Notes

The Effects of Grafting Bisphenol A or Naphthalene Derivative onto Polyurethane with Respect to Shape Memory and Thermal Properties

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Introduction

Molecular interactions, such as hydrogen bonding and dipole-dipole interaction between polyurethane (PU) chains play an important role in determining the polymer's mechanical, thermal, and shape memory properties.[1] The grafting of functional or bulky groups onto PU had been performed to obtain special properties that enable pH-sensitivity, antifungal properties,[2] and low-temperature flexibility.[3] Bisphenol A (BPA), which is used in the manufacturing of polycarbonate, and 1,5-dihydroxynaphthalene (DHN) were selected as grafting functional groups in this investigation because they contain aromatic rings that can be used for the disruption of molecular interactions. Therefore, the effects of grafting BPA or DHN onto PU were examined by comparing the thermal, tensile, and shape memory properties as well as low-temperature flexibility of the modified polymer with those of the unmodified PU.

Experimental

Poly(tetramethylene glycol) (PTMG, M_n~2,000 g/mol, Sigma-Aldrich, St. Louis, MO, USA), bisphenol A (Sigma-Aldrich), 1,5-dihydroxynaphthalene (Sigma-Aldrich), 4,4'-diphenyl-methane diisocyanate (MDI, Junsei, Tokyo, Japan), and 1,4-butanediol (BD, Junsei) were dried overnight under vacuum. The synthesis of PU and sample preparation for the mechanical test followed the literature.[2,3] As for the characterization of

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the PU samples, a Fourier transform infrared spectrometer (FTIR, JASCO 300E, Tokyo, Japan) equipped with an attenuated total reflectance (ATR) accessory was used to measure IR spectra. A differential scanning calorimeter (DSC-Q20, TA Instruments, New Castle, DE, USA) was used to collect calorimetry data for both heating and cooling scans at a rate of 10 °C/min between -50 and 250 °C. Tensile mechanical properties were measured according to the ASTM D638 standard at 25 °C using a universal testing machine (UTM, LR10K, Lloyd Materials Testing, West Sussex, UK) with the following parameters: 20 mm gauge length, 20 mm/min crosshead speed, and 0.5 kN load cell.[2,3] The same UTM equipped with a temperature-controlled chamber was employed for shape memory tests following the literature method.[2,3] The low-temperature flexibility test was conducted in a temperature-controlled chamber of the UTM for a twisted spiral sample frozen at -35 °C for 3 h and was recorded by a video camera (SONY HDR-CX 550, Tokyo, Japan) installed close to the chamber window while the temperature was increased by 10 °C/min.

Results and Discussion

Two series of samples were synthesized by grafting either BPA (B series) or DHN (D series) onto PU (Figure 1) by following previous methods.[2,3] The specific mole ratios are summarized in Table I. PU grafting with the diisocyanate compound is well established and can be carried out under mild reaction conditions.[4,5] The grafting of rigid-structural groups onto PU is known to reduce intermolecular interactions and improve the low-temperature flexibility under freezing conditions compared with the grafting of flexible chains.[3,6] BPA
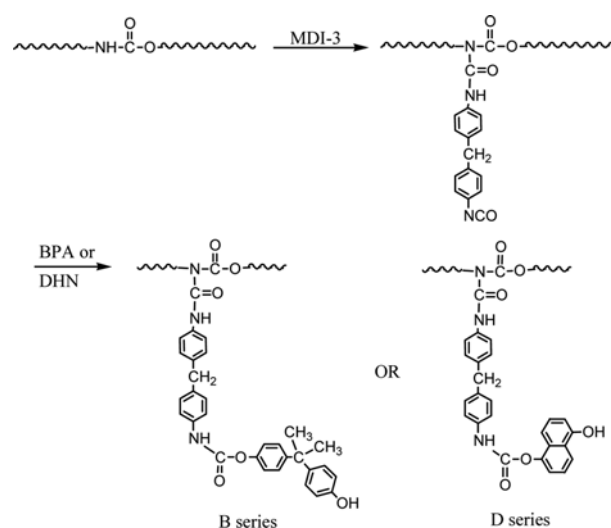

Figure 1. Steps for grafting side groups BPA and DHN onto PU.

Table I. Composition of the PU Grafted with BPA or DHN

Sample Code	Reactant, mmol					
	MDI-1	PTMG	BD	MDI-2	MDI-3	BPA or DHN[a]
L	20	20	30	30	-	-
B-1	20	20	30	30	5	5
B-2	20	20	30	30	10	10
B-3	20	20	30	30	15	15
B-4	20	20	30	30	20	20
D-1	20	20	30	30	5	5
D-2	20	20	30	30	10	10
D-3	20	20	30	30	15	15
D-4	20	20	30	30	20	20

[a]BPA and DHN stand for bisphenol A and 1,5-dihydroxynaphthalene, respectively.

and DHN contain aromatic rings that can disrupt the PU chain alignment and were therefore promising candidates for pendant groups.

The IR spectra for both the B and D series exhibited peaks corresponding to C-H bending at 1530 cm^{-1}, aromatic C-C ring stretching at 1594 and 1413 cm^{-1}, O-H bending at 1363 cm^{-1}, C-N stretching at 1308 cm^{-1}, and C-O stretching at 1219 cm^{-1}. The C=O stretching peaks at approximately 1700 and 1730 cm^{-1} were used to analyze the intermolecular interactions, such as hydrogen bonding and dipole-dipole interactions, between the hard segments. The bonded carbonyl band (1700 cm^{-1}) was observed at a lower wavenumber than the free carbonyl group band (1730 cm^{-1}).[7] The relative intensities of the bonded and free carbonyl stretches indicated the degree of phase separation (DPS), which depends on the molecular interactions between hard segments. The DPS was calculated using the equation DPS=$A_{1700}/(A_{1730}+A_{1700})$, where A_{1700} and A_{1730} are the absorbances at 1700 and 1730 cm^{-1}, respectively. The DPS for the B series changed from 57.3% for L to 54.2% for B-2 and 55.2% for B-4, whereas the DPS for the D series

decreased slightly to 56.7% for D-2 and 54.4% for D-4. Therefore, it was difficult to determine from the IR data alone whether molecular interactions were reduced by the grafted BPA and DHN groups. The UV-Vis spectra for the two series of polymers were compared to analyze the BPA or DHN grafting onto PU. The absorption peak at approximately 268 nm, corresponding to the phenyl group, did not shift but increased in intensity with the grafting of BPA (Figure 2(a)). This was attributed to the BPA phenyl group absorbing at the same wavelength as the MDI phenyl group. However, new absorption peaks at approximately 320 and 333 nm appeared after grafting DHN onto PU (Figure 2(b)). The UV-Vis spectra demonstrated that BPA or DHN groups were proportionally grafted onto PU by the amount of BPA or DHN in the synthesis.

The endothermic peak for soft segment (the PTMG section) melting appeared at approximately 20 °C. The peak area corresponding to the enthalpy change for soft segment melting decreased sharply for the B series, as the BPA content was increased (Figure 3(a)). The D series also exhibited a decrease in peak area; however, the reduction was modest when compared with the B series (Figure 3(b)). The cooling scans indicated the soft segment crystallization of PU, whereas the scans for the B and D series revealed the complete disappearance of the soft segment crystallization peak with the increasing BPA and DHN content, respectively (Figure 3(c) and 3(d)). The decrease in the soft segment melting and soft segment crystallization peaks for the B and D series was due to the disruption of interactions between PU chains by the rigid aromatic structures of BPA and DHN.

The average maximum tensile stress of the linear PU (13.8 MPa) was steeply increased by the grafting of either BPA or DHN: the maximum stress went up to 45.9 MPa for B-1 and 39.9 MPa for D-4. The increase in maximum stresses originated from the light cross-linking induced by the bifunctional BPA or DHN, and the slow decrease in tensile stress observed for the B series could be due to the repulsion between pendant groups at higher BPA content (Figure 4(a)). The tensile strains at break for the B and D series were not significantly affected by the grafting of BPA or DHN: 1458% for
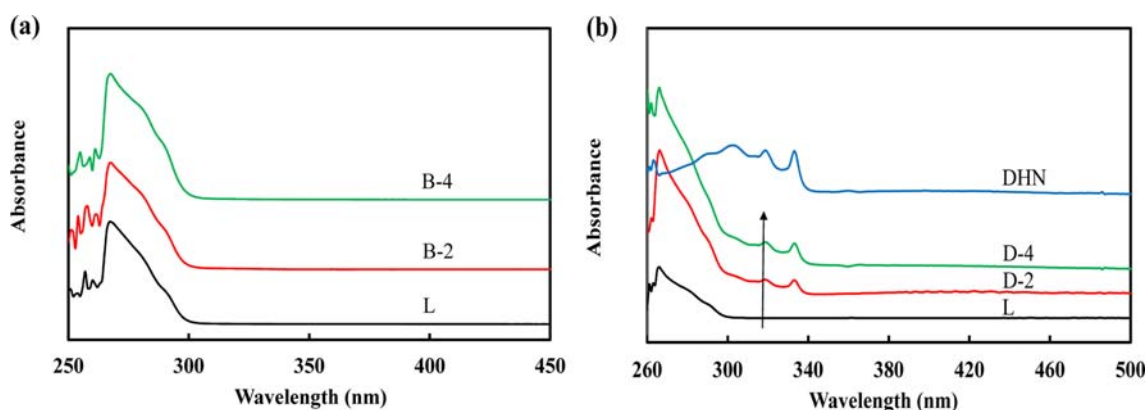
Figure 2. Comparison of the UV-Vis spectra for (a) the B series and (b) the D series.
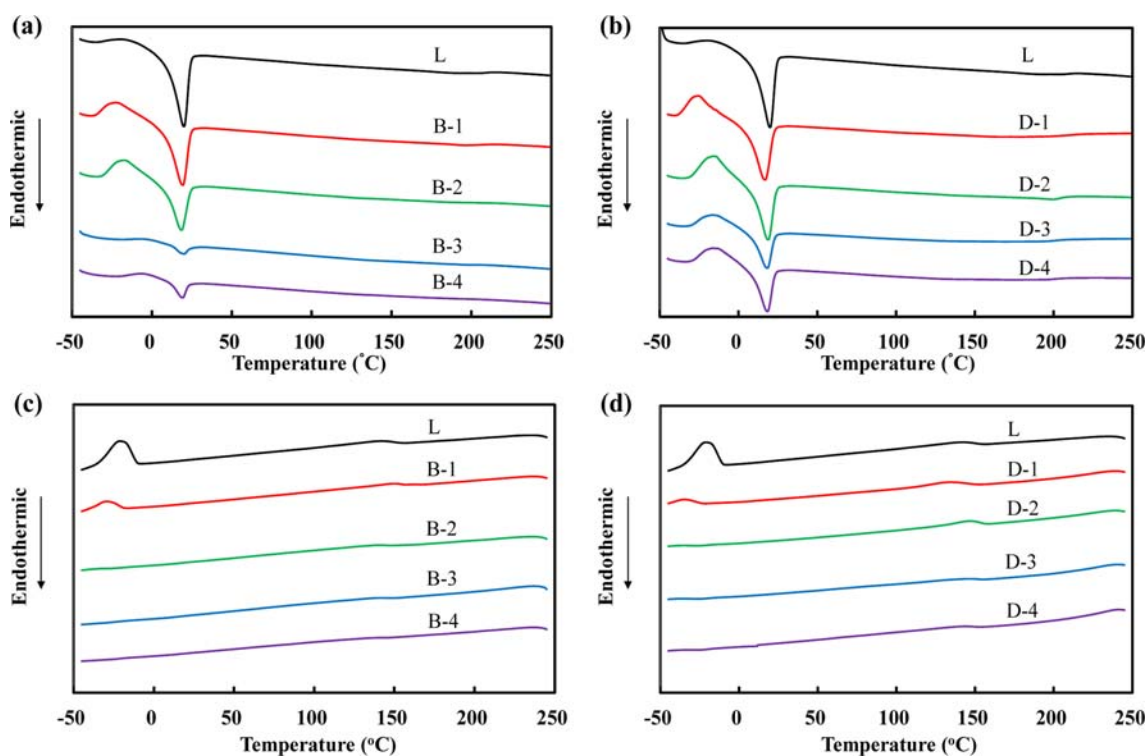
Figure 3. DSC heating scans for (a) the B series and (b) the D series and cooling scans for (c) the B series and (d) the D series.
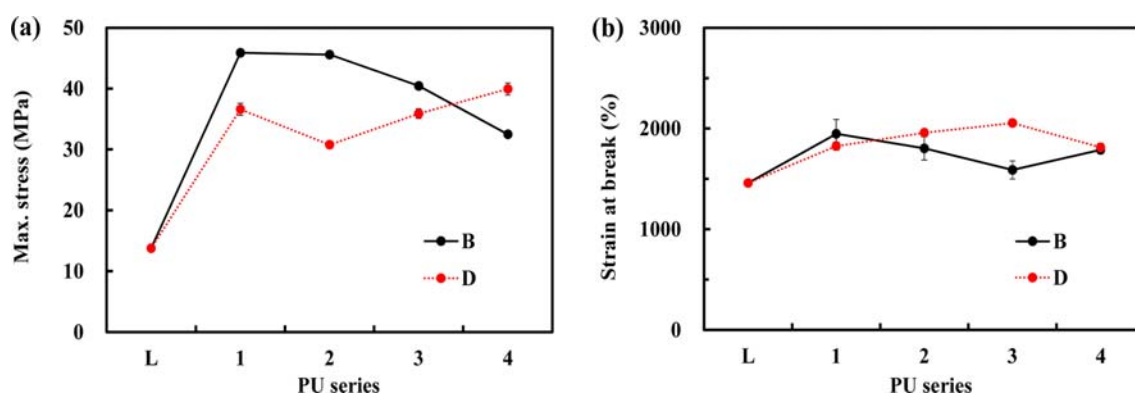

Figure 4. Comparison of (a) tensile stress and (b) tensile strain for the B and D series.

L was changed to 1786% for B-4 and 1812% for D-4 (Figure 4(b)). The tensile strain was not reduced by the grafting of BPA or DHN because the soft segments of PU, which stretched and shrunk during the tensile test, were not structurally modified. The tensile results demonstrated that the maximum tensile stress could be raised without a decrease in tensile strain.

Shape memory properties were tested under stretch-release conditions between -25 and 45 °C, following previous methods.[2,3] Hard segments were important in recovering the original shape after distortion, and the soft segments displayed flexibility by stretching and shrinking. The shape recoveries of the B series and the D series remained approximately 90% regardless of the BPA or DHN content: 90% recovery

for the L form changed to 91.5% for B-4 and 88% for D-4. However, shape retentions of the B and D series noticeably decreased with the increase of BPA or DHN content. For example, 99% retention for the L form decreased to 60% for B-2 and 54% for B-4 in the B series and 67% for D-2 and 51% for D-4 in the D series. The sharp decrease in shape retention at -25 °C resulted from reduced molecular interactions between PU chains, which significantly impacted low-temperature flexibility. Shape memory tests demonstrated that the grafted BPA or DHN mainly affected the shape retention properties of PU instead of shape recovery. The low-temperature flexibility of selected samples (B-4 and D-4) were compared with that of L, as shown in Figure 5. Twisted-spiral samples were allowed to recover their original shapes
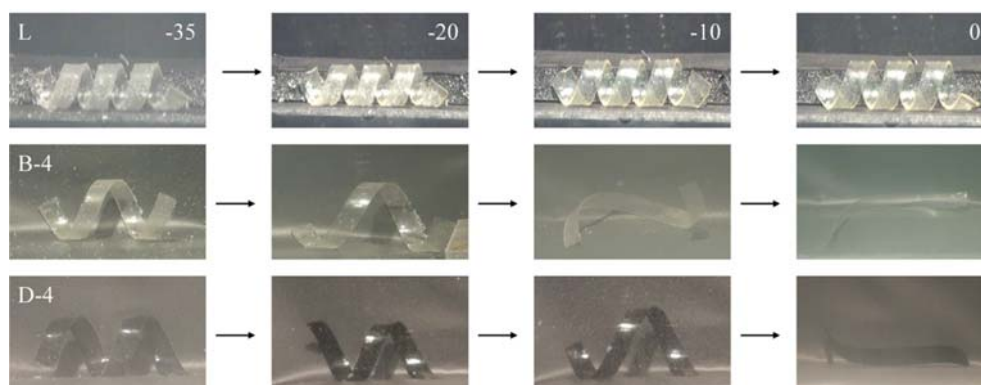
Figure 5. Comparison of low-temperature flexibility for L, B-4, and D-4.

while the surrounding temperature was raised. Even at -35 °C, B-4 and D-4 started unwinding, whereas the L form required warming above 10 °C before recovery initiated. B-4 and D-4 exhibited considerable unwinding even at -20 °C, and full recoveries were achieved below 0 °C. The rigid aromatic structures of the grafted BPA and DHN were very effective at improving the low-temperature flexibility of PU by hindering its intermolecular interactions. Ordinary polymers lose their flexibility below the glass transition temperature (T_g) because their rotational and vibrational movements are restricted, whereas the BPA- or DHN-grafted PU demonstrated the excellent low-temperature flexibility. The aromatic group grafting methods contained within are different from the previous low-temperature flexibility mechanism and can be useful in developing polymers that remain flexible under freezing conditions.

Conclusions

The aromatic groups, BPA (B series) or DHN (D series), were grafted onto PU to control the molecular interactions between polymer chains. The B and D series displayed area reductions for the soft segment melting peak and the disappearance of the peak associated with soft segment crystallization. Furthermore, both series revealed a sharp increase in tensile stress without a decrease in tensile strain. Shape recovery was not affected by the inclusion of rigid pendant groups, but shape retention was significantly decreased by the BPA and DHN grafting. Low-temperature tests confirmed the excellent flexibility of both B and D series polymers under freezing conditions. Therefore, it was demonstrated that control of the molecular interactions between PU chains plays an important role in improving low-temperature flexibility.

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