

The MDI-Mediated Lateral Crosslinking of Polyurethane Copolymer and the Impact on Tensile Properties and Shape Memory Effect

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Polyurethane (PU) has long been investigated due to its excellent mechanical properties, shape memory effect, and biocompatibility,¹⁻³ and was grafted with pendant functional groups to tailor the polymer characteristics without affecting their basic structure. Actually, polyethyleneglycol has been grafted to polyurethane to improve biocompatibility in bio-medical applications,⁴ and low temperature flexibility could be improved by the pendant naphthol group grafted to PU.⁵ In the field of shape memory polyurethane, mechanical and shape memory properties could be improved by terminal crosslinking with glycerol, pentaerythritol, and dextrin.^{6,7} Alternatively, a flexible crosslinking method was devised to demonstrate both high mechanical strength and shape recovery.^{8,9} The carbamate group has been frequently employed as the grafting point due to advantages such as ample linking sites, high reactivity, and mild coupling conditions, and activated with diisocyanate compound.¹⁰ The question is whether the diisocyanate compound used for grafting pendant group to PU chain can crosslink another chain under the mild reaction condition, although such allophanate linking is known to require high temperature.¹¹ In this investigation, the possibility of lateral crosslinking of PU under mild reaction condition and the impact on tensile properties and shape recovery are examined.

The PU was synthesized based on previous methods,^{8,9} wherein 4,4'-methylenebis(phenyl isocyanate) (MDI) and poly(tetramethyleneglycol) (PTMG, $M_n=2000$) function as hard and soft segments, respectively, and 1,4-butanediol

(BD) was used as a chain extender. The specific mole ratios of the reaction mixture are summarized in Table 1. In this investigation, the second MDI was intended to link PU chains through carbamate group and its impact on tensile properties and shape memory effect was tested. The urethane surface grafting with diisocyanate was already well established and could be carried out under mild reaction conditions.¹⁰ In this experiment, the usage of catalyst such as dibutyltin dilaurate or triethylamine was avoided due to the aggregation problem and the grafting reaction could go on homogeneously even without catalyst. The scheme of the MDI-mediated crosslinking is shown in Figure 1. The crosslink density was calculated from a polymer swelling experiment to determine whether the second MDI could really crosslink PU chains, which could explain the unusual tensile properties of the PU.¹² The crosslink density was found to abruptly increase with the inclusion of second MDI

Table 1. Composition of the PU

| Sample code | Composition (mmole) | | | |
|-------------|---------------------|------|----|-------|
| | MDI-1 | PTMG | BD | MDI-2 |
| M-1 | 50 | 20 | 30 | - |
| M-2 | 50 | 20 | 30 | 5 |
| M-3 | 50 | 20 | 30 | 10 |
| M-4 | 50 | 20 | 30 | 15 |
| M-5 | 50 | 20 | 30 | 20 |

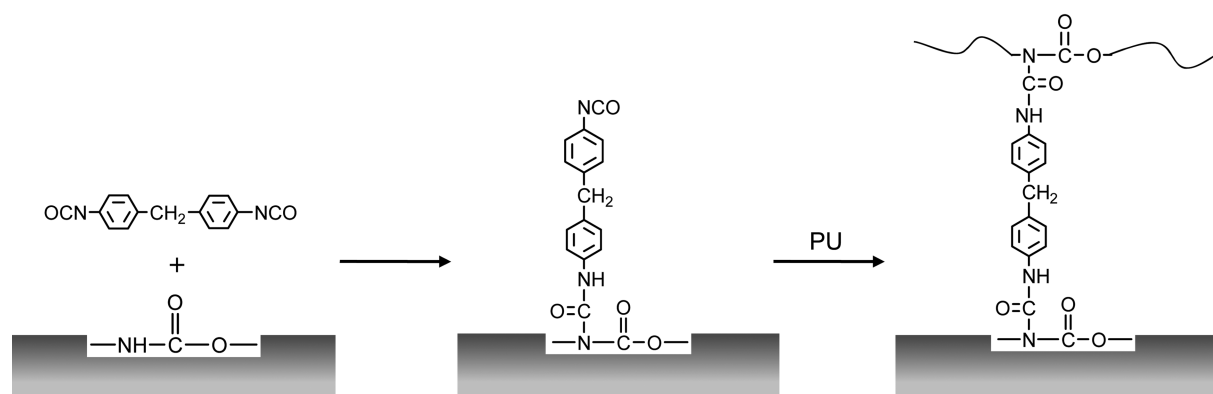


Figure 1. Stylized view of PU linked to other PU by second MDI.

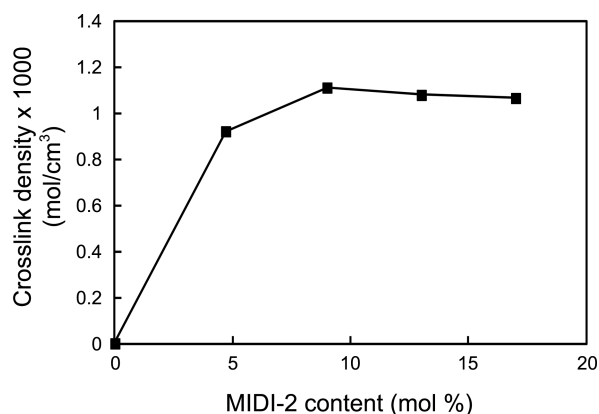


Figure 2. Crosslink density profile of the M series.

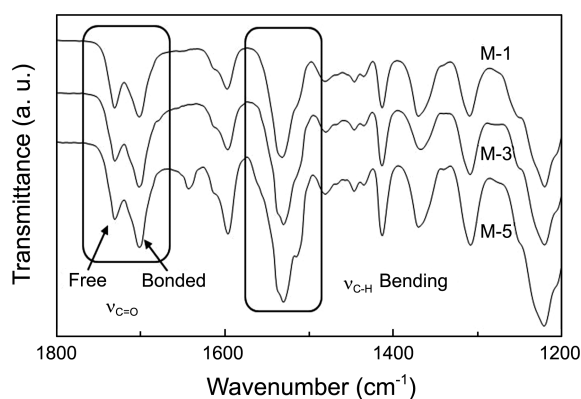


Figure 3. IR spectra of the M series.

(Figure 2).

The IR spectra of the selected M series (M-1, M-3, and M-5) are compared in Figure 3. The new C-H bending peak around 1510 cm^{-1} appeared as the second MDI content increased, which suggests that the crosslinking changed the C-H vibration mode. Intermolecular attraction, such as hydrogen bonding and dipole-dipole interaction, between hard segments can be analyzed from the IR spectra, where the bonded C=O stretching vibration appears at 1699 to 1706 cm^{-1} and is slightly lower than that of the free carbonyl group (1731 to 1733 cm^{-1}).^{13,14} As the second MDI content increased, the bonded carbonyl peak slightly increased compared to the free carbonyl in Figure 3, suggesting that molecular interactions were augmented by crosslinking. It was determined from the IR spectra that the MDI-mediated crosslinking was formed based on the change in vibration mode.

The viscosity of PU solution in *N,N*-dimethylformamide was compared at five different concentrations (0.25, 0.5, 1, 2, and 4%, w/w) in Figure 4. The difference in viscosity between M series was obvious at 4% solution, where the viscosity of M-5, the most highly crosslinked one, was not shown due to the solubility problem. The sudden viscosity increase at high concentration and the insolubility of M-5 suggests that crosslinking was formed as designed.

The average maximum stress abruptly increased with the inclusion of second MDI (Figure 5). For example, the aver-

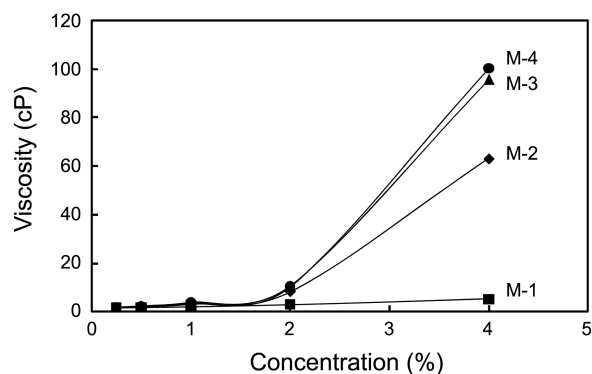


Figure 4. Viscosity profile of the M series.

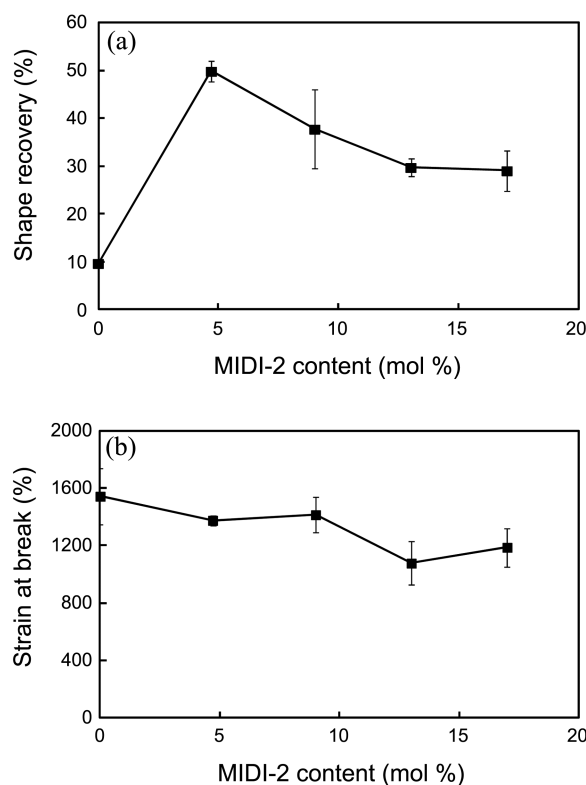


Figure 5. (a) Maximum stress, and (b) strain at break of the M series.

age maximum stress increased from only 9.7 MPa for M-1 to 50 MPa for M-2, and 29 MPa for M-5. The MDI-mediated crosslinking was responsible for the initial increase in the maximum stress, but the maximum stress decreased at high second MDI content because the PU became rigid and vulnerable to external stress if highly crosslinked. The average strain at break slightly decreased with an increase in second MDI content. For example, the strain at break slightly decreased from 1542% for M-1 to 1186% for M-5. It is shown from the tensile results that the MDI-mediated crosslinking improved the maximum stress and strain at break was not significantly reduced by the crosslinking.

Shape memory tests were repeated under cyclic stretch-release conditions between -25 and $45\text{ }^{\circ}\text{C}$, following the same shape memory test conditions of previous PUs.^{8,9} Hard

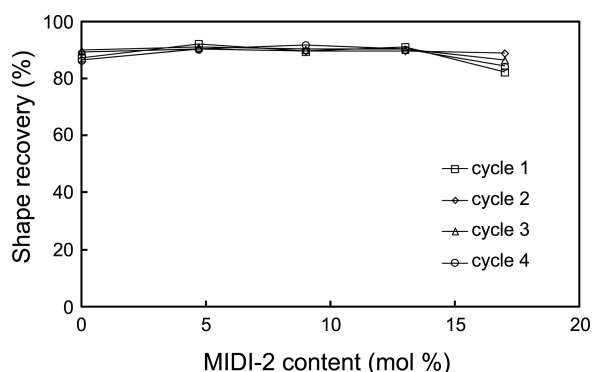


Figure 6. Cyclic shape recovery profile of the M series.

segments retain the distorted shape at $-25\text{ }^{\circ}\text{C}$ and recover the original shape at $45\text{ }^{\circ}\text{C}$. In contrast, soft segments absorb the applied tensile stress by unfolding the entangled chains. However, permanent deformation of the hard segment domain by repetitive stress is known to limit shape recovery.¹ In Figure 6, the cyclic shape memory tests show that shape recovery was reproducible after four test cycles. The shape recovery was approximately 90% and did not significantly decrease or become even better after four cyclic tests. For example, the shape recovery of M-3 changed from 89% in the first test to 91% in the fourth test. In contrast, shape retention was low compared to shape recovery results. For example, the shape retention of M-3 (51%) slightly increased to 55%. Similar to the results for shape recovery, shape retention remained unchanged after cyclic testing. Shape recovery and retention tests demonstrated that the laterally crosslinked PU maintained reliable shape recovery and retention.

In conclusion, the maximum stress and strain at break remained high and stable after MDI-mediated crosslinking. Similarly, shape recovery and shape retention tests also showed excellent and reproducible results. The MDI-mediated crosslinking was responsible for the interesting tensile

and shape memory results. Therefore, it was demonstrated in this investigation that the allophanate type crosslinking, unlike previous misleading informations, was possible under the mild reaction conditions.

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