

Effects of Transitional Phenomena on the Electric Field Induced Strain–Electrostrictive Response of a Segmented Polyurethane Elastomer

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ABSTRACT: The electromechanical properties of a segmented polyurethane elastomer were investigated as functions of temperature and frequency. Two transitional phenomena were observed in the temperature range from -50 to 85°C . In these transition regions, the electric field induced strain coefficient exhibits large increases, which indicate that the effect of the transition processes is significant. The experimental analysis suggests that the transitional processes in the polyurethane are related to the chain-segment motions. From the elastic compliance and the dielectric constant data, the contribution of the uniform Maxwell stress was determined. It was found that the contribution of the Maxwell stress effect to the measured strain coefficient increased from about 10% below the glass transition temperature (T_g) ($\sim -25^{\circ}\text{C}$) to about 50 and 35% for the frequencies of 10 and 100 Hz, respectively, at $\sim 40^{\circ}\text{C}$, which is above T_g . The large difference between the measured strain response and the calculated Maxwell stress effect indicates a significant contribution to the field-induced strain from other mechanisms, such as electrostriction. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1363–1370, 1997

Key words: polyurethane elastomer; electric field induced strain; Maxwell stress; electrostriction; transitional phenomena

INTRODUCTION

Electromechanical coupling effects such as piezoelectricity and electrostriction have been widely utilized in transducer, sensor, and actuator technologies.^{1,2} During the last three decades, electromechanical polymers, especially piezoelectric poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE), have drawn much attention because of their low acoustic im-

pedance, mechanical flexibility, and good processing properties as well as low manufacturing cost.^{3,4} However, their applications have been limited because of the lower electromechanical activity when compared with that of piezoceramic lead zirconate titanate (PZT).^{5,6} The recent development in electromechanical properties of polymers showed that some thermoplastic polymer elastomers, especially segmented polyurethane elastomers, can exhibit very high electric field induced strain response. These electromechanically active polyurethane elastomers have drawn more and more attention and many experimental investigations have been conducted^{7–9} since the large electric field induced strain of this class of polyurethane elastomers was reported.¹⁰

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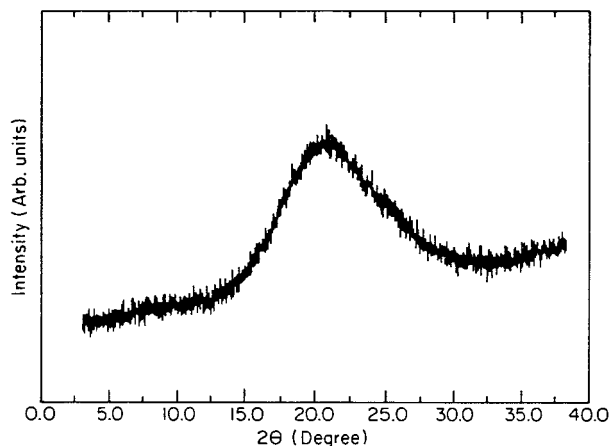


Figure 1 X-ray diffraction data of the polyurethane elastomer at room temperature where the broad halo near 20 degree (2θ) is the reflection of the amorphous phase. No crystalline phase was observed within the data resolution.

The objective of this study is to provide understanding of the possible mechanisms for the observed large electric field induced strain in this class of polyurethane elastomers through investigations of the temperature–frequency dependence of the field induced strain and the dielectric and the elastic properties. In addition, the temperature dependence of the molecular motions in the material were also examined using differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and thermal expansion (TE) techniques to elucidate the property–molecular motion relationship.

EXPERIMENTAL

Sample Preparation

The material used in this investigation was produced by Deerfield Urethane, Inc. using a Dow polyurethane (Dow 2103-80AE). The polyurethane is a segmented elastomer consisting of poly-(tetramethylene glycol) (PTMEG) as the soft segment and methylenedi-*p*-phenyl diisocyanate (MDI) as the hard segment with 1,4-butanediol (Bdiol) acting as the extender. The molar ratio of the components in the polyurethane is 1.8 mol MDI/0.8 mol. Bdiol/1.0 mol. PTMEG. The samples for experimental measurements were prepared by solution casting followed by vacuum-drying for 24 h. The thickness of the sample in this investigation was 2 mm. The gold electrodes were

vacuum-evaporated onto the opposing surfaces of the cast samples.

The result of X-ray diffraction shown in Figure 1, which was obtained by a Philips APD1700 diffractometer, indicates that there is no detectable crystalline phase in the samples investigated within the experimental resolution, or it can be said that the sample is amorphous.

Electric Field-Induced Strain Measurement

A double-beam laser interferometer was employed to measure the strain induced by the applied electrical field at frequencies of 10 and 100 Hz in the temperature range from -30 to 80°C . A detailed description of the technique, including the basic principle, the setup and the sample mounting for the strain measurements was reported with schematic representation in a previous publication.⁸

Dielectric and Elastic Measurements

The temperature–frequency dependence of the dielectric constant of the polyurethane was measured in a temperature-controlled chamber by a lock-in amplifier. The temperature range for the measurement was from -40 to 80°C and the heating rate was $2^\circ\text{C}/\text{min}$. The measurement frequencies were 10 and 100 Hz.⁸

The temperature–frequency dependence of the elastic compliance of the polyurethane was investigated using a Seiko Instruments SDM/5600 dynamic mechanical analyzer (DMTA), from -40 to 80°C with a heating rate of $2^\circ\text{C}/\text{min}$. The measurement frequencies were also 10 and 100 Hz. The sample dimension was 25 mm (length) \times 5 mm (width) \times 2 mm (thickness).

DSC, FTIR, and TE Measurements

To understand how the observed macroscopic properties are related to the molecular structures, molecular motions, and transitional phenomena, DSC, FTIR spectroscopy, and TE measurements of the polyurethane were examined as functions of temperature. A Perkin–Elmer DSC-7 was employed to obtain the DSC curves and a Digilab Model FTS-45 at a resolution of 2 cm^{-1} was used to acquire the FTIR spectra, for which a minimum of 64 scans were signal-averaged. The film used for FTIR examination was sufficiently thin to be within an absorbance range wherein the Beer–Lambert law is obeyed. The temperature range for DSC and FTIR measurement was from 25 to

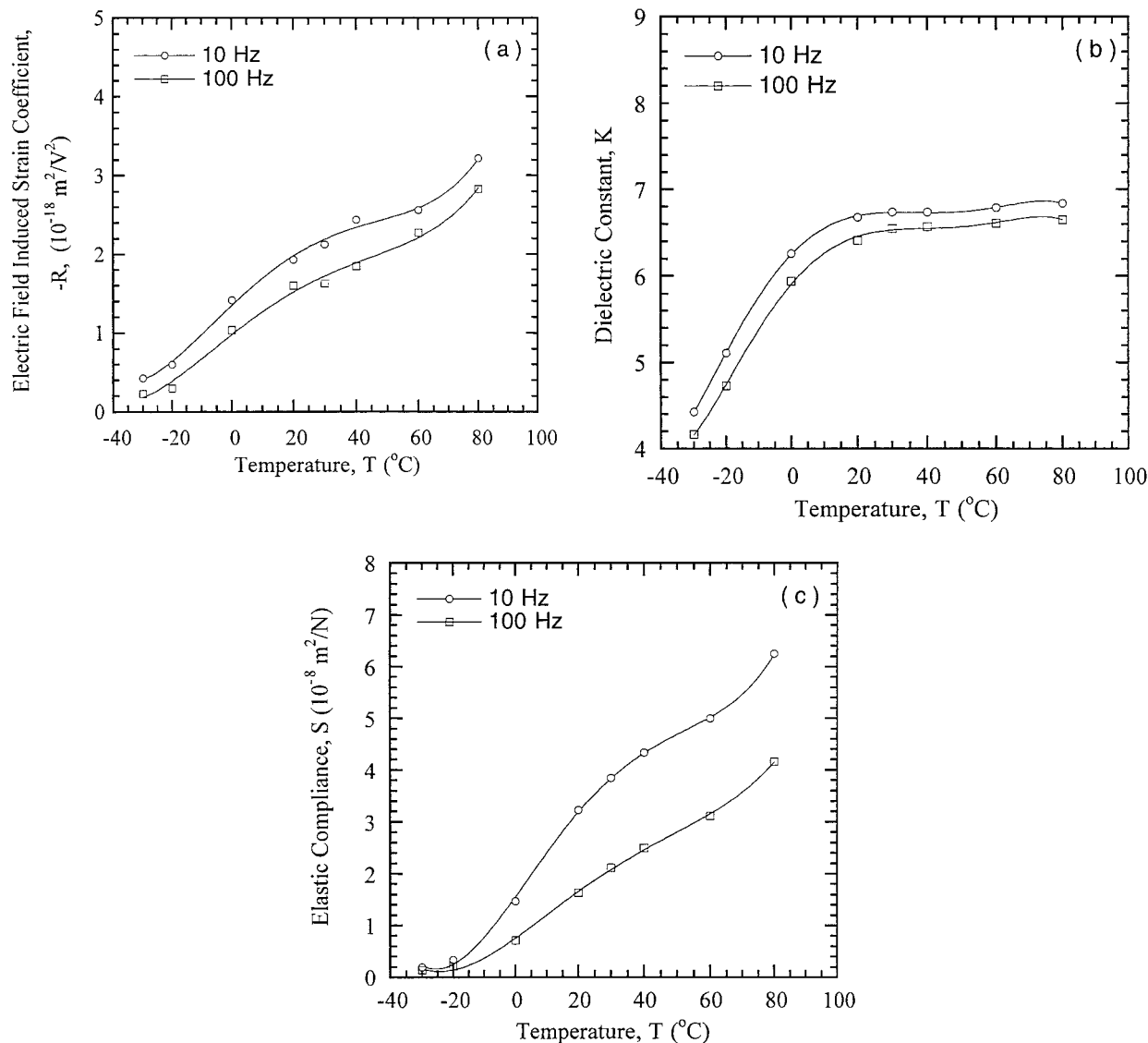


Figure 2 Temperature dependence of (a) the electric field induced strain coefficient, R ; (b) the dielectric constant, K ; and (c) the elastic compliance, s , of the polyurethane elastomer (Dow 2105-80AE) at 10 Hz and 100 Hz. The solid lines are drawn to guide the eye.

190°C and from 25 to 180°C, respectively, whereas for TE the temperature range was from 40 to 100°C. The heating rate was 10°C/min for the DSC and TE measurements.

RESULTS AND DISCUSSION

Temperature and Frequency Dependence and Transitions

The experimental results of the electric field induced strain are presented in Figure 2(a). The strain coefficient, R_{33} ($S_3 = R_{33}E_3^2$, where S is the

strain, E is the applied electric field, and the subscript 3 represents the direction perpendicular to the sample surface), increases with temperature and decreases with frequency. In the temperature range from -30 to 60°C, two relatively sharp increments are observed: one starts at about -20°C and the other at about 50°C. Similar trends are also observed in the dielectric and elastic data shown in Figure 2(b,c), respectively. The dielectric constant, K , shows a rapid increase at about -20°C but a relatively small change at about 60°C, while the temperature dependence of the elastic compliance shows two rapid increases starting at about -25 and 60°C, respectively. The

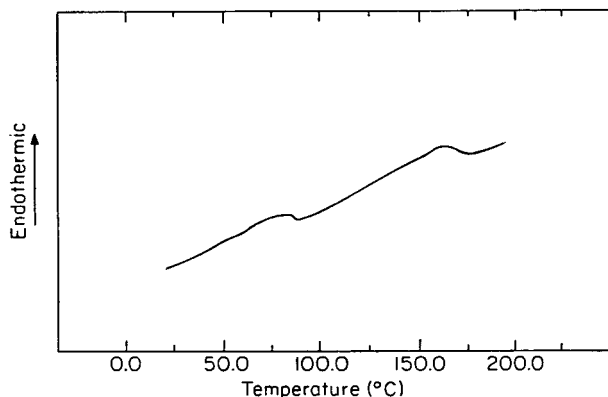


Figure 3 DSC trace of the segmented polyurethane elastomer (Dow 2105-80AE), from 25 to 190°C.

sharp change in the material properties at the lower temperature, observed in these measurements, is related to the glass transition of the polyurethane due to large-scale molecular motions of the soft segments, PTMEG.¹¹ In order to understand the change at higher temperature transition, DSC, FTIR, and TE investigations, which are employed extensively in studies of structures and molecular motions of segmented polyurethane elastomers,¹¹⁻¹³ were carried out. The DSC curve, shown in Figure 3, exhibits an endothermic peak at about 75°C, starting at about 50°C and ending at about 90°C, which is much higher than the glass transition temperature (T_g) (about -20°C) and much lower than the melting temperature (about 170°C), which is reflected by another endothermic peak starting at about 100°C and ending at about 185°C. From the DSC results, the enthalpy change associated with the transition between 50 and 100°C was calculated by assuming the change is associated with the dissociation of the hydrogen bonding in hard segments since previous publications suggested the endothermic peak might be associated with hydrogen bonding dissociation. However, the value obtained (3.71 kcal/mol) is obviously lower than the previously reported enthalpy change due to hydrogen-bond dissociation in segmented polyurethanes having similar chemical structure.¹⁴ The thermal expansion measurement of the segmented polyurethane elastomer also exhibits a characteristic transitional change in the temperature range between 50 and 100°C. As can be seen in Figure 4, the material exhibits a rapid thermal expansion in the temperature range from about 50°C to about 90°C.

The temperature dependence of the absorbency

spectroscopy of the FTIR study on the polyurethane is shown in Figures 5(a-d). The change in the infrared absorption related to the -NH- and -C=O-related hydrogen bonding was investigated at 60, 100, 140, and 180°C. As the temperature is increased from 60 to 100°C, the absorption of bonded -NH (3327 cm^{-1}) associated with the absorption of bonded -C=O (1714 cm^{-1}) shows only a minor decrease. The absorption of unbonded, or free, -NH (3448 cm^{-1}) and the unbonded -C=O (1730 cm^{-1}) shows very little increase in the same temperature range, which indicates that the transitional change observed in the DSC and TE measurements is not associated mainly with the dissociation of the hydrogen bonding in the MDI segments. However, when the temperature is increased from 100 to 140°C, a relatively large change (i.e., a large drop) in the absorption of the H-bonded groups and an increase in the absorption of the unbonded groups can be observed. Further increase of the temperature to 180°C results in a significant dissociation of the hydrogen bonding, which is reflected by the disappearance of the bonded -NH (3327 cm^{-1}) and -C=O (1714 cm^{-1}) absorption peaks, and the large increase of the absorption peak due to the unbonded -NH (3448 cm^{-1}) and -C=O (1730 cm^{-1}). This observation corresponds to the endothermic peak observed in the temperature region from 100 to 180°C in the DSC measurement, which is associated with the hard-segment dissolution (melting) as a consequence of the dissociation of the hydrogen bonding in MDI segments.

The experimental results obtained from the DSC, TE, and FTIR investigations show that the transition between 50 and 100°C, which might be

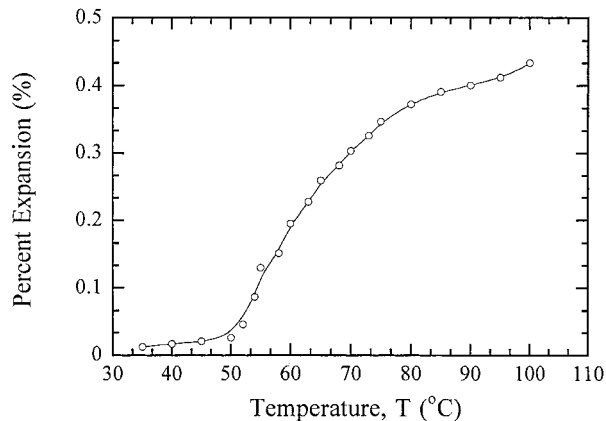


Figure 4 TE measurement of the segmented polyurethane elastomer exhibits a characteristic transitional change in the temperature region from 50 to 100°C.

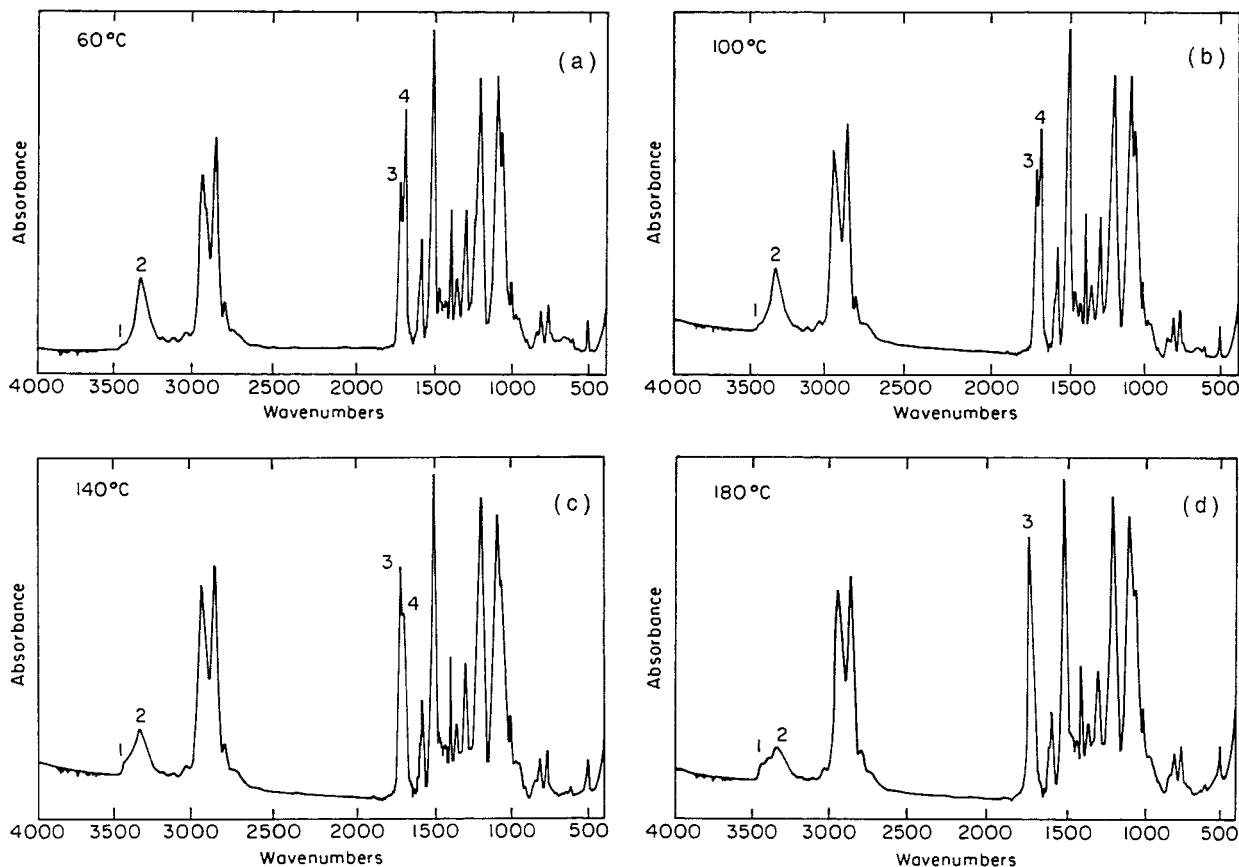


Figure 5 FTIR spectroscopy of the polyurethane elastomer (Dow 2105-80AE) at (a) 60°C, (b) 100°C, (c) 140°C, and (d) 180°C. (Absorbency wave number: 1: 3,448 cm^{-1} ; 2: 3,327 cm^{-1} ; 3: 1,730 cm^{-1} ; and 4: 1,714 cm^{-1}).

the key factor resulting in the increased field-induced strain response of the segmented polyurethane in the temperature region, is neither the glass transition nor the melting if the glass transition reflects the molecular motion of the soft segments and the melting reflects the molecular flow of whole polymer chains when the hydrogen-bond dissociation occurs. The molecular origin of the transition might be related to the molecular motion of the extenders within the hard segments, which might occur without destroying the hydrogen bonding sheet structure,¹² and result in expanding in the direction perpendicular to the hydrogen bonding sheets and increasing free volume. When this happens, it should lead to transitional changes in elastic and thermal expansion properties, as observed in Figures 2(c) and 4, respectively. A similar transition has been observed for similar types of materials and assigned to the glass transition of the amorphous hard-segment domain.¹⁵⁻¹⁷ The asymmetric endothermic peak [i.e., slow increase before the peak

position (about 75°C) and rapid decrease after the peak observed in the DSC curve] could be a result of the restraining of the hydrogen bonding in MDI segments to the extender (Bdiol)-related molecular motion. This restraint can limit the molecular motion of extenders between MDI segments, which results in the slow increase. When the temperature is high enough to cause the motion of or dissociation of the hydrogen bonds in the hard segments to a significant level, the limited molecular motion of the extenders can be accelerated, which results in the rapid decrease.

Contributions from the Maxwell Stress Effect and Non-Maxwell Stress Effects

In general, the electric field induced strain in a nonpiezoelectric material can be from the electrostrictive effect and also from the Maxwell stress effects. The electrostrictive effect is a direct coupling between the polarization and mechanical response in the material. It can be expressed as

the strain change induced by a change in the polarization level in the material:

$$S_E = QP^2 \quad (1)$$

where S is the strain, P is the polarization level, and Q is the electrostrictive coefficient of the material. For a linear dielectric, $P = \epsilon_0(K - 1)E$, so eq. (1) can be rewritten as

$$S_E = Q\epsilon_0^2(K - 1)^2E^2 \quad (2)$$

where K is the dielectric constant of the material, ϵ_0 is the vacuum dielectric permittivity, and E is the applied electric field. On the other hand, Maxwell stress, T , which is due to the interaction between the free charges on the electrode (Coulomb interaction), can also contribute to the electric field induced strain response. For the situation considered here, it is also proportional to the square of the applied electric field and can be expressed as

$$T = -\epsilon_0KE^2/2 \quad (3)$$

Therefore, the dimensional change due to the Maxwell stress is obtained as

$$S_M = -s\epsilon_0KE^2/2 \quad (4)$$

where s is the compliance of the material. As can be seen, the strain induced by the Maxwell stress can be quite substantial for a soft, or high-compliance, material such as the polyurethane elastomer investigated.

From the temperature dependence of the dielectric constant and elastic compliance measurements, the electric field induced strain due to the Maxwell stress effect and the percentage of this contribution to the total strain response were determined, which are shown in Figure 6(a,b), respectively. When the temperature is lower than the T_g , the contribution of the Maxwell stress is relatively small—only about 10%—because the elastic compliance is low. During the glass transition period, which is approximately from -20 to 30°C , the Maxwell stress contribution increases from about 10% to about 35% and 50% for 100 and 10 Hz, respectively, while the elastic compliance, s , increases about one order of magnitude and the dielectric constant, K , increases from 4 to 6.5. From 50 to 80°C , the temperature region for the observed second transition from DSC anal-

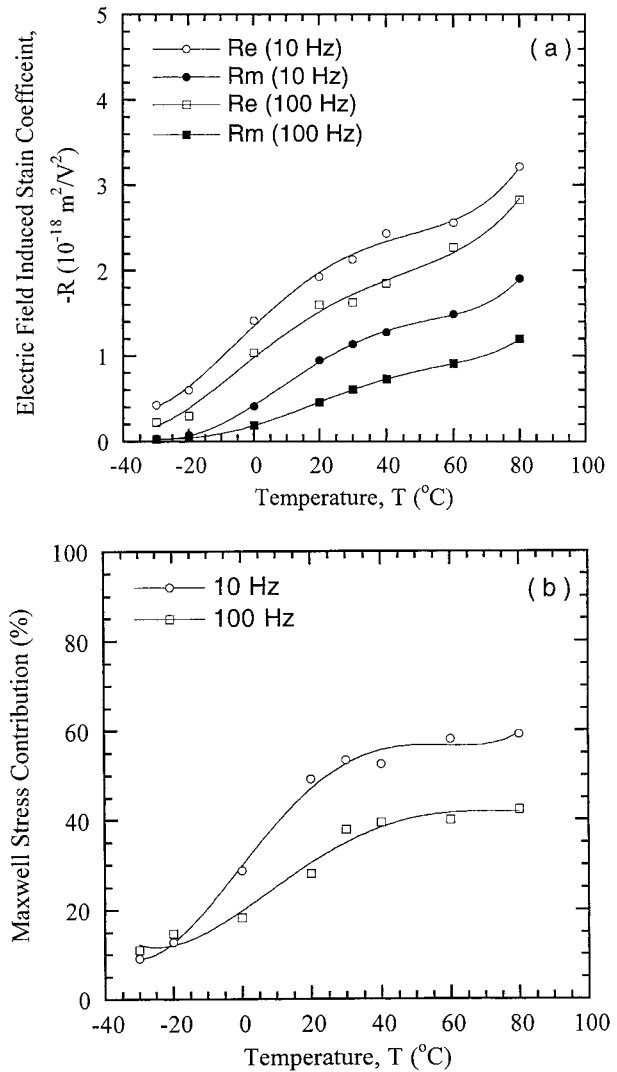


Figure 6 Comparison of the temperature dependence of (a) the total electric field induced strain coefficient, R_e (●, 10 Hz; ■, 100 Hz), and the Maxwell stress-contributed strain coefficient, R_m (○, 10 Hz; □, 100 Hz), and (b) the percentage of Maxwell stress contribution to the total strain coefficient, at 10 and 100 Hz. The solid lines are drawn to guide the eye.

ysis, increased strain is also observed. Associated with this increase, the elastic compliance shows a corresponding increase while the dielectric constant does not show a significant change.

From the discussion above, it can be seen that the Maxwell stress contribution is important for the electric field induced strain, especially when the temperature is higher than the T_g of the polyurethane. On the other hand, the non-Maxwell contribution, which is assumed to be electrostrictive strain, is also very significant. As can be seen in Figure 7(a,b), the non-Maxwell stress part of

the field-induced strain coefficient (represented as $R_e - R_m$, where R_e is the total measured strain coefficient and R_m is the Maxwell stress contribution) shows significant values in the whole temperature region where the measurement was conducted; and when the temperature is lower than the T_g , the electrostrictive contribution dominates (at about 90%). Even though the Maxwell stress contribution is significantly increased when the temperature is raised above 60°C, which is higher than T_g , the electrostrictive strain is still contributing to the total field induced strain of about 40% at 10 Hz and about 60% at 100 Hz.

Temperature and Frequency Dependence of the Electrostrictive Coefficient

The experimental results show that the glass transition plays an important role in the observed large electric field induced strain of the polyurethane investigated. During the transition, both the dielectric and elastic properties show transitional change; therefore the contribution of Maxwell stress effect shows similar characteristics, as discussed. Based on eq. (2), the electrostrictive coefficient Q can be evaluated. The temperature dependence of the coefficient Q at 10 Hz and 100 Hz is presented in Figure 8. As can be seen, when the electrostrictive coefficient Q is examined over the temperature range of the glass transition, it does not show the same temperature dependence as that observed in the Maxwell stress effect, which depends directly on the elastic compliance. However, when the temperature is raised to the second transitional region, the coefficient Q exhibits increase with temperature. Considering the fact that the electromechanical response of a polymer material is contributed by the molecular motions which participate in both the polarization and elastic processes,⁸ the increase in the electrostrictive coefficient Q is a result of the increased elasticity per unit polarization change, which can be caused by lowering the energy barrier for the mechanically related segment motion as reflected by the increase in the elastic compliance in this temperature range, where the dielectric constant does not show much change. On the other hand, when the electrostrictive coefficient Q is examined as a function of the frequency, it is observed that Q measured at 100 Hz is about 25% lower than that measured at 10 Hz. The decrease of the Q with frequency indicates that the component of the polarization motions of high frequency (short relaxation time) does not generate

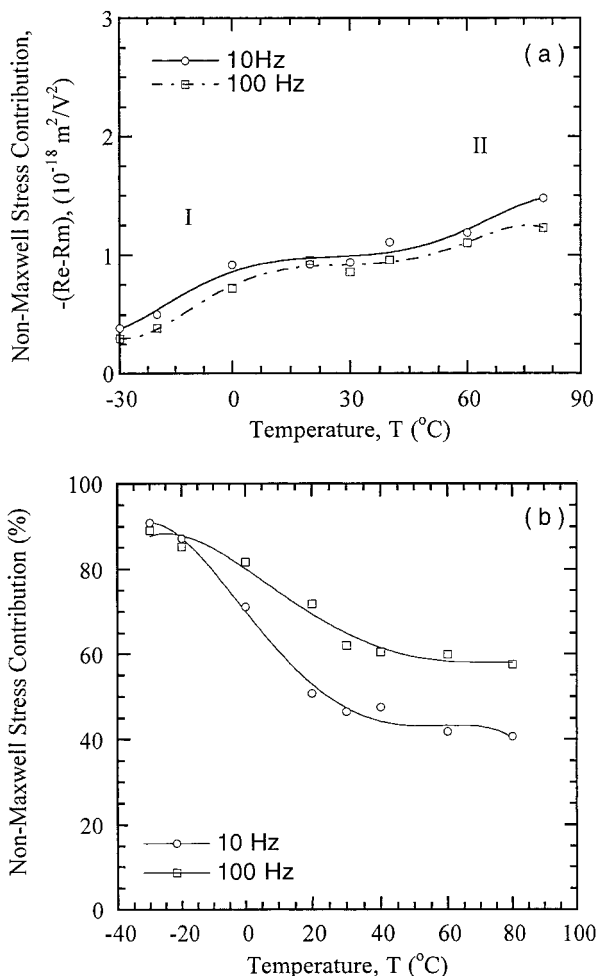


Figure 7 Temperature dependence (a) of non-Maxwell contribution to the electric field induced strain response ($R_e - R_m$) and (b) of the percentage of the non-Maxwell contribution. The solid and dashed lines are drawn to guide the eye.

as much strain in the material and therefore is more like pure dielectric. It should be mentioned that the relatively large data scatter in Figure 8 is due to the fact that the calculated results are obtained from three sets of experimental data (the dielectric constant, the elastic compliance, and the electric field induced strain measurements).

CONCLUSIONS

The temperature and frequency dependence of the electric field induced strain and the dielectric and elastic properties show that both the Maxwell stress effect and electrostriction are important to the electric field induced strain of the polyure-

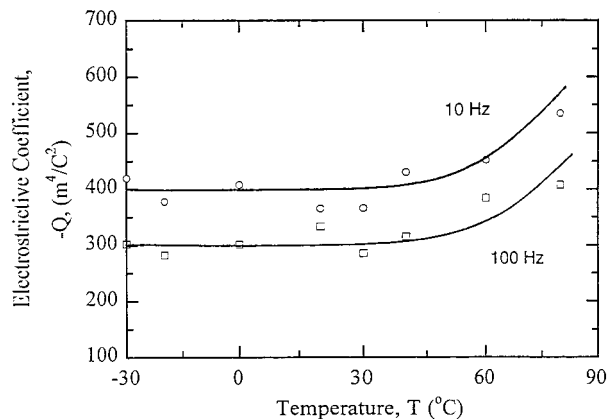


Figure 8 The electrostrictive coefficient Q as a function of temperature at the measurement frequencies of 10 and 100 Hz. The open circles and open squares are data points, and the solid lines are drawn to guide the eye.

thane elastomer investigated. The Maxwell stress contribution increases markedly during the glass transition, along with the sharp increase in the elastic compliance and dielectric constant. In spite of these large changes, the non-Maxwell contribution, such as the electrostrictive coefficient Q , seems to be independent of temperature in the glass transition region. In addition to the glass transition, another transitional change at about 75°C was also observed in the experimental temperature range. The thermal and chemical structural analysis, such as the DSC, TE, and FTIR studies, indicates that the transition might be related to the molecular motion of the extenders in the hard segments. Interestingly, the electrostrictive coefficient Q exhibits an increase with temperature along with the elastic compliance, while there is only a small change in the dielectric constant in the same temperature range. The experimental results show that the two transitional phenomena, which are reflections of the molecular motions of the soft segment and the extender in hard segment, are important for the observed electric field induced strain of the polyurethane elastomer. Even though these transitional phenomena can significantly increase the Maxwell stress contribution, the non-Maxwell stress contribution, such as the electrostrictive coefficient (which seems unchanging with temperature in the glass transition region), is also important for the field-induced strain of the segmented polyurethane elastomer. The different behaviors, observed in the two transitional regions, of the electrostrictive coefficient, the elastic constant, and

the dielectric constant suggest that in this class of the material, the chain-segment motions can be grouped into those related to polarization, those related to the elastic process, and those related to both. The change in the relative activation energies related to these motions with temperature results in the different behaviors in the dielectric and elastic properties and the electrostrictive coefficient.

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