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Electrostrictive response in polyurethane films containing lithium ionic impurities

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The influence of the added lithium ions on the electromechanical response in the unelectroded films of polyurethane based on poly(caprolactone)diol, 1,4-butane diol and isofuran diisocyanate under static electric field was investigated. Longitudinal strain, stress-strain and dielectric measurements were carried out on films with various thicknesses under ambient conditions. On the basis of these measurements the electromechanical parameters such as thickness strain, apparent electrostrictive coefficient, effective pressure, mechanical energy density, response time and Maxwell effect contribution were determined. Induced strain depended quadratically on the electric field, which is consistent with an electrostrictive response. The induced strain increases with film thickness tending to reach a plateau for higher values. As compared to the original samples (no added ions), the added lithium ions enhance the strain response only in films thicker than about 50 µm. The electromechanical parameters are improved in the same thickness domain. The results show that addition of lithium ions can improve the actuation performances of the polyurethane investigated.

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1. Introduction

A special attention has been given to the polyurethane elastomers due to some remarkable elecromechanical characteristics such as large electric field induced strain, high specific energy and fast speed of response for moderate external applied electric field [1-13]. These properties make the material very attractive for many potential induced strain applications [1,2,3,8]. On the other hand, some electrostrictive properties are not well understood.

Few reports are dealing with the influence of the ions impurities on the electrostrictive response of the polyurethane elastomers. These are restricted to the reports of Watanabe at all [14] on the bending electrostriction and Su at all [4] on the transverse electrostriction under alternating electric field. To our knowledge no paper concerned with ionic effects on the longitudinal or transversal electrostriction under an electrostatic field was reported.

Recently, we reported that the polyurethane based on poly(caprolactone)diol, 1,4-butane diol and isofuran diisocyanate shows an remarkable electrostrictive behaviour under static electric field and its electromechanical parameters depend on the film thickness [15].

In this paper we will show the influence of the lithium ionic additives on the longitudinal electrotriction in the same material films of various thicknesses under static electric field.

2. Experimental

From a synthesized polyurethane based on poly(caprolactone)diol, 1,4-butanediol and isofuran diisocyanate with molar ratio 1:2:3, films with various thicknesses were prepared by casting dilute polymer solutions on glass plates. After the films were dried for 24 h at 60 ºC under air atmosphere, they were soaked in an acetone/methanol (80/20, v/v) mixed solution of lithium chloride, dried again and used for measurements.

The static electric field induced strain in thickness direction of the unelectroded films was measured under ambient conditions using a modified Michelson interferometer and a He-Ne laser as light source specially designated for characterising the strain response in unelectroded thin polymer elastomer films [11].

The Young's modulus was determined from the stress-strain curve recorded in air at room temperature with a crosshead speed of 100 mm/min. using a TIRA-Test device. The dumbbell-type specimen was 3.8 mm wide and 42 mm long for the neck.

Dielectric constant measurements were carried out on films with vacuum evaporated silver electrodes by a BM 507 TESLA impedancemeter in the frequency range from 100 Hz to 500 kHz under ambient conditions.

3. Results

Fig. 1 shows the induced longitudinal strain of three representative polyurethane films versus static electric field. Before sample measurement, a preliminary electric field of 10 MV/m for 10 min. was applied. The electric field was brought to zero after each measurement. The strains were entirely recovered as the electric field was off over the whole range considered here. Compression in thickness direction of the film was observed irrespective of the applied electric field sign. Also, a symmetrical strain profile was found against inversion of the electric power polarity.

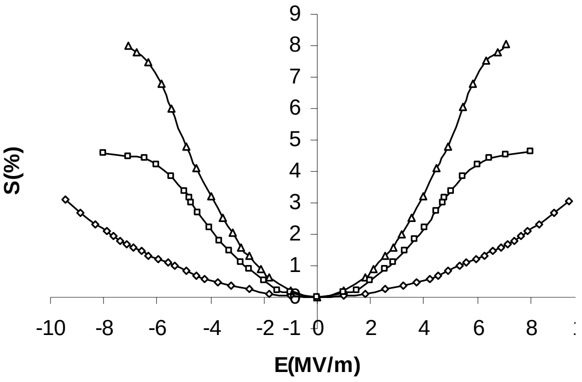

Fig. 1. Dependence of strain on electric field: ◊ - sample 1; □ – sample 4; Δ – sample 5 (Table 1).

The induced strain increases with film thickness tending to reach a plateau for highest values (Fig. 2). Previously [15], we found that the thickness dependence of the induced strain in original films presents a maximum at about 50 μm (Fig. 2).

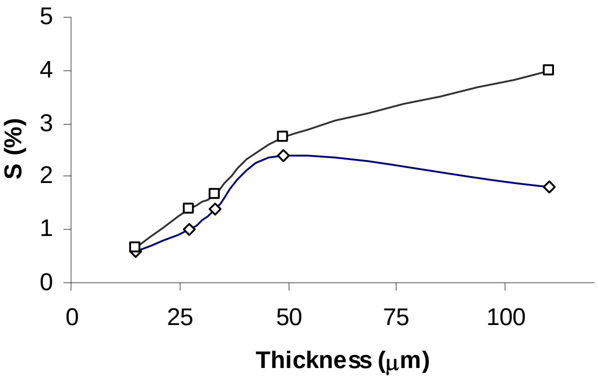

Fig. 2. Thickness dependence of the induced strain in polyurethane films measured at 4.5 MV/m: □ films contaminated with lithium ions; ◊ original films [15].

Up to about 50 μm, lithium ions slightly influence the induced strain, whereas over this value an obvious enhancement occurs with thickness.

The electric field dependence of the strain can be more clearly observed in Fig. 3. Up to a certain value of the electric field, which depends on the film thickness, the induced strain presents a quadratic dependence, whereas at higher values the strain tends to reach saturation.

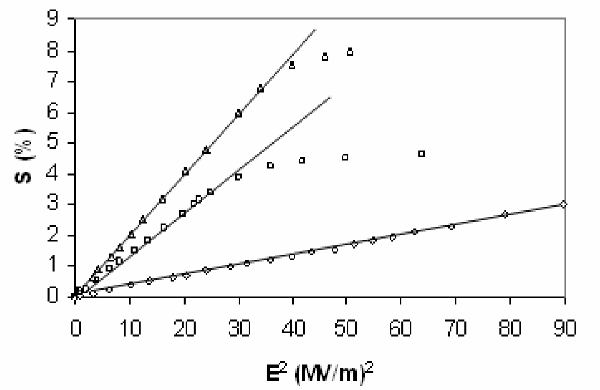

Fig. 3. Dependence of the strain on the square applied electric field; ◊ - sample 1; □ – sample 4; Δ – sample 5 (Table 1).

From the slope of the straight lines, the apparent electrostrictive coefficients were determined (Table 1). The electrostrictive coefficient increases with film thickness. For films up to about 50 μm, the electrostrictive coefficient values are similar to those found in corresponding original films, whereas for thicker films they are much higher [15].

For example, M = 8.92 m^2/V^2 in original sample with 110 μm. This fact could explain the enhanced strain in contaminated films as compared with original samples. The values reported in the literature on unelectroded polyurethane films are similar [11,12,13] or much lower [1].

From the strain-time curves, the response times were determined. A representative example is presented in Fig. 4.

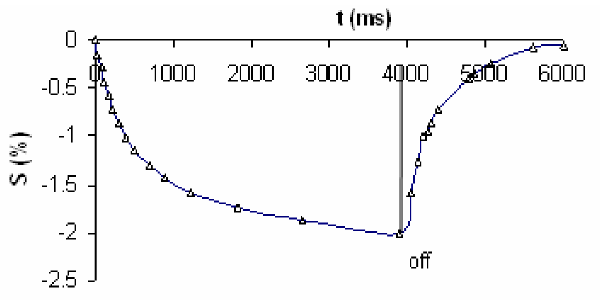

Fig. 4. Time response of contraction and relaxation processes in sample 5 at 3.2 MV/m.

The response times depend on the film thickness (Table 1), present a steady strain and are smaller than those in the original samples [15].

The Young's modulus of the films increases with thickness (Table 1), indicating that in thicker films the phase segregation process into soft and hard domains is more pronounced [16]. Note that films of various thicknesses were obtained by casting polymer solutions of different concentrations. Previously, we reported that mechanical behavior of the polyurethane elastomers depended on the phase segregation degree in polymer films, which in turn could be determined, among other things, by the processing conditions of samples [16].

Table 1. Electromechanical and mechanical parameters of the polyurethane films.

Sample	Thickness (μm)	S (%)	Y (MPa)	*p* (MPa)	*w* 10^3 (J/cm^3)	M 10^{16} (m^2/V^2)	τ (ms)	S$_M$/S (%)
1	15	0.70	4.236	0.029	0.10	3.44	4300	2.82
2	27	1.30	12.285	0.16	1.04	6.60	5000	0.51
3	33	1.70	55.313	0.94	8.00	8.50	5800	0.08
4	49	2.75	52.46	1.44	19.80	13.64	6800	0.06
5	110	4.00	57.87	2.31	46.20	20.00	2640	0.04

Note: values of the electromechanical parameters are determined for *E* = 4.5 MV/m

Young's modulus values are similar to those found for original films [15]. Therefore, it seems that the added ions do not change significantly the morphology of films. As shown in Fig. 5, the dielectric constant was found a little smaller than in original samples and the frequency dispersion is quite appreciable. The dielectric constant does not depend significantly on the thickness.

It may be concluded that the addition of lithium ions improves the electromechanical parameters S, M and τ of polyurethane investigated especially for thicker samples.

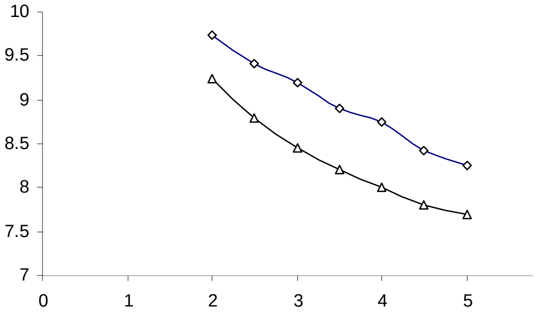

Fig. 5. Dielectric constant vs. frequency: ◊ - original films; Δ - contaminated films.

4. Discussion

When an electric field is applied to unelectroded isotropic dielectric sample, the induced strain is a superposition of pure quadratic electrostriction and strain caused by electrode attraction (Coulomb interaction) [1,6,11]. The contribution of the pure electrostriction can be expressed [6,11] as

$$S_E = -Q\varepsilon_0{}^2(\varepsilon_r - 1)^2 E^2 \tag{1}$$

where S_E denotes the induced strain, E is the electric field strength, ε_r is the relative dielectric constant, ε_0 is the vacuum dielectric permittivity and Q is the pure electrostrictive coefficient.

The electrostatic induced strain (Maxwell effect) is also proportional to the square of the applied electric field. As we previously reported [11], under the actual experimental conditions, the induced strain can be expressed as

$$S_M = -\frac{\varepsilon_0\varepsilon_r}{2Y}E^2 \tag{2}$$

where Y is the Young's modulus.

The measured experimental strain S is

$$S = S_E + S_M = ME^2 \tag{3}$$

where M is apparent electrostrictive coefficient

The percentage of the Maxwell contribution to the global induced measured strain can be evaluated from the relation

$$\frac{S_M}{S} = \frac{\frac{\varepsilon_0\varepsilon_r}{2Y}}{M} \tag{4}$$

which is found from relations (2) and (3).

The Maxwell effect decreases with film thickness (Table 1) and is similar to that found in original samples [15]. This fact could be mainly attributed to higher value of the Young's modulus for thicker samples (see relation 2). On the other hand the global induced strain was found higher for thicker films (Fig. 2). Therefore, according to the relation (3), the pure electrostriction could originate from the hard domains of the films.

If, for low strains, the Hooke's law is supposed to be valid, then other two important electromechanical parameters such as effective compressive pressure *p* and mechanical energy density *w* can be calculated:

$$p = SY \tag{5}$$

$$w = \frac{1}{2}YS^2 \tag{6}$$

Both parameters depended on the film thickness in the same manner occurred in the case of the induced strain (Table 1) and are higher than those found in original samples (p = 1.071 MPa and w = 10^{-2} J/cm^3 in original film 5) [15]. These values are quite remarkable in comparison with those previously reported on others polyurethane elastomers with rigid electrodes; 0.9 MPa and 0.032 J/cm^3 at 16 MV/m [11] and 1.9 MPa and 0.1 J/cm^3 at 160 MV/m [8].

Note that the parameters presented in Table 1 are calculated for a static electric field of only 4.5 MV/m.

5. Conclusion

The addition of the lithium ions improves the electromechanical parameters of investigated polyurethane films especially for thickness higher than 50 µm. This fact could be attributed to the increased values of pure electrostrictive coefficient of hard domains.

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