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Shape-memory effects of polyurethane copolymer cross-linked by dextrin

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Abstract The effects of the dextrin cross-linking and hard-segment content on the shape-memory property of a polyurethane (PU) block copolymer were investigated. Although dextrin was selected due to its large number of free hydroxyl groups and ubiquitous availability, it is unfortunately insoluble in most organic solvents. The insolubility of dextrin was resolved by attaching a phenyl group onto the dextrin to reduce its hydrophilicity. The phase separations of hard and soft segments were not dependent on the dextrin cross-linking and hard-segment content, as per the results obtained from FTIR, DSC, and XRD analysis. An increased content of chemically cross-linked dextrin increased the maximum stress, but did not decrease the strain for most cases. The cross-linking density increased with increasing dextrin content, as expected. After dextrin cross-linking, the shape recovery rate was generally over 90%, and remained the same after four cyclical tests, while a low shape retention rate was observed for most cases. The best shape-memory effect, considering both the shape recovery and retention rate, was found for a PU consisting of 35 wt.% hard segment and 2 wt.% dextrin. Finally, dextrin was compared to other cross-linking compounds, such as glycerol and pentaerythritol, in this investigation.

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Introduction

Polyurethane (PU) has been investigated as a shape-memory polymer (SMP) by many researchers due to its excellent shape recovering property, ease of processing under ordinary conditions, and high solvent resistance [1–6]. An SMP is generally composed of hard and soft segments, wherein the soft segment plays a role as an absorber of external stress, while the hard segment contributes to original shape recovery [3, 4]. Unfortunately, poor shape recovery rates and stiffening of the SMP after cyclical shape-memory tests persist as problems in these materials. Hard-segment cross-linking has been investigated as a possible route to improving the shape-memory effect after repetitive distortion and recover cycles [7]. The cross-linker has usually been selected based on its reactivity to other reactants, miscibility in the reaction mixture, and density of accessible functional groups. Cross-linkers, such as glycerol, pentaerythritol, sorbitol, glucose, melamine, and maleicanhydride, have been already investigated [8, 9]. Dextrin is a compound composed of, on average, three glucose units, and generally has been used as a binding or thickening agent in industrial applications. Dextrin is considered to be a promising cross-linker, as there are enough hydroxyl groups for coupling, and the cyclical structure can potentially reduce the congestion of PU chains around the cross-linker. Unfortunately, dextrin is also highly soluble in water and insoluble in organic solvents, such as dimethylformamide (DMF), the favored solvent used for PU synthesis. A phenyl group was attached to dextrin to reduce its hydrophilicity, and thereby increasing its solubility in organic solvents and preventing the congestion of PU chains around the dextrin. In this article, the impact of dextrin on PU shape-memory effects are discussed in the framework of the aforementioned analytical techniques.

Experimental

Materials and methods

Dextrin and phenylisocyanate were purchased from Aldrich and used without further purification. 4,4′-Diphenylmethanediisocyanate (MDI, TCI) and poly(tetramethylene glycol) (PTMG, MW = 2000 g/mol, Aldrich) were dried overnight under high vacuum (0.1 torr) before use. 1,4-Butanediol (BD, Duksan Chemical, Korea) was stored over a 4 Å molecular sieve. *N*,*N*-Dimethylformamide was distilled over CaH_2 before use.

Synthesis of polyurethane

A mixture of molten MDI and PTMG was stirred at 50 °C for 2 h in a 500-mL four-necked flat-bottomed flask, equipped with a condenser, mechanical stirrer, and nitrogen blanket, to prepare a prepolymer. 1,4-Butanediol, dissolved in 20 mL of DMF as a chain extender, was added to the flask and allowed to react for another hour under the same conditions. Meanwhile, dextrin was reacted with phenylisocyanate in 20 mL of DMF for 2 h, in a separate flask to reduce the hydrophilicity of the dextrin. Additional dextrin was added to the solution and allowed to react for an additional hour. The final PU product was dried for a week to completely remove any remaining DMF. Specific mole ratios of the reaction mixture are summarized in Table 1.

Specimen preparation

The specimen for the mechanical and shape-memory test was prepared by pouring a solution of PU and DMF (10 g of PU in 100 mL of DMF) into a Petri dish (12 cm × 1 cm), and then drying at 60 °C for 60 h to fabricate a thin film. The specimen was made from the thin film according to the specification of ASTM D638.

Table 1 Composition of cross-linked PU block copolymer

Sample code	Composition (mol%)					Hard segment (wt.%)
	MDI (mol%)	PTMG (mol%)	BD (mol%)	Dextrin (wt.%)	P[a] (wt.%)	
H30D0	5.0	2.0	3.0	0	0	30
H30D1	5.2	2.0	3.0	1.0	2.0	
H30D2	5.2	2.0	3.0	2.0	4.0	
H30D3	5.2	2.0	3.0	3.0	6.0	
H35D0	5.0	1.5	3.5	0	0	35
H35D1	5.2	1.5	3.5	1.0	2.0	
H35D2	5.2	1.5	3.5	2.0	4.0	
H35D3	5.2	1.5	3.5	3.0	6.0	
H40D0	5.0	1.2	3.8	0	0	40
H40D1	5.2	1.2	3.8	1.0	2.0	
H40D2	5.2	1.2	3.8	2.0	4.0	
H40D3	5.2	1.2	3.8	3.0	6.0	

[a] Phenylisocyanate

Mechanical and shape-memory analysis

The tensile mechanical strength of the specimen was measured according to ASTM D638 by a universal test machine (UTM) equipped with a temperature-controlled chamber (Lloyd Instrument, Model LR50K), with a gage length of 25 mm, cross-head speed of 10 mm/min, and load cell of 2.5 kN. The UTM was also used to measure the stress and strain of the specimen at various temperatures to investigate the of shape-memory effect. The shape retention, L_1, was measured by drawing the specimen 100% at 20 °C above T_g for 5 min, and letting it shrink at 20 °C below T_g for 30 min. The shape recovery, L_2, was measured after incubating the specimen at 20 °C above T_g for 10 min, and cooling at 20 °C below T_g (Fig. 1). The measurements were repeated three times, and the shape retention and recovery rates were calculated using L_1 and L_2 in the following equations:

$$\begin{aligned}&\text{Shape retention rate} = (L_1 - L_0) \times 100/L_0\,(\%)\\&\text{Shape recovery rate} = (2L_0 - L_2) \times 100/L_0\,(\%)\end{aligned} \qquad (1)$$

General analysis

A differential scanning calorimeter (DSC-2010, TA instrument) was used for the heating and cooling scan at a rate of 10 °C/min between temperatures of −100 °C and 250 °C. An FTIR spectrometer (JASCO 300E) equipped with an ATR was used to measure the IR spectrum of the PU sample using the scan parameters of 4 cm^{-1} resolution, 25 scans, and 2 mm/s scan speed. The X-ray diffraction spectra were recorded using a wide-angle X-ray diffractometer (Rigaku) in the 2θ range of 10°–30°, using CuKα, at 40 kV, and at 30 mA.

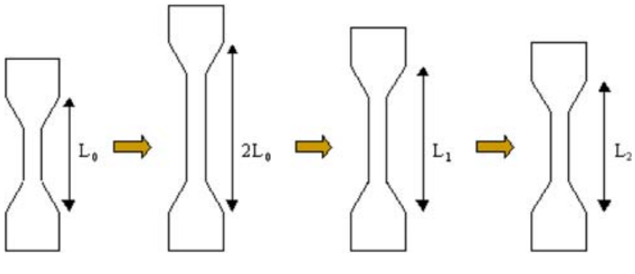

Fig. 1 Shape retention and recovery test, where L_0 = initial specimen length, $2L_0$ = length of L_0 strained 100% at above T_m, L_1 = deformed length at below T_m after load removal, and L_2 = final specimen length at above T_m

Results and discussion

Synthesis

Polyurethane was synthesized based on previous methods [3–5], wherein MDI and PTMG work as hard and soft segments, respectively, and BD is used as a chain extender. Dextrin is composed of a few glucose units and, as a chemical cross-linker, is able to connect the hard segments of PU chains through the copious number of available hydroxyl groups in glucose. The congestion of the PU chains around the cross-linker can be reduced because the remote hydroxyl group, in contrast to a tri-functional cross-linker such as glycerol, is available after one PU chain is connected to the dextrin. Practically, dextrin is not soluble in our reaction solvent, DMF, and it thus needs to be modified to be used as a cross-linker. A phenyl group was attached to some of the dextrin hydroxyl groups to reduce the hydrophilicity by using phenylisocyanate as the reacting agent. It was found from separate experiments that dextrin became soluble in DMF if more than ca. 25% of the available hydroxyl groups were coupled with phenyl groups. The phenyl groups attached to dextrin also prevented the congestion of PU chains when the incoming PU chains reacted with the hydroxyl groups of dextrin. Once dextrin became soluble in DMF, polymerization of PU was unencumbered. The compositions of the PUs synthesized in this investigation are summarized in Table 1, and the proposed cross-linked structure of the PU is depicted in Fig. 2.

The cross-link density was calculated from a polymer-swelling experiment. The interaction parameter, χ, between the toluene solvent and the polymer was found from the following expression [10]:

$$\chi = (\delta_1 - \delta_2)^2 V_1/RT, \tag{2}$$

where δ_1 and δ_2 are solubility parameters of solvent and polymer, respectively, V_1 is the molar volume of the solvent; R is the gas constant; and T is the absolute temperature.

The solubility parameters of toluene, δ_1, and PU, δ_2, were 18.2 and 20.5 $(\mathrm{MPa})^{1/2}$, respectively. The degree of cross-linking was calculated from the Flory–Rehner equation (3):

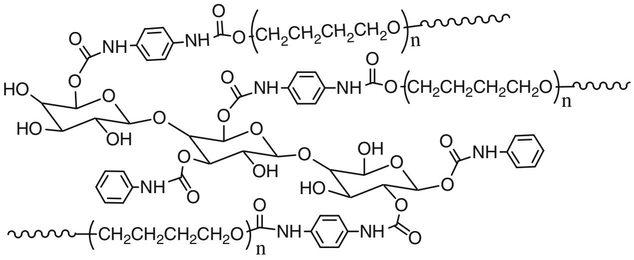

Fig. 2 PU structure cross-linked by dextrin

Table 2 Cross-link density of SMPU by swelling experiment

Sample code	ρ[a] (g/cm^3)	Q[b]	v_2[c]	$10^3 n$[d]
H30D1	1.064	2.745	0.113	1.353
H30D2	0.992	2.916	0.11	1.298
H30D3	1.061	2.623	0.125	1.539
H35D1	1.152	2.158	0.171	2.340
H35D2	1.107	2.249	0.164	2.209
H35D3	1.108	2.221	0.169	2.288
H40D1	1.154	1.971	0.209	3.068
H40D2	1.171	1.944	0.212	3.130
H40D3	1.073	1.954	0.23	3.509

[a] ρ is the density

[b] Q is the degree of swelling

[c] v_2 is the volume fraction of polymer

[d] n is the cross-link density

$$-[\ln(1 - v_2) + v_2 + \chi v_2^2] = V_1 n[v_2^{1/3} - 1/2 v_2], \tag{3}$$

where v_2 is the volume fraction of polymer in the swollen mass; χ is the interaction parameter; and n is the cross-link density.

The cross-link density was found to increase with increasing dextrin content, suggesting that the dextrin participated in the cross-linking (Table 2).

FTIR analysis

Intermolecular attraction, such as hydrogen bonding and dipole–dipole interaction, between polymer hard segments can be analyzed from IR spectra, wherein the stretching vibrational modes of the bonded carbonyl groups appear at 1699–1706 cm^{-1} and are slightly lower than that of the free PU carbonyl group (1731–1733 cm^{-1}) [3]. The FTIR spectra can also be used to analyze the phase separation of hard and soft segments by comparing peak shifts in the range of 1700–1750 cm^{-1}. The FTIR spectra of all the PU series are compared in Fig. 3. Although the hard segment and dextrin content varied, the two peaks corresponding to bonded and free carbonyl did not change. From this data, we can conclude that the interaction between the hard segments and the phase separation was not affected by dextrin cross-linking.

Thermal analysis

The effects of dextrin cross-linking and hard-segment content on the phase transition of the soft segment were investigated from the differential scanning calorimetry (DSC) data depicted in Fig. 4. The T_m of the soft segment copolymer was not affected by the dextrin cross-linking and hard-segment content, compared to uncross-linked soft

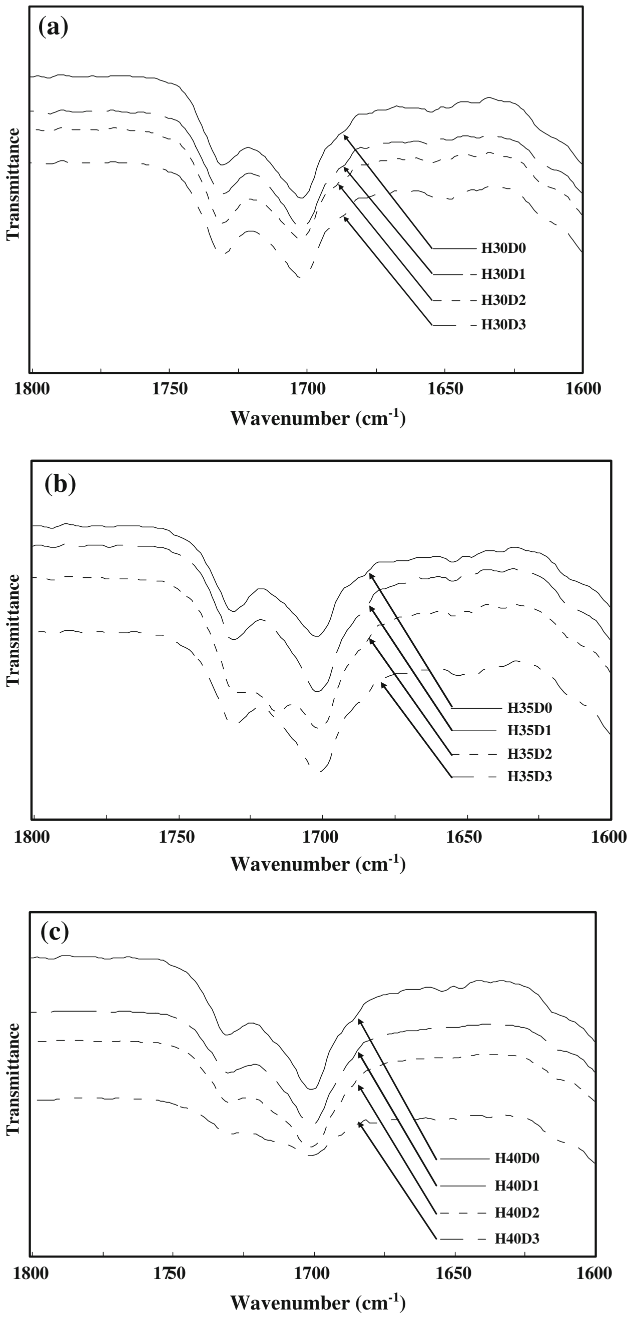

Fig. 3 IR spectra of (**a**) H30, (**b**) H35, and (**c**) H40 series

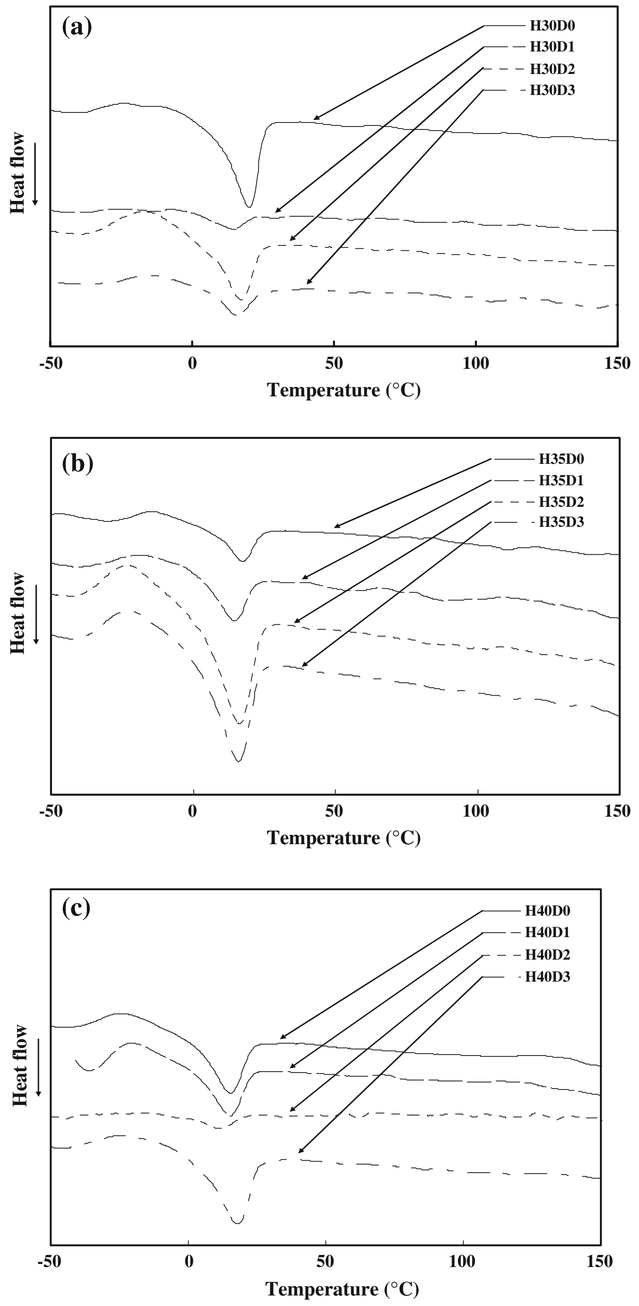

Fig. 4 DSC thermograms of (**a**) H30, (**b**) H35, and (**c**) H40 series

segment copolymer. Although some of the hard segments were cross-linked by the different contents of dextrin, the soft segment was not bound to dextrin, and thus, permitted an unrestricted movement of the soft segment comparable to uncross-linked polymer. Additionally, an increase in the hard-segment content did not change T_m, since the soft segment was separated from the hard segment despite an increased hard-segment content. Therefore, the T_m was not appreciably impacted by changes in the dextrin and hard-segment content. Controlling T_m is practically important since the ideal phase transition temperature for the shape-memory effect should be around room temperature, that is, the working temperature range of an SMP.

XRD analysis

Previous studies have demonstrated that the partially crystalline structure of PU can exhibit diffraction peaks [11]. The X-ray diffraction spectra of the PU investigated in this study exhibited a major diffraction peak at $2\theta = 19.5°$ that did not shift as a function of varied dextrin and hard-segment content (Fig. 5). The observed XRD peaks originate from the partially crystalline structure of hard domains scattered around the PU chains. It is challenging to clearly distinguish different diffraction peaks, since the PU chains are dynamic, and the degree of interactions between hard segments varies the hard domain structure; however, the appearance of the diffraction peak at $2\theta = 19.5°$ partially supports the presence of hard domains in the PU chains.

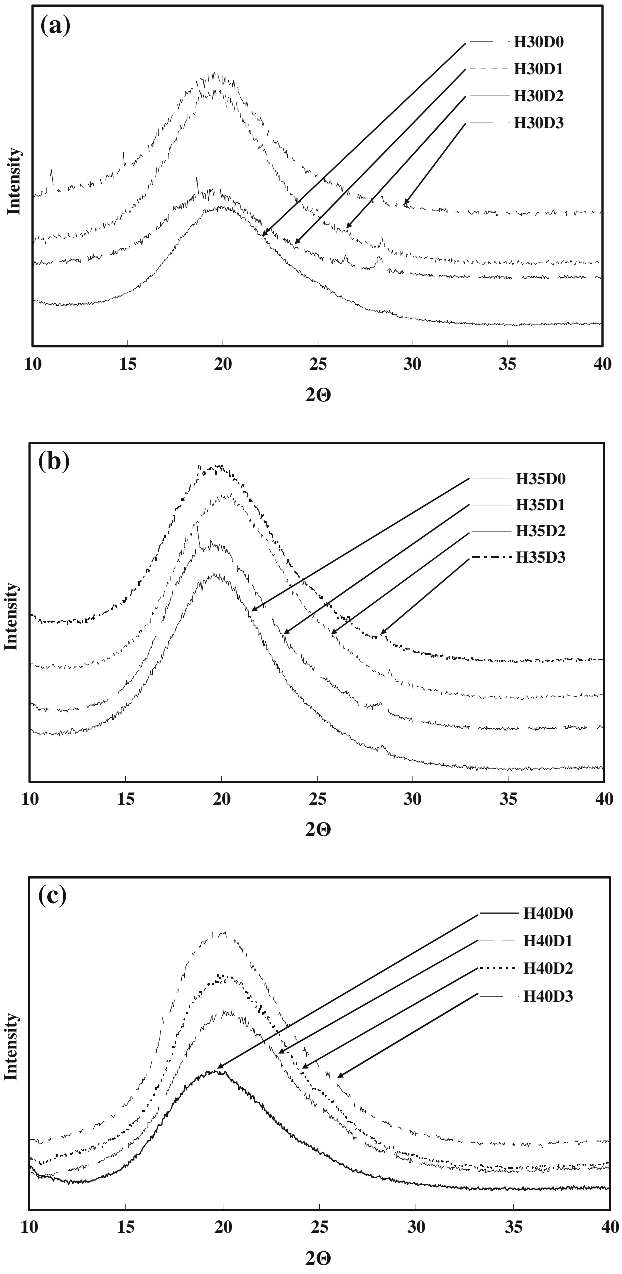

Fig. 5 XRD spectra of (**a**) H30, (**b**) H35, and (**c**) H40 series

Mechanical property

The tensile mechanical properties of the investigated PU depend on the dextrin and hard-segment contents, as represented by the stress–strain curves in Fig. 6, and as summarized in Table 3. The maximum stress was observed to increase with increasing dextrin and hard-segment contents. For example, the maximum stress of a PU, consisting of a 30 wt.% hard segment and a 0 wt.% dextrin (H30D0), increased from 4.8 to 19.3 MPa when the dextrin and hard-

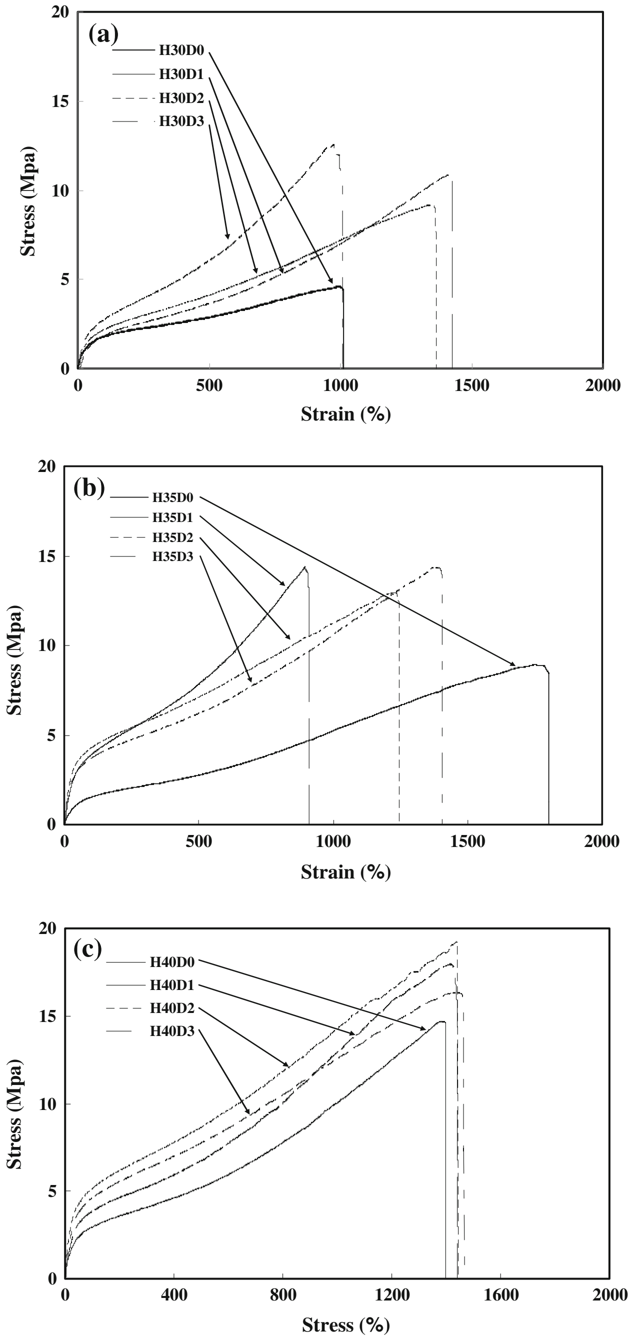

Fig. 6 Stress–strain curves of (**a**) H30, (**b**) H35, and (**c**) H40 series

Table 3 Tensile mechanical properties of PU cross-linked by dextrin

Hard segment (wt.%)	Dextrin content (wt.%)							
	0		1		2		3	
	Max. stress (MPa)	Strain at break (%)	Max. stress (MPa)	Strain at break (%)	Max. stress (MPa)	Strain at break (%)	Max. stress (MPa)	Strain at break (%)
30	4.8	1011	12.6	1426	8.1	1366	13.5	1007
35	8.0	1803	16.0	909	12.7	1247	14.3	1406
40	13.1	1397	19.3	1439	17.2	1442	15.4	1466

segment contents were increased to 40 and 1 wt.% (H40D1), respectively. The strain at break increased, in some cases, with an increase in dextrin and hard-segment contents. For example, the strain at break of the H30D0 increased from 1011% to 1466% for the H40D3. In the H30 series, the maximum stress improved with increasing dextrin content, while strain initially increased at 1 and 2 wt.% dextrin, and remained the same at 3 wt.% dextrin. In the H35 series, the maximum stress improved for all dextrin contents; however, the strain decreased, since dextrin was involved in cross-linking. In the H40 series, the maximum stress increased moderately as more dextrin was included, and remained comparable to the uncross-linked polymer. The best case dextrin cross-linked PU exhibited an increase in both stress and strain with increasing dextrin content, although strain generally decreased with increased cross-linking. The maximum stresses of previously investigated glycerol and pentaerythritol cross-linked PUs were 12 and 17 MPa, respectively [4, 5], with strain at breaks of 1100% and 1200%, respectively. Compared to these two cross-linked PUs, the dextrin cross-linked PU exhibited a higher maximum stress and strain at break.

Shape-memory property

A cyclical shape-memory test was used to compare the shape recovery and retention rates under repetitive stress-release conditions at a soft segment T_m range of ±20 °C. Since the soft segment T_g was too low and it was too difficult to control the temperature around it, the shape-memory test was conducted around the T_m of the soft segment as an alternative. In the shape-memory mechanism, the hard segment plays an important role in retaining the distorted shape below the transition temperature, as well as in shape recovery after distortion at a temperature above the transition temperature. The soft segment, which determines the transition temperature, absorbs the applied tensile stress by unfolding the entangled chains. Permanent deformation in the hard-segment domain by repetitive stress-release cycles may limit the shape-memory effect [2, 12]. In Fig. 7,

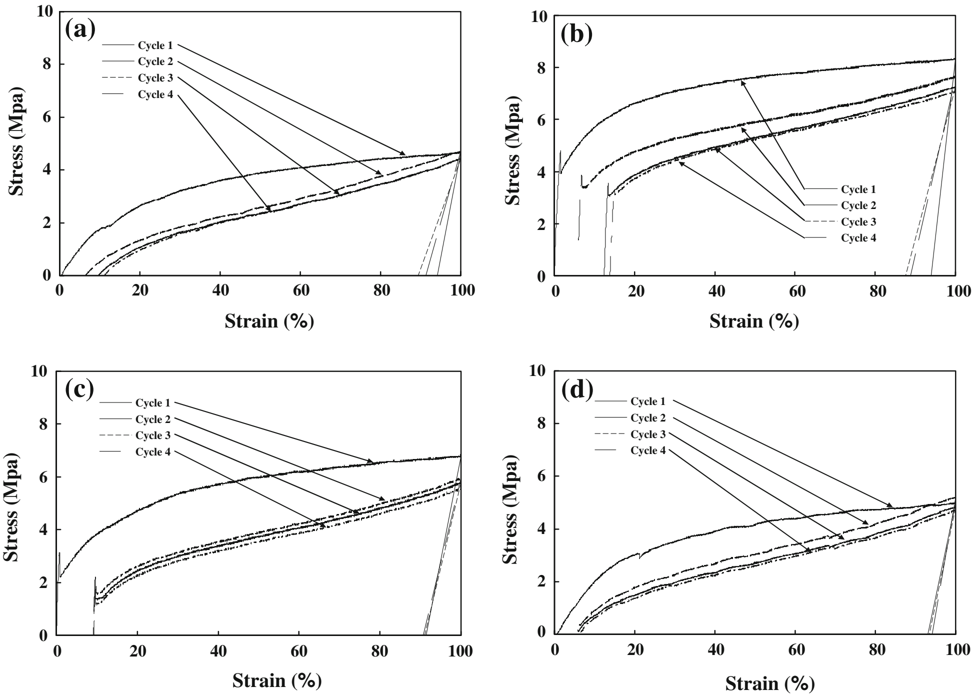

Fig. 7 Cyclical shape-memory tests of (**a**) H40D0, (**b**) H40D1, (**c**) H40D2, and (**d**) H40D3

the representative cyclical shape-memory tests of the H40 sample series demonstrates that the shape of the stress–strain curve did appreciably change, indicating that the shape recovery process was reproducible even after four repetitive test cycles. Figure 8 compares the shape recovery rates of the H30, H35, and H40 series specimens. Shape recovery rates were over 90% for most of the PUs, and remained the same if the dextrin cross-linking content was high. For example, the PU consisting of 40 wt.% hard segment and 3 wt.% dextrin (H40D3) exhibited shape recovery rates of 94% (first cycle), 94% (second cycle), and 93% (third cycle). In contrast, the shape recovery rates of H30D0 were 90% (first cycle), 85% (second cycle), and 69% (third cycle). Therefore, dextrin cross-linking maintained a high PU shape recovery rate compared to the uncross-linked PU. Figure 9 compares the shape retention rates of the H30, H35, and H40 series specimens. Shape retention rates were generally poor compared to shape recovery rates, and heavily depended on the dextrin and hard-segment content. In the case of the H30D0 series,

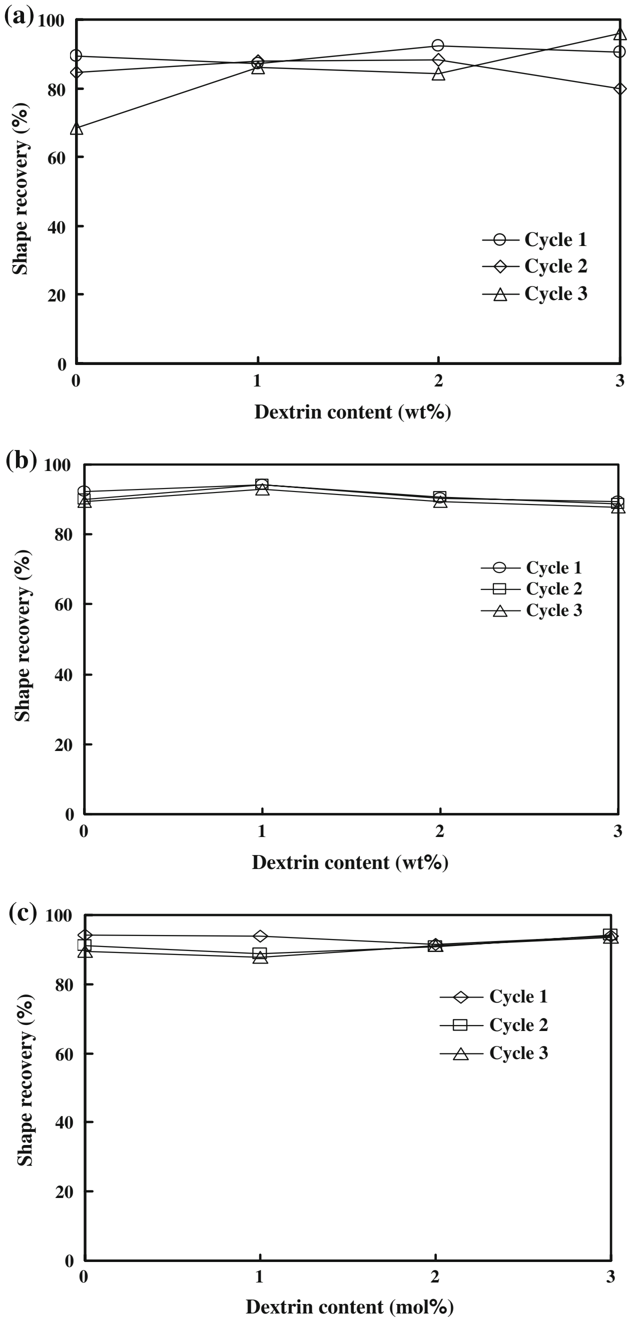

Fig. 8 Shape recovery rates of (**a**) H30, (**b**) H35, and (**c**) H40 series

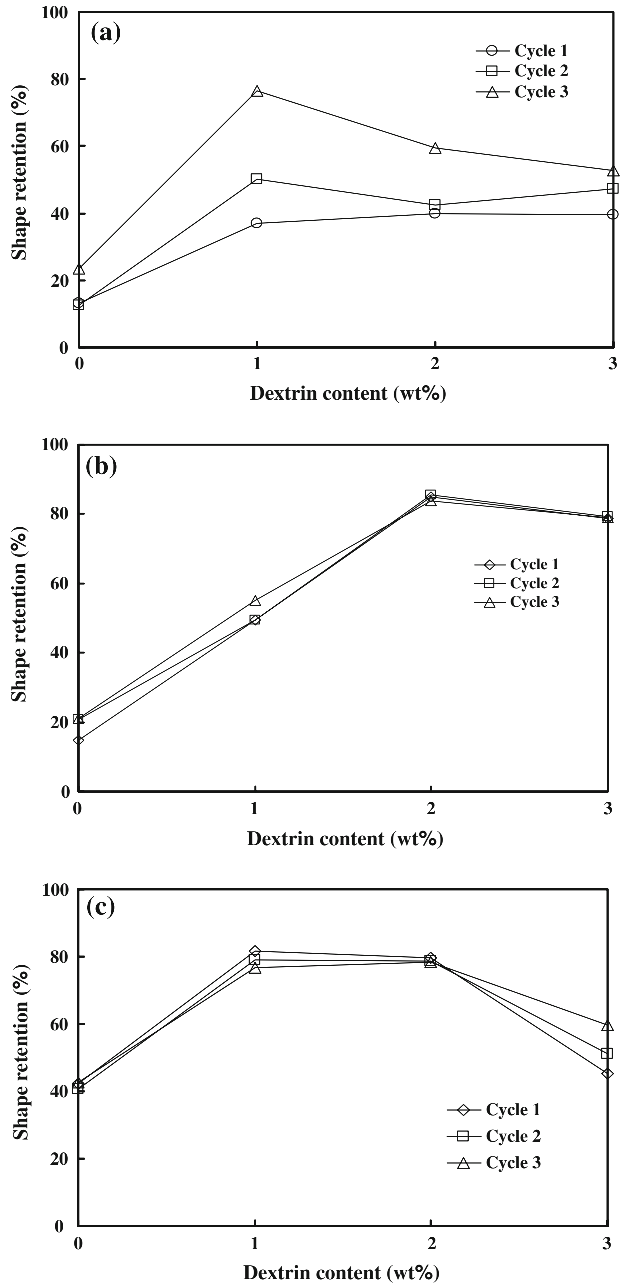

Fig. 9 Shape retention rates of (**a**) H30, (**b**) H35, and (**c**) H40 series

Table 4 Cyclical shape-memory test of PU cross-linked by dextrin

Hard segment (wt.%)	Test cycle	Dextrin content (wt.%)							
		0		1		2		3	
		Shape retention[a]	Shape recovery[a]	Shape retention	Shape recovery	Shape retention	Shape recovery	Shape retention	Shape recovery
30	1	13	90	37	87	40	92	40	91
	2	13	85	50	88	42	88	47	80
	3	24	69	77	86	60	84	53	96
35	1	15	92	49	94	85	91	79	89
	2	21	90	49	94	85	91	79	89
	3	21	90	55	93	84	90	79	88
40	1	42	94	82	94	80	91	45	94
	2	41	89	79	89	79	91	51	94
	3	77	88	77	88	78	91	60	93

[a] Shape retention and recovery rates in %

shape retention rates were 13% (first cycle), 13% (second cycle), and 24% (third cycle). In contrast, the shape retention rates of H35D2 were 85% (first cycle), 85% (second cycle), and 84% (third cycle). Considering that shape retention rates generally get reduced if shape recovery rate is increased, it is remarkable that the shape retention rate substantially increased after dextrin cross-linking, while also maintaining high shape recovery rates. The shape recovery rates of glycerol and pentaerythritol cross-linked PUs were 93% and 94%, respectively, while the shape retention rates were 90% and 80%, respectively. Therefore, dextrin cross-linked PUs demonstrate comparable shape recovery and retention rates to those observed for PUs cross-linked by glycerol and pentaerythritol. Shape recovery and retention rates generally deteriorate with repeated cyclical tests due to the deformation of hard-segment domains; however, chemical cross-linking with dextrin reduces the deformation of hard-segment domains (Table 4).

Conclusion

Dextrin was selected as a cross-linker for PUs composed of MDI, PTMG, and BD, due to the cyclical structure of glucose, and to the numerous hydroxyl groups available for cross-linking therein. The insolubility of dextrin in DMF was resolved by attaching a phenyl group onto the dextrin to reduce its hydrophilicity. Hard-segment interaction and the phase transition temperature were not affected by the dextrin content, as per data derived from FTIR, DSC, and XRD analysis. The maximum stress increased with increasing dextrin content, while strain remained the same. Shape recovery rates did not appreciably decrease after four cyclical shape-memory tests for PUs cross-linked by dextrin, while shape retention rates substantially increased in some cases. If a proper dextrin and hard-segment content is selected, a high shape memory and retention rate can be achieved.

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