

Surface Molecular Mobility of Crosslinked Polyurethane by Scanning Force Microscopy

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Introduction

Surface properties of polymer materials are closely related to molecular mobility and chemical composition at the top surface. For the linear polymers, it is revealed that surface molecular mobility is activated in comparison with bulk. However, the study on crosslinked polymers has never done yet. It is inferred that another factors, for example, crosslinking density and dangling chain density, need to be thought to understand. In this study, surface molecular motion of the crosslinked polyurethanes was investigated in terms of their crosslinking density and the number of dangling chains.

Experimental

Chemically crosslinked polyurethanes (PUs) with different crosslinking density were synthesized from poly(oxypropylene) triol (PPT) and, 4,4'-diphenylmethane diisocyanate (MDI) or tolylene-2,4-diisocyanate (TDI) by a one-shot method. Surface molecular mobility of PUs was investigated using lateral force microscope (LFM) at various temperatures.

Results & Discussion

In differential scanning calorimetry (DSC) thermograms, T_g of bulk was clearly observed at around -60 °C for both PPT-TDI- and PPT-MDI-based PUs. α -Relaxation of the PPT chains was detected in LFM measurement, and the relaxation temperature observed shifted to the lower temperature region in comparison with bulk measurement. This might be attributed to surface localization of dangling chains, decreasing crosslinking density and surface effect. Figure 1 shows temperature dependence of apparent activation energy for α -relaxation of PUs. Apparent activation energy for surface was much lower than that for bulk. Therefore, it seems reasonable to conclude that the surface molecular mobility of crosslinked polyurethane is activated compared with the bulk one.

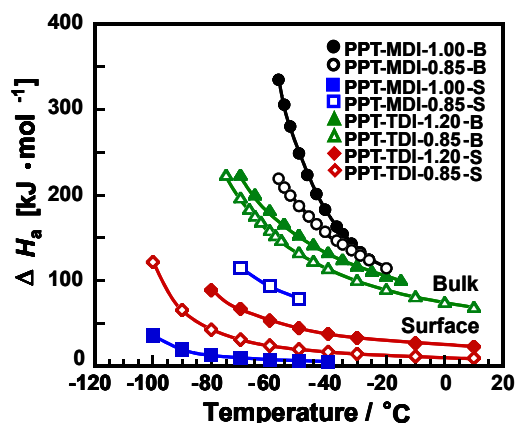


Figure 1. Apparent activation energy of PUs. Nomenclature denotes the name of polyol, diisocyanate, the ratio of $K = [\text{NCO}]/[\text{OH}]$. The symbol "S" and "B" represent data for surface and bulk, respectively.