Electrostrictive Effect in Polyurethanes

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ABSTRACT: Polyurethane electrostriction was investigated by measuring the tensile electromechanical coupling coefficients of structurally different materials. True values of the strain coefficients M_{3311}, M_{3322}, and M_{3333} were obtained for four types of polymer: one commercial polyurethane (DOW 2103-80 AE) and three polyurethanes synthesized at the Naval Surface Warfare Center, including two phase-separated (PS) materials with molecular weights of 1000 and 2000 and one phase-mixed (PM) material with a molecular weight of 2000. Measurements were performed at 2 kHz under a bias field of 4 MV/m at room temperature. Measured values of M_{3333} ranged from -9.4×10^{-18} to -74.6×10^{-18} m^2/V^2, with the PM material exhibiting the largest coefficient. The electrostatic interaction (Maxwell stress) did not account for more than 15% of the total electromechanical activity in any of the materials. Furthermore, at the macroscopic level, an empirical relationship was established to predict the values of the electrostrictive coefficients from the dielectric constants and the compliance coefficients of the material. Finally, results indicated that, at the microscopic level, the phenomenon of electrostriction in polyurethanes could be best explained by the presence of charges inside the material (space–charge theory). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 399–404, 2003

Key words: polyurethanes; elastomers; stress; dielectric properties; electrostriction

INTRODUCTION

Since the discovery of a large electrostrictive effect in some polyurethane elastomers,[1] relatively few advances have been reported in either the fundamental understanding of the phenomenon or its practical application. Furthermore, the number of articles currently available that deal with the measurement of polyurethane electrostrictive properties is quite limited.[2–5]

Several macroscopic models have been introduced in an attempt to derive theoretical relations between electrostrictive coefficients and other macroscopic properties such as dielectric constants and elastic compliances. Popular references on this topic include Anderson,[6] who evaluated electrostrictive coefficients using a model dielectric of linearly polarizable point dipoles and a Lorentz cavity approach; Katz and Nelson,[7] who developed a model for the susceptibility of the material, taking into account the orientation of urethane group dipoles in an electric field; and Shkel and Klingenberg,[8,9] who proposed a new approach based on mean-field calculations and the consideration of probability distribution functions to model an amorphous microstructure. Unfortunately, all of these models predict much smaller coefficients than those experimentally measured.

At a more fundamental level, there exist two microscopic hypotheses that propose to explain the basic mechanisms responsible for polyurethane electrostriction. One hypothesis, put forth by Balizer and colleagues,[10,11] is a mechanism that relies on phase separation in the typical polyurethane morphology, which is that of hard (polar) segments embedded in a soft, stretched matrix. This hypothesis indicates that electrostriction is due to the relaxation of the matrix under an electric field by induced crystallization. A second hypothesis, introduced by Su et al.,[12] suggests that the presence of electrical charges inside the material is mostly responsible for the large electrostrictive strains. Neither of these two hypotheses have been thoroughly tested, although some evidence points to space charges as responsible for the phenomenon of bending electrostriction.[13–16] To definitely identify a mechanism, Balizer proposed that two different morphologies of polyurethanes be compared: a phase-separated (PS) semicrystalline morphology and a homogeneous, phase-mixed (PM) morphology that could not crystallize. It was the goal of this study to assess the validity of the proposed hypotheses by the presentation and analysis of electrostrictive coefficient data obtained on these structurally different polyurethane materials. These data, which represent a com-

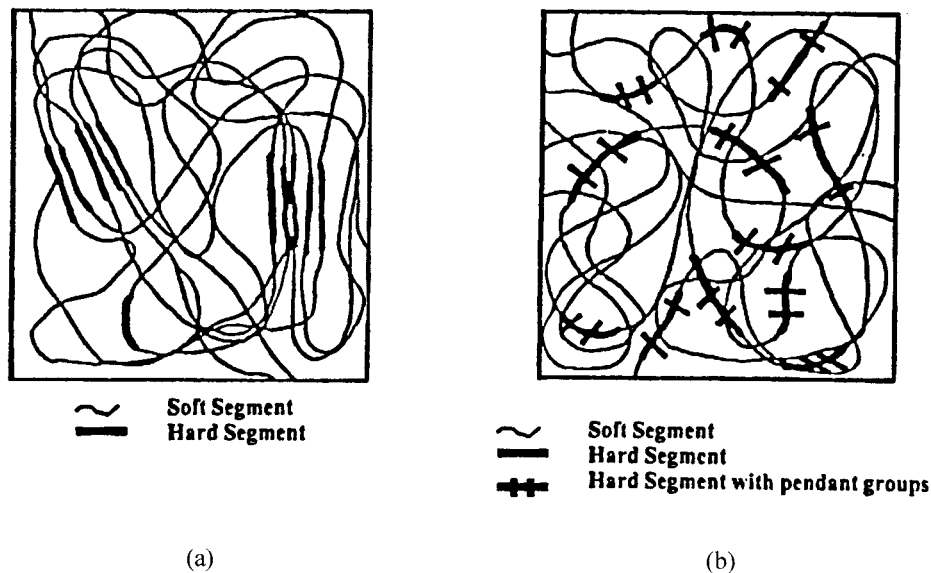(a)   (b)

Figure 1 Polyurethane morphologies: (a) PS and (b) PM.

plete set of true material properties, were also used to evaluate the role played by Maxwell stress in electrostriction and to derive an experimental relationship between electrostrictive coefficients and the dielectric and elastic constants.

EXPERIMENTAL

The experimental method used in this study was described in detail in previous publications.[17,18] Its main features are briefly summarized next. Small square polymer films (3 mm^2) were sandwiched between an aluminum plate (acting as a rigid backing and as an electrode) and a piece of aluminum foil (acting as a moving electrode) with a soft silicone rubber. The samples were subjected to an alternating-current driving voltage combined with a large direct-current bias voltage, which induced electromechanical strains. These strains were optically measured in three directions by a laser Doppler vibrometer and the data were input into a Rayleigh–Ritz energy minimization procedure implemented symbolically in Mathcad. By considering the appropriate energy functional (which includes elastic, electrostrictive, and electrostatic contributions), the method provides the three tensile electrostrictive strain coefficients of the polymer, M_{33ii} [the electrostrictive strain coefficients (M_{ijkl}) relate the strains (S_{kl}) to the square of the electric field (E_iE_j)]. The unique feature of this approach is that it yields the true polyurethane coefficients, because the mechanical boundary conditions and the strain contribution from Maxwell stress are precisely taken into account in the energy functional and are factored out in the coefficient computation by the Rayleigh–Ritz procedure. Therefore, the method provides the true electrostric-

tive material properties of the polyurethanes, and because it is the only method capable of producing such data, it is the ideal tool to investigate the origins of electrostriction in polyurethanes.

Polyurethane materials

Four different types of polyurethanes were used in this work: one of them was a commercially available material, and the other three were synthesized specifically for this study. Before each type is presented, we take a more detailed look at the molecular structure of the polyurethanes. As mentioned previously, their molecular chain consists of two segments: one is a soft segment, and the other is a highly polar hard segment. This causes the material to have a two-phase microscopic structure. The hard segments control the dielectric properties of the polymers, whereas the soft segments, being more "rubbery," are responsible for the elastic properties of the polymers. When the material is synthesized, the hard segments tend to aggregate together and form distinct regions. To create these regions, the hard segments pack themselves close to one another, stretching the soft portions of the molecules. This results in a two-phase microscopic morphology where hard, polar regions are embedded in a soft, stretched matrix. This morphology, represented schematically in Figure 1(a), is the common one for these materials and is referred to as a PS structure. However, it is possible to synthesize the polyurethanes in such a way that the two segments mix together, which results in a PM structure, as illustrated in Figure 1(b). In this configuration, methyl pendant groups are attached to the hard segments, to render them more chemically similar to the soft segments,

TABLE I
Properties of Various Electrostrictive Polyurethanes and Comparison with the Piezoelectric PVDF Polymer

Material	Density (kg/m^3)	Young's modulus (MPa)	Dielectric constant	Film thickness (10^{-6} m)	Electrostrictive coefficients (10^{-18} m^2/V^2)	% Electrostriction to total strains	d_{333} at 4 MV/m (10^{-12} m/V)	k_{333} at 4 MV/m
PS 2000	1091.9	33.8	6.1	81	$M_{3311} = 5.0$	86		
					$M_{3322} = 4.4$	84		
					$M_{3333} = -9.4$	85	-74	0.059
PS 1000	1099.3	20.3	7.2	75	$M_{3311} = 18.4$	92		
					$M_{3322} = 14.4$	90		
					$M_{3333} = -32.2$	92	-253	0.167
PM 2000	1080.0	7.2	7.8	76	$M_{3311} = 41.5$	90		
					$M_{3322} = 34.1$	87		
					$M_{3333} = -74.6$	88	-587	0.190
DOW	1130.0	30.1	7.1	56	$M_{3311} = 14.0$	94		
		30.1			$M_{3322} = 11.4$	93		
		27.9			$M_{3333} = -16.3$	90	-128	0.088
PVDF	1760	2300.0	12.0	110	N/A	N/A	-37	0.165

N/A = not applicable.

resulting in mixing of the two phases. The presence of these groups makes it more difficult for the hard segments to aggregate and sterically hinders crystallization of the polymer chains.

The types of material that were used are now presented. Polyurethanes were synthesized at the Naval Surface Warfare Center (NSWC), Carderock Division; all of these materials were unoriented and, therefore, isotropic. The first one was a PS material with a soft-segment molecular weight of 2000; it is referred to as PS 2000. The second material was a PM polyurethane, also with a soft-segment molecular weight of 2000; it is referred to as PM 2000. The third material was PS 1000, with a soft-segment molecular weight of 1000. Finally, a commercial polyurethane, DOW 2103-80 AE, was also studied; this material was naturally PS, but it was biaxially stretched, and this stretching introduced some partial phase mixing in the material. For the PS material, the hard segment resulted from the condensation of 4,4'-diphenylmethane diisocyanate with 1,4-butadeniol (BDO); the soft segment was poly(tetramethylene ether)glycol (PTMG). The PM system was of similar chemistry, except that 2,2-dimethyl-1,3-propanediol (DMPD) was substituted for the BDO (the two methyl groups on the DMPD promote the solubility between the hard and soft segments). The polymer precursors were mixed under vacuum at 70°C, were then poured and drawn down with a blade on drawn-down tables equilibrated in a preheated oven (100°C), and were left for 48 h to complete curing. The films were characterized by thermal analysis and small-angle neutron scattering.

MEASUREMENT RESULTS

Measurement results are summarized in Table I. For reference purposes, the properties of the electrostric-tive polyurethanes were compared with those of a piezoelectric polymer [polyvinylidene fluoride (PVDF)]. Measurements were performed at 2 kHz with a bias field on the order of 4 MV/m inside the polyurethane (the exact value of the field depended on the thicknesses of the films and of the rubber layers and on their respective dielectric constants). The densities, Young's moduli, and dielectric values of the DOW material were taken from ref.[19]. The densities and dielectric constants of the PM and PS materials were measured at the NSWC, and their Young's moduli were measured at the Georgia Institute of Technology. The film thicknesses and the electrostrictive strain coefficients on all of the materials were also measured at the Georgia Institute of Technology. The percentage quantities in Table I refer to the contribution of the electrostrictive response to the the total strains experienced by the samples in all three directions and, therefore, quantify the contribution of intrinsic electrostriction with respect to that of the Maxwell stress effect. The equivalent piezoelectric coefficient is provided to facilitate the comparison of the electromechanical activity of the electrostrictive polyurethanes and PVDF and is given by $d_{333} = 2M_{3333}E_3$, where E_3 is the bias electric field. The last column of the table displays values of the coupling factor (k_{333}) which is a measure of the efficiency of the energy conversion process (i.e., an indication of how much electrical energy is converted into mechanical energy by the transduction mechanism); it is given by $k_{333} = d_{333}/\sqrt{S^E_{3333}\varepsilon^X_{33}}$, where S^E_{3333} is the elastic compliance coefficient and ε^X_{33} is the dielectric permittivity coefficient.

All of the polyurethanes exhibited more electromechanical activity than PVDF, and in particular, the PM electrostrictive response was extremely large, resulting in an equivalent piezoelectric coefficient about 16 times larger than that of PVDF (at 4 MV/m). The PM

2000 coupling factor, however, was not substantially higher than that of PVDF. This was because the PM materials are very compliant. Although this could be considered a disappointing result, one should keep in mind that in the electrostrictive case, the coupling factor is directly proportional to the bias field and that it is evaluated in Table I for a relatively low bias value. For example, doubling the value of the bias field to 8 MV/m (which is still quite small) would result in a coupling factor twice as large. Although this reasoning does not take into account the likely variations of the electrostrictive coefficients with the bias field, the results clearly indicated that materials such as PM 2000 and PS 1000 (which has a lower piezoelectric coefficient but a larger Young's modulus and, therefore, a coupling factor comparable to that of PM 2000) had better performances than PVDF.

RESULTS AND DISCUSSION

Maxwell stress contribution

The results presented in Table I reveal that the deformations due to the Maxwell stress effect accounted for less than 15% of the total strains. This is an important finding that proved that most of the electromechanical activity in the polyurethanes stemmed from intrinsic electrostriction. This was in contrast with the findings of other researchers that claim that Maxwell stress is responsible for approximately 50% of the polyurethane strain response.[2,3] This discrepancy between our results and theirs is most likely due to the fact that they used electroded samples and, therefore, measured a constrained response (the Maxwell contribution is calculated and is independent of the measuring technique). On the basis of the values that we obtained, it is our conclusion that the electrostatic attraction is in fact a minor factor in the mechanical response of a polyurethane film to an applied electric field.

Elastic and dielectric effects

An empirical relationship between electrostrictive, dielectric, and elastic constants was already established by Eury et al.[20] for a variety of dielectric materials, including glasses, ceramics, single crystals, and polymers. The findings of these researchers indicated that the hydrostatic electrostriction coefficient (Q_h) is linearly related to the ratio of the elastic compliance to the dielectric permittivity, $s/\varepsilon_0\varepsilon_p$ (where ε_0 is the permittivity of the vacuum and ε_p is the dielectric constant of the material). The electrostrictive coefficients Q_{ijkl} relate the strains S_{ij} to the square of the polarization $P_k P_l$ and are also related to the strain coefficients M_{ijkl} through $Q_{ijkl} = (\varepsilon_{kl} - \varepsilon_0)^{-2} M_{ijkl}$. Hence, in the case of our polyurethanes, the following relationship

applies: $M_{3333} = \varepsilon_0^2 (\varepsilon_p - 1)^2 Q_{3333}$, which, together with the observations of Eury and her coworkers, suggests that the M_{3333} coefficient is proportional to $\varepsilon_0 (\varepsilon_p - 1)^2/Y_3\varepsilon_p$ (where Y_3 is the Young's modulus in the 3-direction). This was confirmed by Figure 2, which shows a plot of $|M_{3333}|$ as a function of $\varepsilon_0(\varepsilon_p - 1)^2/Y_3\varepsilon_p$ for the four types of materials studied in this work. This proportionality relationship, now also established for soft polyurethane elastomers, provides an approximate formula to predict electrostrictive coefficients.

Microscopic effects

One proposed mechanism to explain electrostriction relies on the PS morphology of the polyurethane:[10,11] because this structure corresponds to hard-segment domains embedded in a stretched matrix of soft segments, the explanation for the observed large strains was the relaxation (by crystallization) of the matrix under electric field. It was to test this hypothesis (and also to assess the general effects of the polymer structure on electrostriction) that samples with the PS and PM structures were synthesized at NSWC. Because both types of samples had a measurable electrostrictive response, phase separation alone could not completely account for the phenomenon. In fact, results on the PM 2000 material indicated a larger electrostrictive activity in these materials than in the ones with the PS structure. Therefore, we conclude that the proposed mechanism based on phase separation cannot be validated as solely responsible for electrostriction (although we have not established that it does not contribute at all) and that the latter is actually enhanced by phase mixing.

Another proposed microscopic theory relies on the space–charge hypothesis:[12] this theory claims that the large observed strains can be explained by the presence of charges inside the sample; these charges create a nonuniform electric field across the film thickness, which in turn, can be shown to enhance the electrostrictive strain response. These charges come from impurity ions in the samples and from charge injection (of electrons) from the electrodes (however, this second source of charges is not likely to play a role in our samples because of the layer of silicone rubber between the electrodes and the polymer itself). To test this theory, Su et al. measured the response of samples made from filtered and unfiltered solutions, with the filtering process capable of removing some of the impurities, and they observed that the unfiltered samples showed the largest strains. At this point, two observations should be made: (1) the interfaces between the soft-segment and the hard-segment regions are space–charge trapping sites, and (2) the number of these interfaces is substantially larger in the PM
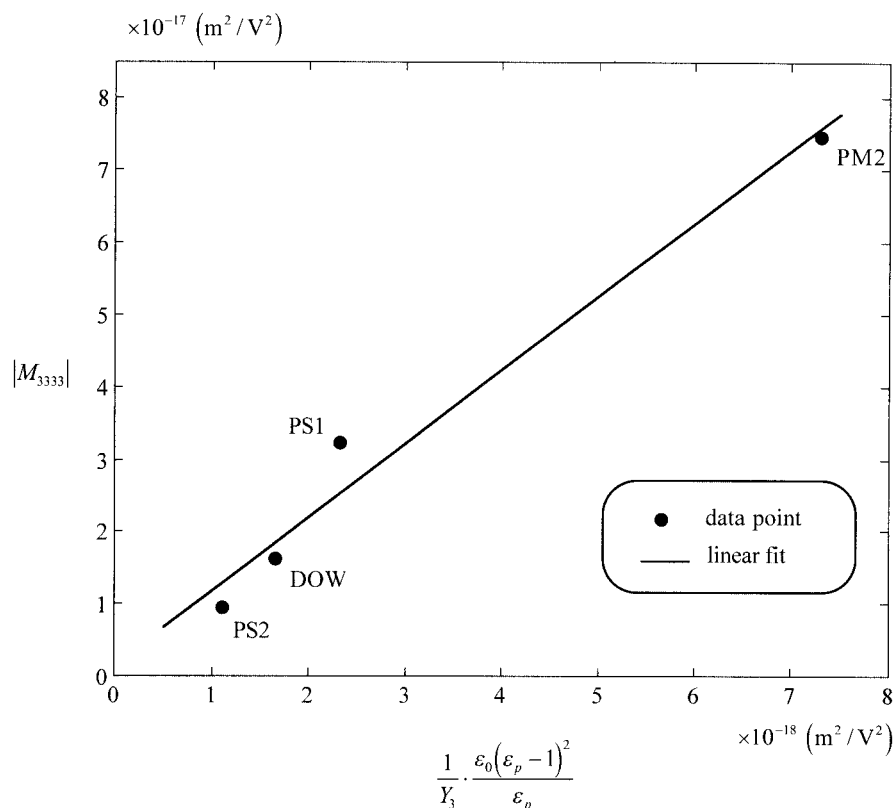
Figure 2 Dependence of polyurethane electrostrictive coefficients on the dielectric and elastic constants.

morphology than in the PS one because in the former, the hard segments are dispersed throughout the material instead of forming clusters. Therefore, the PM morphology is likely to contain a larger amount of charges, resulting in a higher electrostrictive response for this type of samples. Our data were in agreement with this prediction and, therefore, tended to reinforce the validity of the suggested space–charge theory. However, to definitely establish the validity of this theory, a more quantitative study should be undertaken, where the relative amount of space charges is evaluated and used to estimate the magnitude of the resulting nonuniform electric field. The field nonuniformity should also be taken into account in subsequent attempts to model polyurethane electrostriction, as this may be one of the missing key features of the current macroscopic models.

CONCLUSIONS

In this article, we report that a method previously introduced to measure electrostrictive coefficients was successfully implemented to characterize the electromechanical properties of various types of polyurethanes. All of the materials exhibited a substantial electrostrictive activity, and the PM morphology possessed the largest coefficients. The effects of Maxwell stress were assessed, and intrinsic electrostriction was determined to be responsible for at least 85% of the measured response, depending on the material. Our results provided an empirical prediction formula for the electrostrictive strain coefficients, on the basis of the knowledge of the elastic and dielectric constants of the material. Finally, we discovered that field-induced soft-segment crystallization in the PS polyurethanes was not required for electrostriction to occur and that the space–charge theory offered an explanation for the phenomenon that was compatible with our observations.

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