Solidification Thickness Dependent Electrostriction of Polyurethane Films

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To obtain large electrostriction (S_{max}) at low electric field (E_{max}), a dependence of the solidification thickness (L) on S_{max} was investigated for polyurethane films. Thinning the films remarkably enhanced S_{max} at high E_{max} at 20 MV/m, whereas thick films apparently exhibited higher S_{max} at low E_{max} of less than 3 MV/m. The L dependent S_{max} from 5.01% for 140 µm thickness to 30.99% for 28 µm thickness exhibited linear relationship of pure polyurethane. Considering crystalline volume fraction and crystalline periodicity, the L dependent S_{max} was explained.

Keywords: electrostriction, electro active, crystalline periodicity

1. Introduction

Polyurethane (PU) is one of the most versatile materials in the world today. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances to thermoplastic pure PU used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interiors.¹)

Over the last two decades, the field of electrically controllable polymer actuators has developed significantly because their performances are comparable to those of natural muscles. Pure PU elastomers are one of the most important class of polymers due to some remarkable electromechanical characteristics such as large electric field induced strain, high specific energy and fast speed of response.²–⁶) This makes the material very attractive for many electromechanical applications. Many electroactive strain properties of the PU were investigated but the fundamental mechanisms which are responsible for the electrostriction have not been yet well understood.⁷)

We found that the thermal absorption on melting of DSC thermal analysis often corresponds to data of electrostriction. Crystalline volume fraction may contribute to the electrostriction. If the volume fraction of surface crystallization on solidification is controlled by solidification thickness, the experimental error can be explained to obtain the reproducible data. Thus, the influence of solidification thickness on electrostriction has been investigated for pure polyurethane before making composites to confirm the standard to prepare the composite films.

The purpose of the present paper is to report the influence of solidification thickness on electrostriction of the pure polyurethane films.

2. Experimental Procedure

2.1 Pure polyurethane films

Pure polyurethane (PU) film was prepared by a simple solution cast method.⁸–¹²) One gram of PU granules (Noveon Estane 58888 NAT021, Lubrizol Corporation, Wickliffe, OH, USA) was dissolved in approximately 20 ml of N,N-dimethylformamide (DMF) at 85°C for 45 min. The solution was poured onto a glass plate and dried at 60°C at atmospheric pressure for 1 day. The obtained films were removed from the plate with ethanol. Subsequently, they were placed in a ventilated oven at 130°C for 4 h in order to eliminate residual solvent. The thicknesses of the films varied between 28 and 140 µm. For the electromechanical characterization measurements, metal electrodes were placed on both sides of disc-shaped specimens (25 mm in diameter).

2.2 Thickness strain measurements

The field-induced thickness strain (S) was measured by a laser interferometer (Agilent 5519A) with a precision on the order of 5 nm. The induced electric field (E) was a sawtooth wave for 2-cycles at 0.1 Hz. Its maximum (E_{max}) was varied with an upper limit at 20 MV/m. The film samples were placed on a horizontal brass disc (20 mm in diameter) in order to avoid measuring a parasitic flexural motion, and a second brass disc placed on the upper side of the film rendered it possible to apply a bipolar electric field. A function generator (Agilent 33220A) delivered the corresponding bipolar voltage amplified by a factor of 1000 through a high-voltage lock-in amplifier (Trek 10/10B). The ground current between the sample holder and the ground was measured using a current amplifier (Stanford Research Systems SR570).

2.3 Characterization

X-ray diffraction (XRD; D8 ADVANCE, BRUKER) was used to confirm the internal structures of periodicity of pure PU films with different thicknesses. The change in strain probably corresponds to the periodicity perfection of hard and soft segments. To evaluate the periodicity perfection, X-ray diffraction was carried out. The peak width corresponds to the periodicity perfection. Differential scanning calorimetry (DSC: 131Evo, SETARAM, France) analysis was used to confirm the volume fraction of crystalline of pure PU films with different thicknesses. The endothermic heat is usually generated by transformation from crystal to liquid on melting. It corresponds thus to volume fraction of crystalline form in material. The fusion enthalpy values were obtained by area of endothermic peak.
3. Results

Figure 1 compares the typical strain outcome for pure PU for two different thicknesses of 28 µm for Fig. 1(a) and 140 µm for Fig. 1(b). The image of the electric field is represented in the figure by a bold line.

A comparison between Figs. 1(a) and 1(b) shows that the electrostrictive strain, measured at constant electrical field, is strongly depends on the sample thickness. Ratio around 6 can be found on the strain amplitude and it is clear that decreasing the thickness leads to a huge strain enhancement. For low field values, the strain presents a triangular shape similar driving field. For high field level, the curvature is inversed.

Figure 2 shows the strain amplitude (S_max) versus the applied field (E_max) for different pure PU films with different thicknesses. As mentioned earlier the thickness effect is obvious. Thinning the films remarkably enhance the S_max more than 30% at high E_max at 20 MV/m, whereas thick films apparently exhibit the higher S_max at low E_max of less than 5 MV/m.

The strain saturation (S_max: 5.22%) occurs at 3 MV/m for thick sample. On the other hand, although the thin sample shows the high S_max value, the strain saturation can not be found.

4. Discussion

4.1 Thickness dependent electrostriction at 20 MV/m

Figure 3 shows the logarithmic linear relationship between the thickness (L) and the maximum strain (S_max) at 20 MV/m of pure PU films. Thinning the films enhanced the S_max. The linear relationship between logarithmic L from 140 to 28 µm thicknesses and logarithmic S_max from 5.01 to 30.99% was obtained for the pure PU film.

The starting point of the convergence occurred at a lower electric field for the thick films as opposed to for the thin films. There are thin sample which do not have convergence. Particularly, the 28 µm thin pure PU film does not show clear convergence till 20 MV/m. It was able to generate a strain of more than 30%. Such a strain level is not surprising for actual EAPs. But important is that traditional EAPs must require much higher electric field to generate such strain level.

The films presented herein can thus generate a significant S_max change with E_max from 5 to 20 MV/m. This should render possible applications in associated with other electric devices.
The extremely low $S_{\text{max}}$ values of extremely thin film with 28 $\mu$m thickness is found in the Fig. 3. As the comment of final sentence at the end of discussion, it is explained by thickness reduction of crystalline.

4.2 Surface crystallization model from glass to crystalline form of hard segments

The results show that the $S_{\text{max}}$ of films depends on thickness. The thin pure PU film shows high strain at 20 MV/m. In order to evaluate volume fraction of crystalline, the DSC analysis is performed. The fusion enthalpy values were obtained for thin and thick PU films.

DSC analysis was carried out to see the fusion enthalpy value of thin and thick films, 18–22 $\mu$m and 126–135 $\mu$m, respectively. These selected thicknesses correspond to the ones of Fig. 2 shown in Fig. 4.

Endothermic heat from crystal to liquid on melting of thick pure PU film is smaller than that of thin pure PU film. The fusion enthalpy value (12.1 J/g) of thin pure PU film is 1.24 times higher than that (9.78 J/g) of thick pure PU film. Thus, it is clear that the high electrostriction of pure PU thin films can be contributed by high volume fraction of surface crystalline.

Although the crystalline volume fraction strongly contributes to the electrostriction, the large change in electrostriction quantitatively cannot correspond to the volume fraction. Thus, the crystalline periodicity should be considered.

Figure 5 shows the X-ray diffraction peaks of thin and thick pure PU films. Most of the sharp peaks are related to thin pure PU film, whereas the broad peak is related to the thick pure PU film. The big broad peaks from 12 to 29 degree for thick film and from 16 to 26 degree for thin film were found at about 20 degree for soft segments. The sharpness with intensity and width of the peak corresponded to an enhancement of the periodicity. An additive effect to compressive electrostriction could be gotten, when the periodicity enhancement raised the polarizability. Namely, the angle width of thin pure PU film is smaller than the thick one. The angle width corresponds to the periodicity of soft segments.

In addition, remarkable sharp peaks at 28.7 and 26.7 deg of hard segments were found in thin films, whereas they were not observed in thick film. Thus, it is possible that thin film enhances the molar volume and/or their preferred orientation ratio of hard segments and probably enhances the polarizability, resulting in an additive effect to compressive electrostriction.

The pure PU (thin and thick) films show thickness effect. Furthermore crystallized volume fraction and crystal perfection were confirmed to have changed by thickness difference. In other terms, we can say that constituting thin film presents different characters from thick film.

These films were fabricated by solution cast method. The films were solidified on a clean surface. After the films were removed from the glass plate, they were dried again in high temperature. Two surfaces were in contact with heated air at that time. Explanation can be given. One is the thermal conductivity in material and the other is the oxidation from the surfaces. It is possible that formation of a crystal starts from the surfaces due to the thermal gradients. A property gradient takes place (For instance ratio soft/hard segment...). Outside of film can have different morphology to the one of inside. In other terms, film can have skins. Neither DSC nor XRD can see the different of layers in material, but the results do not against to this hypothesis. The crystallized volume fraction and crystalline perfection of thin film are higher than thick film.

Figure 6 is inferred from there result. There are only skins of thin sample. There are skins and inner layer for thick sample from the fact that there were no out-plane motion when electric field was inducted. The model was done with three layers to keep the symmetry in thickness direction. In this model, the polymeric material is considered to have a skin effect that might have occurred during the fabrication processing. The large strain of thin films is estimated being generated by the strong isotropy, when the hard segments like the crystal structure. On the other hand, when the volume
fraction of crystallization in material is not so high in the thick film, the low strain can be obtained because of its anisotropy. The layer model can be the method to explain the thickness dependence on electroactive strain.17)

5. Conclusion

In order to obtain the large electrostriction ($S_{\text{max}}$) at low electric filed ($E_{\text{max}}$), a dependence of the solidification thickness ($L$) on $S_{\text{max}}$ was investigated for pure polyurethane films.

1. Thinning the films remarkably enhanced the $S_{\text{max}}$ at high $E_{\text{max}}$ at 20 MV/m.
2. Thick films apparently exhibited the higher $S_{\text{max}}$ at low $E_{\text{max}}$ of less than 5 MV/m.
3. The $L$ dependent $S_{\text{max}}$ from 5.01% for 140 µm thickness to 30.99% for 28 µm thickness at 20 MV/m exhibited linear relationship of pure polyurethane.
4. The starting point of the convergence occurred at a lower electric field for the thick films as opposed to for the thin films. Thin samples do not have convergence until 20 MV/m.
5. Considering with crystalline volume fraction and crystalline periodicity, the $L$ dependent $S_{\text{max}}$ was explained.

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