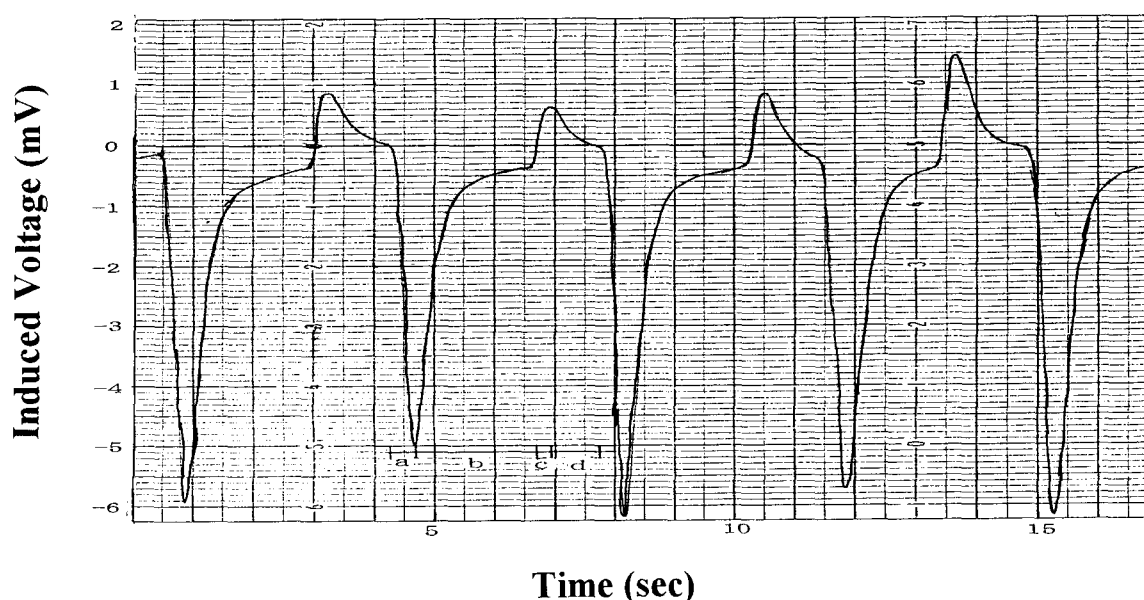


Fig.6 Response curves on the induced voltage by pulling at the fullerene doped PUE films.
(a): pulling, (b)-(d): releasing, (c): appearing of inverse voltage, (d): returning to 0 voltage

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