Molecular Mobility of Soft Segment of Polyurethane Elastomers under Elongation

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Abstract. In this study, we investigated molecular mobility of a soft segment in the poly(oxypropylene) glycol (PPG), 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butane diol (BD)-based polyurethane elastomers (PUE) with and without elongation by dynamic viscoelastic property measurement and pulse nuclear magnetic resonance (NMR) measurement. The peak position of the loss tangent (tanδ) curves shifted to the lower temperature region with increasing elongation. In the pulse NMR measurement, the long spin-spin relaxation time (T_2) component appeared at -18.0 ($\varepsilon = 0$) and -26.0 °C ($\varepsilon = 1.5$), respectively, with increasing temperature. Since this temperature seems to be related to the glass transition temperature (T_g) of the soft segment in the PUE, it is likely to consider that the T_g decreased with increasing strain. These results might be attributed that the size of cooperative motion during the glass transition decrease due to the orientation of the soft segment, and the soft segment phase approach to a pure phase on account of the extraction of the hard segment from the soft segment phase.

Keywords: Polyurethane, Glass Transition Temperature, Elongation
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INTRODUCTION

The glass transition of the rubbery molecules under elongation is pivotally intriguing in terms of not only academic but industrial aspects. Some groups have worked on this topic using natural rubber [1-3] and cycloaliphatic polyester networks[4,5] using dynamic viscoelastic properties measurement, volume dilatometry, broad line nuclear magnetic resonance (NMR), stress-temperature measurement and so on.

Polyurethane elastomer (PUE) is an important elastomer as well because it possesses quite high abrasive and rubbing resistances. Generally, the PUEs form the microphase-separated structure, which consists of hard segment domains and a soft segment matrix.[6] Since the PUEs possess a simplified structure, it seems suitable for investigation of the relation between the glass transition and elongation.

In this study, we investigated the relation between the glass transition of the soft segment chain and elongation of the PUE using dynamic viscoelastic measurement and pulse NMR measurement.

EXPERIMENTAL

Synthesis of PUEs

The PUEs were synthesized from poly(oxypropylene) glycol (PPG: M_n=2000 and 4000), 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butane diol (BD) by a prepolymer method. The sample name denotes the abbreviation of raw materials and the thousand digit of PPG.

Dynamic Viscoelastic Property Measurement

Temperature dependence of dynamic viscoelastic properties was measured with a dynamic mechanical analyzer (DMS 6100, Seiko Instruments, Co., Ltd.). The size of samples used is 30 mm x 5 mm x 2 mm. Measurement was performed in the temperature range from -150 to 250 °C with a heating rate of 2 °C min^{-1} with nitrogen atmosphere. Imposed strain and frequency were set to be 0.2 % and 10 Hz, respectively.

Pulse Nuclear Magnetic Resonance (NMR) Measurement

Molecular mobility of the soft segment of the PUE was evaluated with a Pulse NMR (JNM-MU25AH, JOEL, Co., Ltd. Japan). A solid echo method was employed for measurement. Measurement was performed at various temperatures in the range from -70 °C to room temperature.

RESULTS AND DISCUSSION

Dynamic Viscoelastic Properties of Polyurethanes under Elongation

Figure 1 (a) shows temperature dependence of dynamic storage modulus (E') and loss tangent (tanδ) of PPG-MDI-BD at various strains. The E' curve at ε=0 decreased at around glass transition region of the soft segment and exhibited the rubbery plateau region and terminal flow. The terminal region is assignable to melting of crystallized hard segment domains. As the strain increases, the rubbery plateau region disappeared and the temperature of the terminal region decreased. In the tanδ curves, the maximum magnitude decreased with increasing strain and it looks like the peak position shifted to lower temperature region. Figure 1 (b) shows temperature dependence of normalized tanδ. The peak position shifted to the lower temperature region and the peaks width broadened with increasing static strain. Figure 1 (c) shows strain dependence of the onset temperature of tanδ peak obtained from Figure 1 (b). The onset temperature for PPG2-MDI-BD decreased greater than for PPG4-MDI-BD. This is related to not only conformation of the soft segment but the change in the degree of microphase separation induced with elongation.
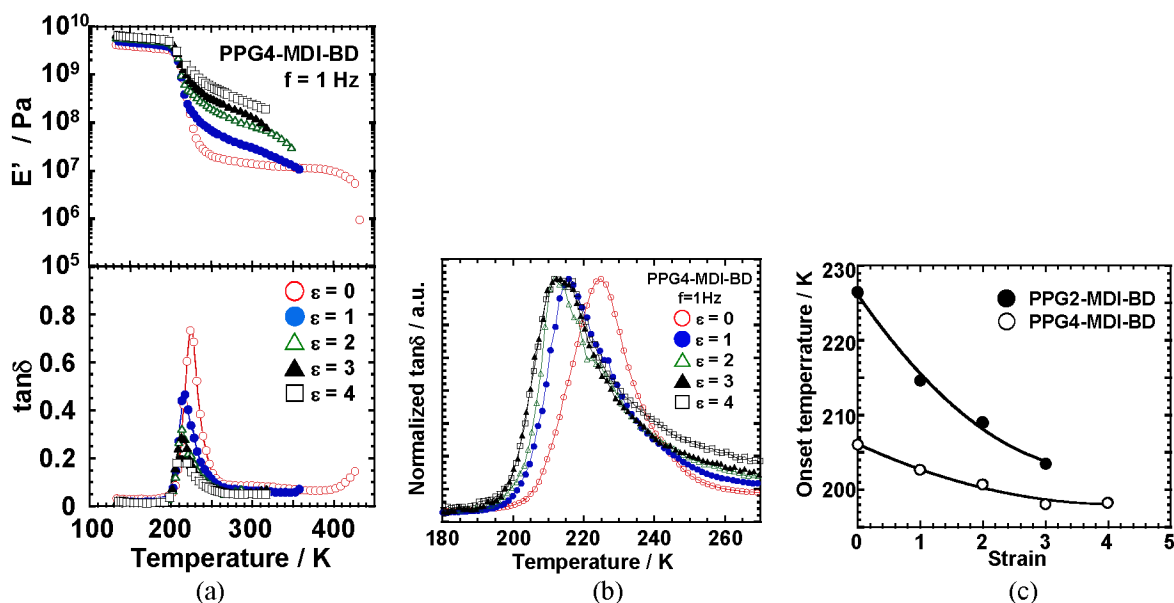

FIGURE 1. (a) Temperature dependence of dynamic storage modulus (E') and loss tangent (tanδ) for PPG4-MDI-BD at various static strains. (b) Temperature dependence of normalized tanδ. (c) Onset temperature of tanδ peak-strain relation for PPG2-MDI-BD and PPG4-MDI-BD.

Figure 2 shows FID curves of spin-spin relaxation time (T_2) of PPG2-MDI-BD measured at various temperatures at a strain (ε) of (a) 0 and (b) 1.5. In the FID curves, fast and slow decay components generally exhibit Gaussian and Lorenzian functions. In the case of the polyurethane, the soft segment in the rubbery state and the hard segment component in the crystalline state correspond to the slow and fast decay components, respectively. At low temperature region, no slow decay component was observed because all the components are in the glassy and crystalline state. As the measurement temperature increases, the slow decay component appeared as a linear component at the longer time region (-18.0 °C for ε=0). The temperature, at which the linear component was observed, was different between two strains. The temperatures were -18.0 and -26.0 °C for ε=0 and 1.5, respectively. If we assume this temperature can be defined as the glass transition temperature (T_g) of the soft segment, this result clearly implies that the T_g decreased with increasing strain. This might be attributed that the size of cooperative motion during the glass transition decreases with due to the orientation of the soft segment, and the soft segment phase approach to a pure phase on account of the extraction of the hard segment from the soft segment phase.
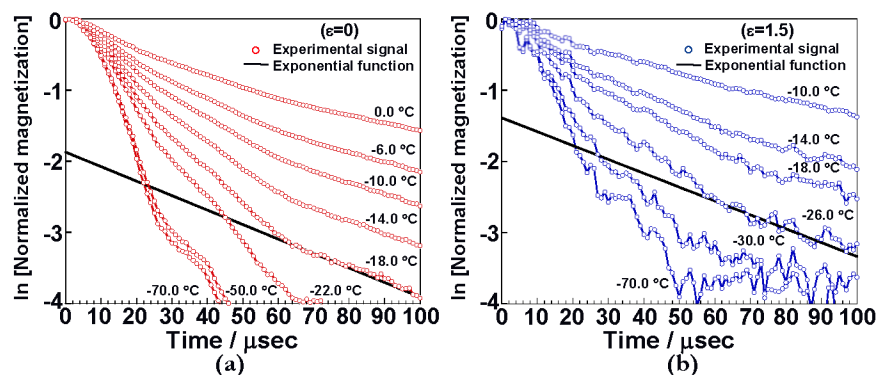

FIGURE 2. FID curves of spin-spin relaxation time (T_2) of PPG2-MDI-BD measured at various temperatures at a strain of (a) 0 and (b) 1.5.

Figure 3 shows temperature dependence of T_2 for PPG, PPG2-MDI-BD measured at ε=0 and ε=1.5. As can be clearly seen, T_2 at ε=1.5 gradually increased with the measurement temperature in comparison with ε=0. Thus, this result obviously suggests that the molecular mobility is suppressed although the T_g of the soft segment decreased with increasing strain.
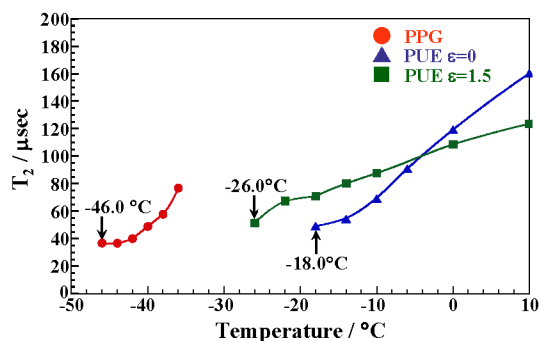

FIGURE 3. Temperature dependence of T_2 for PPG, PPG2-MDI-BD measured at ε=0 and 1.5.

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