Physical and Mechanical Properties of Polyurethanes Crosslinked by [3]Rotaxane

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Abstract

We report here physical and mechanical properties of three polyurethanes (PU11, PU33 and PU0) with and without azobis(dibenzo-24-crown-8 ether) ABC, which acts as a mechanical bonding cross-link point possessing a [3]rotaxane structure.

Introduction

One of the most interesting properties of rotaxanes arising from a mechanical bond is that the ring molecule can move freely along the axis molecule since no covalent bond exists between the ring and axis molecules (Fig. 1).\textsuperscript{1,2} It is expected that introduction of the mechanical bonding crosslink instead of the hydrogen bonding one into the hard segments of PU elastomers (PUEs) leads to control the mechanical properties and development of novel functions of PUEs.

In this presentation, we describe characterization of three PUs with and without a [3]rotaxane as a mechanical bonding crosslink point by spectral, thermal, and mechanical measurements.

Results and Discussions

Glass transition temperatures ($T_g$) of the soft segment chains in PU0, PU11 and PU33 were observed at $-62$, $-61$ and $-59$ °C, respectively. The $T_g$ values are gradually shifted to higher temperature with increasing the content of ABC while the difference was small. The shift would be expected that the decrease of the formation of hydrogen...
bonding between the PU chins induced by the introduction of ABC would involve decreasing both the hard-segment and pure soft-segment phases. In fact, the ATR-FT-IR spectra of the PUs revealed that relative intensity ratios of the carbonyl groups ($I_{\text{ν}(C=O)H\text{-bond}}/I_{\text{ν}(C=O)\text{free}}$) of the PUs decreased with increasing the content of ABC.

Figure 2 shows the stress-strain curves for the PU0, PU11 and PU33. Young’s moduli for PU0 and PU33 were 11.1 and 10.8 MPa, respectively, whereas that for PU11 was 1.8 MPa. Remarkably, PU33 possesses the best tensile strength and strain at break. Even if the interaction between a crown unit of ABC and an ammonium unit of Ax is broken by tension, the crown unit can slide on the chain and interact with neighbor ammonium unit of Ax. Therefore, we believe that this sliding behavior causes the unique tensile properties. These tensile strength and elongation properties are the evidence for the existence of the mechanical bond crosslink point via the rotaxane in the structure of PU33.

Conclusions

The content of 33 % for ABC in PU33, in which some of them act as the mechanical bond crosslink point, is enough to develop the properties originated from the mechanical bond crosslink point. In fact, incorporation of the enough amount of the mechanical bond crosslink point via the rotaxane structure causes the best tensile strength and elongation among the PUs. In contrast, the content of 11 % for ABC in PU11 is unsatisfying to form the network structure.

References