



# A Comparison of the Dielectric Behavior of Aromatic and Aliphatic Polyurethanes in Relation to Transitional Phenomena

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The dielectric properties of two polyurethanes (PUs) with different hard segments, i.e., aromatic methylene di-*p*-phenyl diisocyanate (MDI) and aliphatic hexamethylene diisocyanate (HDI), were investigated in the temperature range of -100 to 100°C and in the frequency range of 1 Hz to 3 kHz. The  $\alpha$ -relaxations induced by the glass transition of the equivalent soft segments in the two PUs occurred at relaxation times of  $\tau = 3.46 \times 10^{-3}$  s for MDI-PU and  $\tau = 3.39 \times 10^{-2}$  s for HDI-PU at -20°C, in accord with the temperature-frequency superposition principle, resulting in similar shifting factors. However, different I-relaxations were observed for the two PUs. The I-relaxation of MDI-PU occurred due to the mobility of the chain extenders near 80°C with a slower shifting rate than the  $\alpha$ -relaxation. On the other hand, I-relaxation arising from both the extender and the unconstrained hard segments of HDI-PU occurred at 70–100°C, indicating complicated dielectric behavior due to partial interaction with the  $\alpha$ -relaxation at high frequencies. Thus, the I-relaxation of HDI-PU did not follow the superposition principle. The dielectric behaviors of the PUs were mainly influenced by their phase transitions, which were affected by the structure and components of the materials.

**Keywords :** MDI-polyurethane, HDI-polyurethane, Dielectric relaxation, Temperature-frequency superposition principle, Shifting factor

## 1. INTRODUCTION

As smart materials, a group of electrostrictive polymers that are non-piezoelectric in nature are known to exhibit a pseudo-piezoelectric effect when exposed to a large direct current (DC) bias electric field. These polymers have several advantages, such as high mechanical flexibility, that allow them to withstand high levels of strain, and also have low acoustic impedance, light weight, excellent processing properties, and low manufacturing cost. Their disadvantages, including their low actuation force, low conversion efficiency, and low dielectric constant, do not preclude their application in electromechanical areas such as sensors and transducers and these polymers have been used for artificial muscles

and to mimic the movements of humans, animals, and insects to produce biologically inspired devices, and robots [1–7].

Among these electrostrictive polymers, certain polyurethane elastomers undergo a large strain induced by an electric field and have attracted much attention [8,9]. Attempts have been made to construct acoustic transducers by using these dielectric elastomer films [10–12]. In general, the electric field-induced strain in non-piezoelectric materials is attributed to the electrostrictive effect and the Maxwell stress effect [12–14]. The electrostrictive strain is proportional to the square of the dielectric constant for a linear dielectric, and the strain caused by the Maxwell stress is linearly proportional to the dielectric constant [14]. Thus, evaluation of the temperature- and frequency-dependence of the dielectric response can provide more information about the mechanisms underlying the activity for the application of these polymers in electromechanical systems.

Although polyurethane is a non-piezoelectric material with a low dielectric constant, evaluation of its dielectric transition is important due to its high mechanical flexibility that induces a high strain. Generally, the dielectric transition, at which an abrupt dielectric change

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occurs through the appearance of a new dielectric relaxation or/ and the disappearance of the pre-existing dielectric relaxation, is connected to the phase transition. The dielectric relaxation process is characterized by an effective relaxation time and a parameter describing the distribution of relaxation. Researchers have explored this subject using various polymer systems [15–18].

In this study, the dielectric behavior of two polyurethanes (PUs) having different hard segments are investigated. PU is a block copolymer composed of a soft segment (S) and a hard segment (H), in which the hard segment is connected by a chain extender (E) such as  $-S_n-H-E-H-$ . The dielectric responses and the possible relaxation mechanisms of polyurethane are explored in the temperature range of  $-100$  to  $+100$  °C to characterize the temperature-dependence of the relaxation processes, including the  $\alpha$ -relaxation process at the glass transition temperature ( $T_g$ ), where the soft segment is mobilized from a rubbery state to a glass state. The hard segment comprising aliphatic isocyanate is found to be more flexible, UV-stable, and less susceptible to oxidation and degradation than the hard segment composed of aromatic isocyanate [19]. Aliphatic isocyanates are rubbery materials with high elongation and low tensile strength compared with aromatic isocyanates [20]. Their dielectric dispersions are examined in the low frequency range from 1 Hz to 3 kHz, which is selected based on the nature of the polymer system that has long chains and a high molecular weight. The dielectric constant and the elastic compliance of polymeric materials are well known to be dispersive at low frequencies, reflecting the relatively high activation energies of the motions of the molecular units and chain segments. Further, the conformance of the dielectric relaxation times and shifting factors of these polymers to the temperature-frequency superposition principle [21] is discussed.

## 2. EXPERIMENTS

The two PU films used in this study were obtained from Deerfield Urethane Inc., USA. The films were composed of poly (tetramethylene glycol) (PTMEG) as the soft segment and aromatic methylene di-*p*-phenyl diisocyanate (MDI) as one hard segment and aliphatic hexamethylene diisocyanate (HDI) as the other hard segment, which were connected by the extender, 1,4-butanediol (Bdiol). The mole ratio of the components was approximately 1.8 mol MDI/HDI: 0.8 mol Bdiol: 1.0 mol PTMEG. The polyurethane films were prepared by solution casting onto a glass plate and drying at 60 °C in a vacuum oven. The film thickness was 0.43 mm for MDI-PU and 0.51 mm for HDI-PU. The structures are presented in Fig. 1, where the soft segment (PTMEG) is  $-(OCH_2CH_2CH_2CH_2)_n-O-$ ,  $n \approx 13$  and the structure of the chain extender connecting the hard segments is  $-O-(CH_2)_4-O-$ . As seen in Fig. 1,  $-C=O\cdot$  and  $NH\cdot$  of the MDI/HDI hard segment bind strongly to  $\cdot HN-$  and  $\cdot O=C-$  of the neighboring

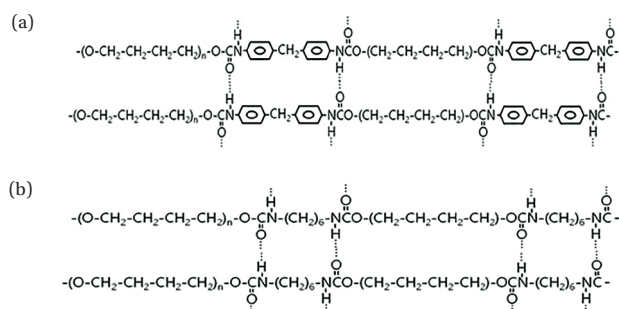


Fig. 1. Structures of (a) MDI-PU and (b) HDI-PU. The dotted lines are hydrogen bonds connecting the molecular chains.

molecular chains, where the hard segments are embedded in the soft matrix.

Before evaluating the dielectric properties of the polymers, gold electrodes with a thickness of 300 Å were sputtered onto both sides of the polyurethane film. A Perkin-Elmer DSC-7 instrument was used to determine the phase transition temperature and a Phillips APD1700 X-ray diffractometer was used to investigate the crystallinity of the films. The dielectric constant was measured over the temperature range of  $-100$  °C to  $100$  °C with the use of temperature controller (Lakeshore 321 Autotuning) and a lock-in amplifier (SR850), which measured the phase for the loss tangent, the amplitude of the voltage, and the current applied to the sample. For this experiment, the capacitances and the losses of the films were measured at a constant voltage of 5 V. The frequency was varied at a fixed temperature under atmospheric conditions. In order to obtain subzero temperatures, liquid nitrogen was used with a sample holder that was specially designed for the experiment.

## 3. RESULTS AND DISCUSSION

The temperature-dependence of the real part ( $k'$ ) of the relative dielectric constant and the dielectric loss ( $D$ ) at 10 Hz and 1 kHz for the PU films with different hard segments are presented in Fig. 2(a) and 2(b). An increase in  $k'$  with a loss at  $-40$  °C to  $10$  °C and a high loss at temperatures above  $40$  °C were observed in the figures. It has been reported that the change near  $-15$  °C is related to the glass transition temperature ( $T_g$ ), at which  $\alpha$ -dielectric relaxation occurs due to the mobilization of the soft segment from a rubbery state to a glass state, and the I-relaxation process at about  $80$  °C is related to the glass

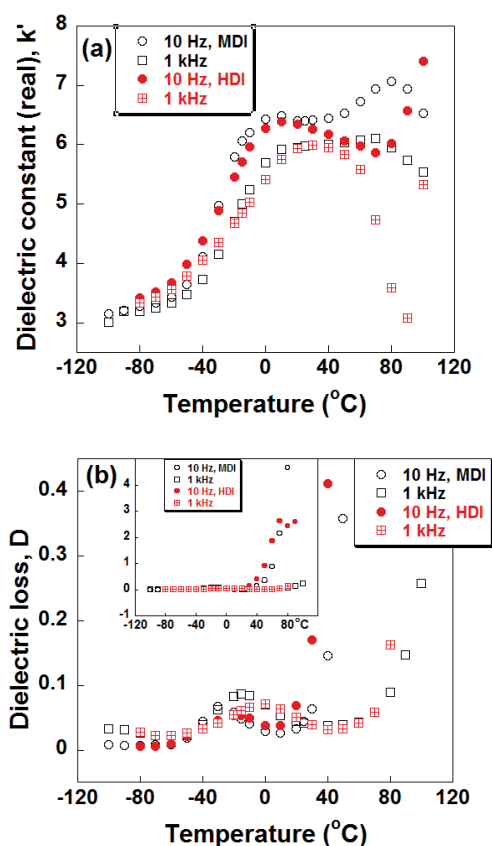


Fig. 2. Temperature-dependence of dielectric (a) constants and (b) losses at 10 Hz and 1 kHz for MDI/HDI-PU. The inset in (b) is scaled down.

transition temperature of the chain extender connecting the hard segments in MDI-PU [22]. It is implied that the dielectric transition directly reflects the phase transition of the material. In general, the dielectric constant is high at low frequencies because polymers with long chains can fluctuate sufficiently at low frequencies, but some of the fluctuations cannot follow the wave motions at high frequencies, inducing a decrease in the dielectric constant. As shown in the figure, the dielectric trends were similar in the temperature range of  $T_g$  for both the MDI-PU and the HDI-PU. However, the change in the dielectric behavior of HDI-PU at around 80 °C was much larger than that of MDI-PU, especially at 1 kHz (Fig. 2(a)), which indicates that the phase transitions of the two PUs near 80 °C occur by different mechanisms. MDI-PU and HDI-PU have an equivalent chain extender and its glass temperature is quite high because the hard MDI/HDI connected to the chain extender is linked to the other chains with strong intermolecular forces, as indicated in Fig. 1. Thus, the extender chain requires high energy for mechanical fluctuation, and the I-relaxation temperature of the extender is near 80 °C, as shown in the differential scanning calorimetry (DSC) curve in Fig. 3.

In Fig. 3, MDI-PU shows two endothermic phase transitions, i.e., the glass transition of the chain extender at about 80 °C and

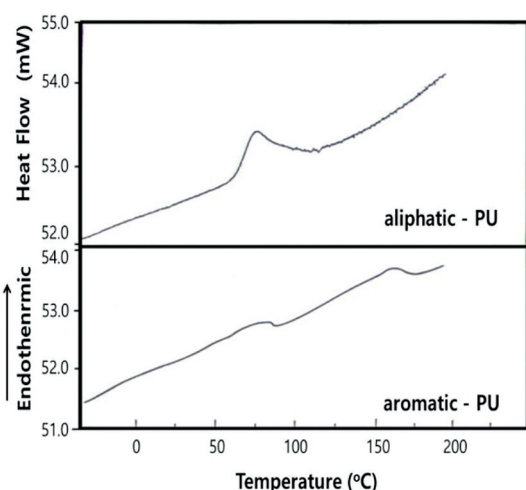


Fig. 3. DSC curves of the HDI- and MDI-polyurethane films.

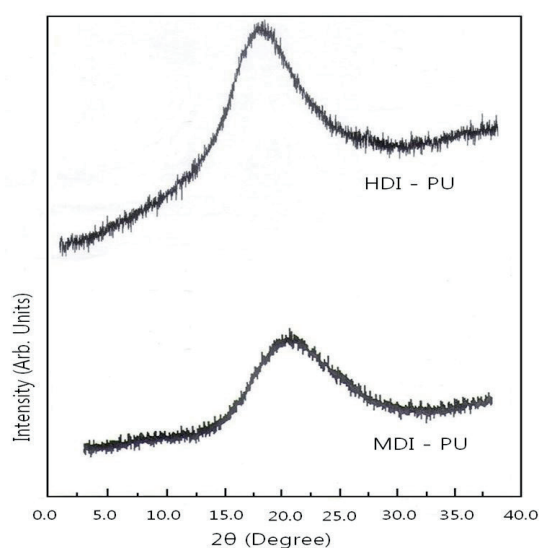


Fig. 4. XRD patterns of the HDI- and MDI-polyurethane films.

that of the rigid domain in PU close to 160 °C, where the hydrogen bond between  $-NH \cdots$  and  $\cdots O=C-$  in the aromatic MDI segments is dissociated [22]. In other words, the chain extenders connecting the hard MDI segments fluctuate without destroying the hydrogen bonding sheet-like structure in the polymer at approximately 80 °C, which is called the I-relaxation process. However, HDI-PU shows only one large endothermic peak, demonstrating that the hydrogen bond dissociates at 70–100 °C, where the chain extender is also mobilized. That is, the glass transition temperature of the chain extender and that of the rigid hard segment are the same in the HDI-PU system. Therefore, the I-relaxation in the HDI-PU occurs via fluctuations of both the chain extenders and rigid hard segments. In fact, the polyurethane comprising aliphatic isocyanate (HDI) is more flexible than that with the aromatic isocyanate (MDI) hard segment. Hence, a different I-relaxation mechanism is expected in the HDI-PU system compared with the MDI-PU system, although their crystallinities are similar, as observed in Fig. 4.

Figure 4 shows the X-ray patterns of the two PUs; no detectable crystalline phases were found in the samples, reflecting their amorphous states. The broad peak near  $2\theta = 20^\circ$  is due to the soft segment, PTMEG [23]. The crystallinities of the HDI-PU and the MDI-PU species are similar, meaning that the orders of the molecular arrangements in the respective chains are similar.

As a consequence of the dissociation of the hydrogen bonds in the HDI segments, a sharp decrease in the dielectric constant was observed at about 80 °C in Fig. 2(a) and the dielectric constant of HDI-PU increased again at temperatures above 90 °C due to an increase in the polarization motion from flipping of the unconstrained-dipoles to the favorable direction with high endothermicity. The large change in the dielectric constant was accompanied by a dielectric loss near 80–90 °C, resulting in conduction, thermal absorption, or/and a large change in the strain, where the I-dielectric relaxation is observed.

The dielectric constants in the frequency range of 1 Hz to 3 kHz at different temperatures are shown in Fig. 5. The largest changes in the dielectric constant with variation in the frequency were observed for HDI-PU at 80–90 °C, which is in good agreement with the results in Fig. 2, reflecting the difference in the I-relaxation mechanism relative to that of MDI-PU. That is, the elongated chains composed of the extenders and unconstrained hard segments fluctuate slowly, resulting in the large dielectric reduction with increasing frequency compared with that of MDI-PU, where only the extender is mobilized at 80–90 °C. On the other hand, both MDI-PU and HDI-PU show a similar dielectric tendency at -15 °C with variation of the frequency as both have the same soft segment, PTMEG. Thus, the  $\alpha$ -relaxations of the two PUs show an equivalent type of dielectric response around

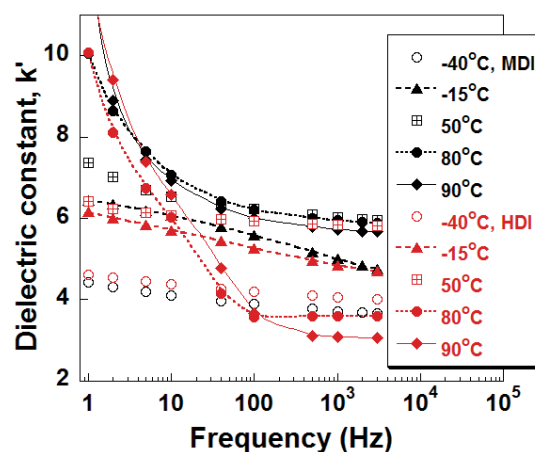


Fig. 5. Frequency-dependence of dielectric constants at -40, -15, 50, 80, and 90 °C in MDI/HDI-PUs.

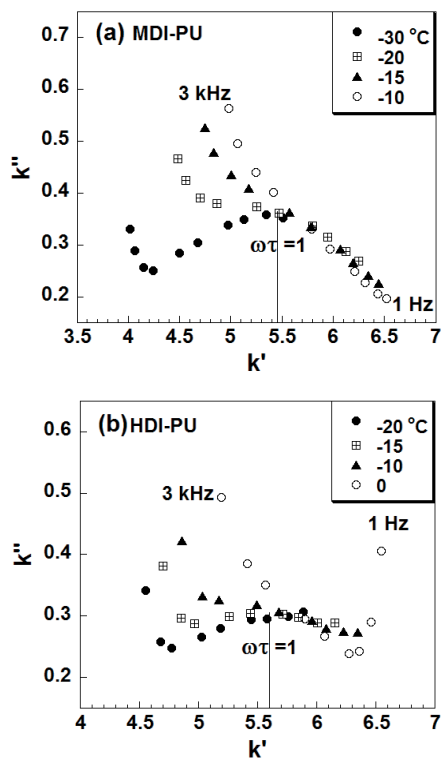


Fig. 6.  $k''$  vs.  $k'$  Cole-Cole plots (a) at -30 to -10°C for MDI-PU and (b) at -20 to 0°C for HDI-PU.

the  $T_g$  (-15°C).

Based on the Cole-Cole equation [24], the relaxation frequency of the dielectric absorption maximum,  $f_{max}$ , is expressed as:

$$2\pi f_{max}\tau = 1 \quad (1)$$

where  $\tau$  is the effective relaxation time. The dielectric dispersion (real part,  $k'$ ) and absorption (imaginary part,  $k''$ ) curves are symmetrical about the position  $\omega\tau = 1$  in the plot of  $k''$  vs.  $k'$  (Fig. 6), where  $\omega$  ( $= 2\pi f$ ) is the angular frequency and  $k''$  is the imaginary part of the relative dielectric constant, described by the relation,  $k'' = k'D$ . The position of  $\omega\tau = 1$  is indicated for MDI-PU in the temperature range of -30 to -10°C (Fig. 6(a)) and that of HDI-PU in the range of -20 to 0°C (Fig. 6(b)), illustrating the shift of their relaxation frequencies to higher frequencies as the temperature increases. The plots indicate the same relaxation mechanism, i.e.,  $\alpha$ -relaxation, which is observed as a part of a depressed semicircle. Thus, the experimentally obtained  $f_{max} = 46$  Hz for MDI-PU and 4.7 Hz for HDI-PU at -20°C could be used to determine the relaxation time ( $\tau = 3.46 \times 10^{-3}$  s for MDI-PU and  $\tau = 3.39 \times 10^{-2}$  s for HDI-PU) at -20°C.

Figure 7(a) shows a part of the large semicircle at low frequencies, which is derived from the I-relaxation of MDI-PU in the temperature range of 60–100°C. A trace of the  $\alpha$ -relaxation was still observed at high frequencies and the magnified section in the figure shows the part of the semicircle derived from  $\alpha$ -relaxation, which shifted towards high frequencies as the temperature increased, where the  $\alpha$ -relaxation frequency ( $f_{max}$ ) at 90°C was a little above 3 kHz. The plot in Fig. 7(b) shows a unique semicircle at 80–90°C, where the relaxation frequency is in the range of 200–400 Hz. This relaxation is attributed to the coupling of the I-relaxation at low frequencies with the  $\alpha$ -relaxation at high frequencies. In other words, all the segments in the HDI-PU begin to mobilize close to 90°C after dissociation of the hydrogen bond and the motions match at a certain frequency (200–400 Hz). The  $\alpha$ -relaxation induced by the soft segment

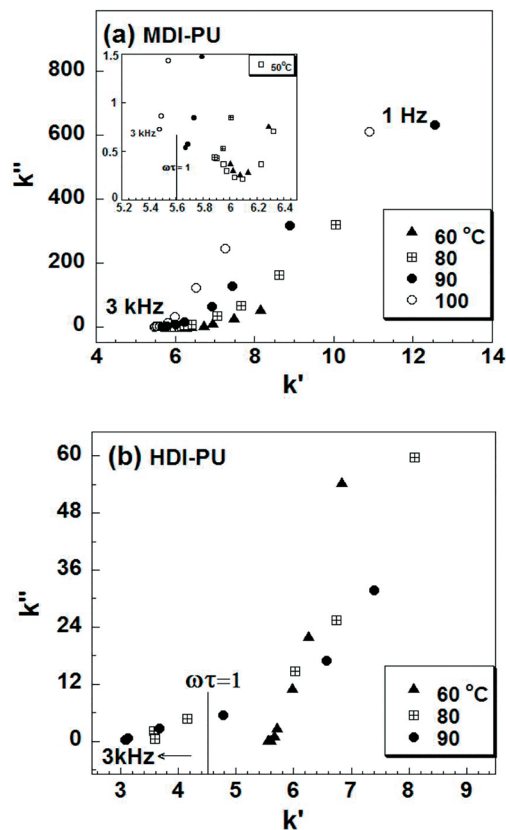


Fig. 7.  $k''$  vs.  $k'$  Cole-Cole plots (a) at 60 to 100°C for MDI-PU; the region at high frequencies is magnified in the inset and (b) at 60 to 90°C for HDI-PU.

appears from about -20°C and shifts towards high frequencies as the temperature increases, then interacts with the newly appearing I-relaxation produced by the extenders and rigid hard segments at about 80–90°C. Thus, the dielectric behavior of HDI-PU is more complicated than that of MDI-PU in the temperature range of 80–90°C.

The dielectric responses over the frequency range of 1 Hz to 3 kHz in the temperature range of -30 to 0°C are presented in Figs. 8(a), 8(b). The dielectric dispersion shifted to higher frequencies as the temperature increased. Using the temperature-frequency superposition principle [21], the data at other temperatures were well matched to those at -20°C, where the frequency was shifted by the factor,  $a(t) = \tau_t / \tau_r$ , which is the ratio of the relaxation time at a certain temperature ( $t$ °C) to the relaxation time at the reference temperature ( $r$ °C); the reference temperature is -20°C. The values of the shifting factor  $a(t)$  obtained for MDI-PU at -30, -15, and -10°C to -20°C were 26, 0.26, and 0.11, respectively. The  $a(t)$  values for HDI-PU at -15, -10, and 0°C to -20°C were 0.27, 0.08, and 0.011, respectively, which provide information on the migration rate of the relaxation time with variation of the temperature. When the dielectric dispersions at 70 and 90°C shifted to 80°C, as shown in Fig. 8(c), the  $a(t)$  values were 1.28 and 0.89 for MDI-PU. However, the dielectric dispersions did not match well in the case of HDI-PU and did not follow the temperature-frequency superposition principle, especially at high frequencies, because the I-relaxation interacts with the  $\alpha$ -relaxation as described in relation to Fig. 7. After dissociation of the hydrogen bond, the elongated molecular chains of the soft segments, extenders, and hard segments in HDI-PU cannot oscillate in resonance with the high wave frequency provided, resulting in an abrupt reduction in the dielectric constant at high frequencies,

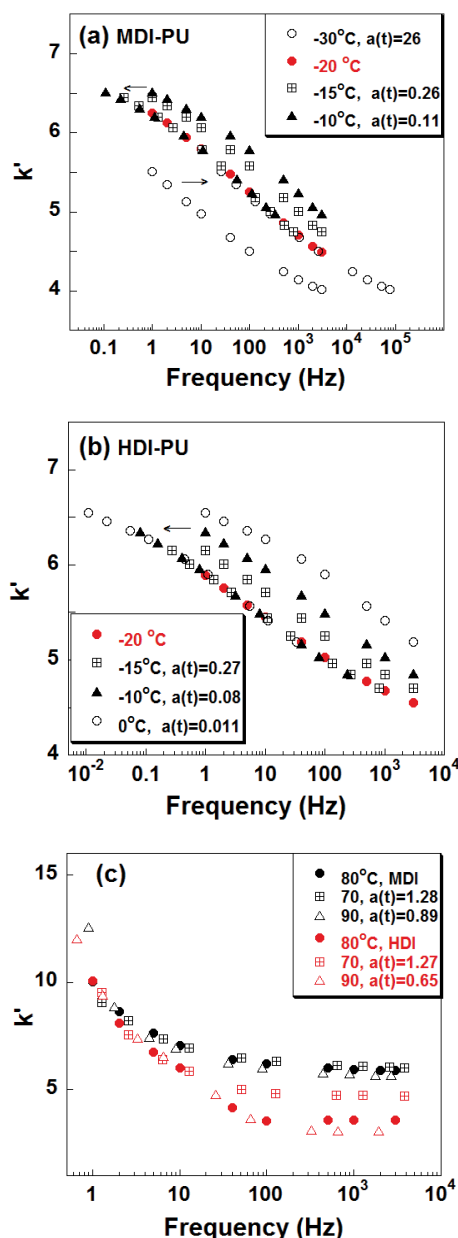


Fig. 8. Frequency-dependence of dielectric constants (a) at -30 to -10°C and curve shift to -20°C for MDI-PU, (b) at -20 to 0°C and curve shift to -20°C for HDI-PU, and (c) curve shift to 80°C from 70 and 90°C in the MDI/HDI-PU.

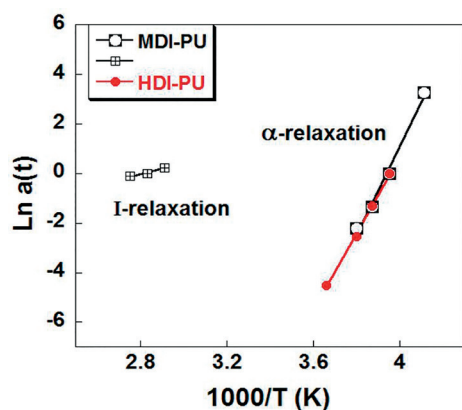


Fig. 9.  $\ln a(t)$  of dielectric relaxation vs.  $1000/T$  (K) for MDI/HDI-PU.

as observed in Fig. 5. Thus, the dielectric constants of HDI-PU at 80-90°C in Fig. 8(c) are lower than that at 70°C at high frequencies, even though the dispersion curve at 70°C is shifted to 80°C, which fails to obey the temperature-frequency superposition principle.

Figure 9 shows the relation between the shifting factor and the temperature for the dielectric relaxations of the two PUs that follow the superposition principle, in which the  $\ln a(t)$  is positively linearly related to the inverse of the temperature. The shifting ratios of the  $\alpha$ -relaxation for the two PUs with variation of the temperature were similar, meaning that as the temperature increases, the  $\alpha$ -relaxation migrates towards higher frequencies with a similar rate because both PUs have the same soft segment. Compared with the  $\alpha$ -relaxation, a slower migration of the I-relaxation was observed for MDI-PU.

#### 4. CONCLUSION

The dielectric behavior of two polyurethane films having different hard segments, i.e., MDI and HDI, but having an equivalent soft segment, chain extender, similar crystallinity, and film thickness, was examined to investigate the relationship of the temperature and frequency to the phase transitions of the polymers. The two PUs adopted amorphous morphologies with similar  $T_g$ s in the region of -20 to -15°C. Their  $\alpha$ -relaxations followed analogous patterns with a similar shifting rate due to the similarity of the soft segment, except that the relaxation time was slightly longer for HDI-PU. Two transitions were observed for aromatic MDI-PU, i.e., one at about 80°C owing to the glass transition of the chain extender and another close to 160°C due to that of the rigid hard segment. However, only one transition (near 70-100°C) was observed for aliphatic HDI-PU because the glass transitions of the chain extender and the hard segment occurred in the same temperature range. Thus, the I-relaxation of HDI-PU was attributed to fluctuation of the long chain extender and unconstrained hard segment. In addition, the I-relaxation of HDI-PU was coupled with the  $\alpha$ -relaxation which shifted towards high frequencies at 70-100°C, resulting in a different I-relaxation mechanism from that of MDI-PU. Therefore, the  $\alpha$ -relaxations of the two PUs and the I-relaxation of MDI-PU followed the temperature-frequency superposition principle, whereas the I-relaxation of HDI-PU did not. The shifting rates of the  $\alpha$ -relaxations were faster than that of the I-relaxation in the case of MDI-PU. These results demonstrate that the dielectric responses are influenced mainly by the phase transition of the material, which is affected by the structure and components of the molecule. The arrangements of the molecular chains and the number of defects, such as grain boundaries, also influence the dielectric properties of the material to a certain extent.

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