Flexible Cross-Linking by Both Pentaerythritol and Polyethyleneglycol Spacer and its Impact on the Mechanical Properties and the Shape Memory Effects of Polyurethane

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ABSTRACT: A series of polyurethane (PU) polymers cross-linked laterally by pentaerythritol and polyethyleneglycol (PEG) spacers were compared with linear PU. The PU was composed of 4,4′-methylenebis(phenylisocyanate) (MDI), poly(tetramethyleneglycol), 1,4-butanediol (BD), pentaerythritol, and PEG-200 as a spacer. PEG-200 connected the pentaerythritol hydroxyl groups of two PU chains with MDI as a connecting agent. The phase separation between hard and soft segments was disrupted by the PEG crosslinking, and T_m did not change with an increase in cross-linking content. Instead, the cross-link density increased with an increase of pentaerythritol content. A significant increase in maximum stress compared with linear PU was attained, together with an increase in strain. The combination of both pentaerythritol and PEG-200 in the PU resulted in the improvement of both stress and strain, unlike in the conventional cross-linking method. The shape recovery increased to 90% and did not decrease after three test cycles. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2800–2808, 2009

Key words: polyurethane; crosslinking; shape recovery; pentaerythritol; network structure

INTRODUCTION

The first shape memory polymer was developed by the Nippon Zeon company, and since then other types of shape memory polymers, such as poly(isoprene-butadiene-styrene), polyurethane (PU), and polystyrene series, have followed.[1–4] A shape memory PU was widely researched because of its excellent properties, such as a wide shape recovery temperature range, a high shape recovery rate, easy processing conditions, and possible biocompatibility.[3,5–7] A shape memory PU has a phase-separated structure of hard and soft domains due to the difference in intermolecular attraction between the two segments. The hard domain recovers its original shape after distortion, whereas the soft segment absorbs external stress and keeps the polymer resilient at low temperature.

If not crosslinked, PUs cannot withstand repeated distortion and recovery cycles. To bypass this problem, the authors and other researchers have adopted cross-linking as a possible solution.[7–10] Flexible cross-linking method was attempted before, in which some of the chain extender, specifically 1,4-butanediol, is replaced with glycerol as a connecting point in PU chain and polyethyleneglycol (PEG)-200 was used as a linker because of its flexibility and short chain length.[11] Pentaerythritol, a four way cross-linker, was tried for glycerol in this investigation, because additional flexible cross-linking point could be secured and better mechanical properties were expected. The target PU differs from the conventionally cross-linked ones in that PU chains are linked at multiple points along the chain, and not at the chain ends. By using a flexible PEG linker, the strain at break was not reduced by cross-linking and substantial improvements in the mechanical and shape memory properties were possible. In this article, the PU made by the flexible cross-linking method employing pentaerythritol is compared with the method without cross-linking. In particular, the effect of flexible cross-linking by PEG-200 on the shape memory and mechanical properties is investigated.

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TABLE I
Composition and Molecular Weight of Cross-Linked SMPU

Sample code	Reactant (mmole)					wt % of Penta	[b]M.W. (g/mol)
	MDI	PTMG-2000	BD	[a]Penta.	PEG-200		
P-0	50.0	18.0	32.0	–	–	0	9400
P-5			30.4	1.6	0.8	5	19,500
P-10			28.8	3.2	1.6	10	28,700
P-12.5			28.0	4.0	2.0	12.5	35,800
P-15			27.2	4.8	2.4	15	63,400
P-17.5			26.4	5.6	2.8	17.5	55,800
P-20			25.6	6.4	3.2	20	69,500

[a] Pentaerythritol was used as a connecting agent.
[b] The molecular weight was determined by the intrinsic viscosity method.

EXPERIMENTAL

Materials

Poly(tetramethyleneglycol) (PTMG, M_w = 2000 g/mol; Aldrich) and polyethyleneglycol (PEG-200, M_w = 200 g/mol; Duksan Chemical, Korea) were dried at 50°C under high vacuum (0.1 Torr) for 12 h before use. Pentaerythritol (Aldrich), 4,4′-methylenebis (phenylisocyanate) (MDI; Tokyo Kasei, Japan) and 1,4-butanediol (BD; Junsei, Japan) were also dried at room temperature for 12 h under high vacuum. Dimethylformamide (DMF; Duksan Chemical, Korea) was distilled over CaH_2 under nitrogen before use.

Polymer synthesis

In a 500 mL four-neck cylindrical flask, a mixture of MDI and PTMG was allowed to react by mechanical stirring under nitrogen purge at 50°C for 2 h to prepare a prepolymer. The prepolymer was then dissolved in 30 mL of dried DMF, to which BD and pentaerythritol were added. This mixture was subsequently stirred under the same conditions for 1 h. The amount of each reactant used is shown in Table I, where the hard segment content is fixed at 30 wt %. To decide the molarity of the free hydroxyl groups in the prepolymer, the hydroxyl number was found by the titration method shown in the following section. An exact amount of MDI based on the hydroxyl number was added to the above prepolymer solution, and the reaction mixture was stirred under the same conditions for 1 h. Subsequently, an amount of PEG-200 equivalent to half the mole of MDI was added, and the mixture was stirred under the same conditions for 1 h. The final product was dried at 60°C for 40 h to remove the DMF. As a control, linear PU without pentaerythritol was prepared for comparison. The PU structures are shown in Figure 1. The specimen used for mechanical tests was prepared by a solvent casting method as follows: the DMF in a PU solution was slowly evaporated at 70°C for 60 h to obtain a 0.7–0.9 mm thick PU sheet. The specimen was prepared from the sheet according to ASTM D638.

Number of hydroxyl groups

The number of free hydroxyl groups in the PU chain after pentaerythritol addition was found by following the titration method found in the literature.[12] A phthalic anhydride solution was prepared by dissolving 14 g of phthalic anhydride in 91.5 mL of DMF. The phthalic anhydride solution (5 mL) was then added into 2 mL of the PU reaction mixture. The mixture was the sonicated for 10 min at 45°C, incubated at 98°C for 15 min, and allowed to cool to room temperature. After the addition of 10 mL of DMF and 2 mL of distilled water, the mixture was titrated with 0.1*N* NaOH using a drop of 1% phenolphthalein indicator. A blank titration of phthalic anhydride solution was carried out without the reaction mixture by the same procedure. An average of five titrations was used for the hydroxyl number calculation. The exact mass of the PU in a sample reaction mixture was found by weighing the residue after complete evaporation of DMF in a vacuum oven for 30 h. The hydroxyl number was calculated from the following equations:

$$0.1(\mathrm{B} - \mathrm{A})/\mathrm{PU\ mass} = \mathrm{Hydroxyl\ number\ (mmole/g)} \quad (1)$$

where A, titration volume of PU; B, blank volume.

$$\mathrm{Hydroxyl\ number} \times \mathrm{Total\ mass} = \mathrm{Total\ hydroxyl\ group} \quad (2)$$

Characterization

An FT-IR spectrometer (JASCO 300E, Tokyo, Japan) equipped with ATR was used to take the IR

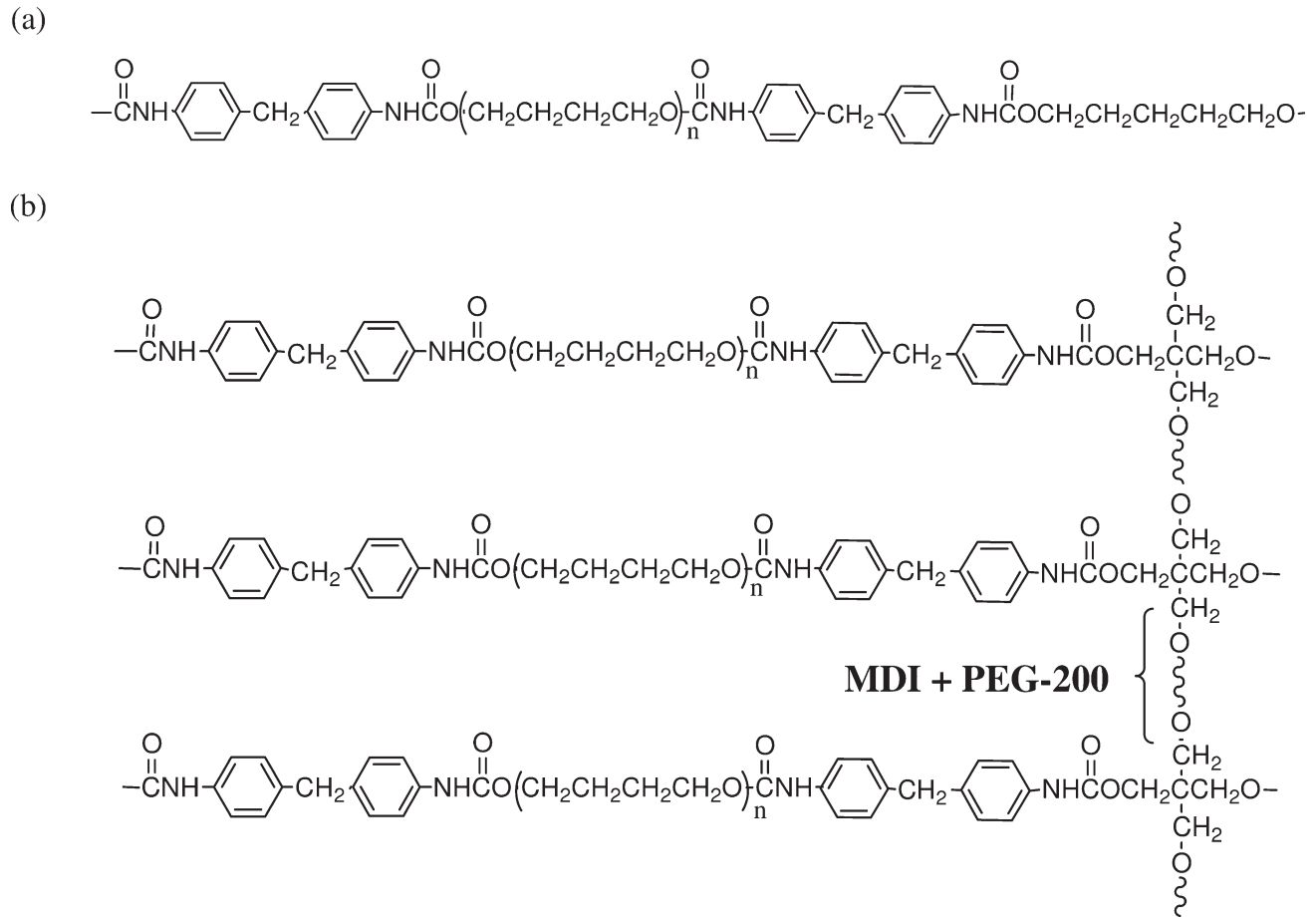

Figure 1 Structures of (a) linear SMPU and (b) pentaerythritol cross-linked SMPU.

spectrum of the thin PU sample on KBr disk under the following conditions: 4 cm^{-1} resolution, 25 scans, and 2 mm/s scan speed. X-ray diffraction spectra were scanned under the following conditions: $2\theta = 5°–40°$ and 1°/min by a wide-angle X-ray diffractometer (WAXD, Rigaku Rint 2000, CuKα, 40 kV, and 30 mA) (Osaka, Japan). A differential scanning calorimeter (DSC-2010, TA instrument, New Castle, DE) was used for the heating and cooling scans at a rate of 10°C/min between −100°C and 200°C. The tensile mechanical properties were measured by a Universal Testing Machine (LR50K, Lloyd instrument, UK) according to ASTM D638 under the following conditions: 25 mm gauge length, 10 mm/min crosshead speed, and 2.5 kN load cell. The crosslink density was calculated according to the Flory-Rehner equation for a specimen ($25 \times 25 \times 1$ mm^3) swelled in toluene. A more detailed explanation of this calculation will appear in the results section.

Shape memory test

UTM equipped with a temperature-controlled chamber was used for the cyclic shape memory test. The specimen with a length L_0 in a temperature-controlled chamber was drawn 100% to $2L_0$ at T_m + 20°C for 2 min and stayed at T_m + 20°C for 5 min. After the upper grip is released, the specimen in the chamber was cooled to T_m − 20°C with the help of liquid nitrogen for 10 min and the shrunk length (L_1) was measured after 20 min of stay at T_m − 20°C. Shape retention (%) was calculated by the eq. (3) using L_0 and L_1. The specimen in the chamber was heated to T_m + 20°C for 5 min and the length (L_2) was measured after 10 min of stay at T_m + 20°C. Shape recovery (%) was calculated by eq. (4) using $2L_0$ and L_2. The shape memory test was repeated three times for the same specimen.

$$\text{Shape retention } (\%) = (L_1 - L_0) \times 100/L_0 \quad (3)$$

$$\text{Shape recovery } (\%) = (2L_0 - L_2) \times 100/L_0 \quad (4)$$

RESULTS AND DISCUSSION

Synthesis

Previous cross-linking of PU was carried out by connecting the chain ends with a three-way or a four way linker in a random manner, where the strain

was sacrificed in spite of the improved stress result. It was reported by the authors that the connection of PU chains by a flexible crosslinker and the control of the crosslink density could improve both strain and stress and shape memory properties due to the flexible linking and additional linking points.[12] The flexible linking was so successful that additional PEG linking by adopting a four way linker was included in this investigation. In this flexible crosslinking design, some of BD was replaced with pentaerythritol and the extra free hydroxyl groups of pentaerythritol, because MDI content was controlled just enough for linear chain formation, were used as cross-linking points. The free hydroxyl groups on the PU chain were activated by MDI and linked by PEG-200, which connected the MDI-activated PU chains. Because the PU chain was connected at various points along the PU chain, a substantial increase in stress and strain was possible compared with the linear PU. The free hydroxyl group on the PU chain was found by the titration method and used for the calculation of the required MDI and PEG-200 for cross-linking.

The free hydroxyl groups attack the phthalic anhydride to form a polymer–phthalic acid intermediate. The excess phthalic anhydride is hydrolyzed with water to give phthalic acid. The carboxyl groups from the phthalic acid were titrated with a NaOH solution using a phenolphthalein indicator, and a blank titration was performed without the PU polymer. The difference in NaOH volume between the blank and PU titrations was used for the calculation of the free hydroxyl groups.[10] The hydrolysis of phthalic anhydride was finished in 2 min, judging from the fact that the volume of NaOH was almost constant after 2 min. An aliquot of the reaction mixture after pentaerythritol addition was taken from the reactor at 10 min intervals, and the amount of free hydroxyl groups remaining after pentaerythritol addition was followed by the above titration method. As the pentaerythritol reaction progressed, the number of free hydroxyl groups decreased. The number of carboxyl groups from the phthalic anhydride hydrolysis, which occurred during the titration, increased due to the decrease of the free hydroxyl groups. The pentaerythritol reaction was completed in 30 min as the NaOH volume reached the maximum, as shown in Figure 2. The free hydroxyl groups present in the reaction mixture were calculated from the titration result. For example, the hydroxyl number of P-10 was 0.13 mmole/g, and the total hydroxyl group in reaction mixture was then 6.7 mmole that was close to the 6.4 mmole (a theoretical amount derived from the added pentaerythritol (3.2 mmole) where two hydroxyl groups are available per pentaerythritol). An equivalent amount of MDI was added to activate these free hydroxyl groups. Last, PEG-200 was used for the crosslinking of MDI-activated PU chains.

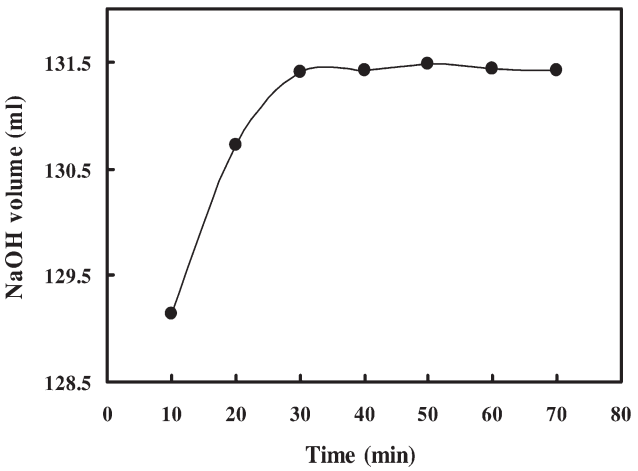

Figure 2 Titration of the periodically sampled reaction mixture after pentaerythritol addition.

Cross-link density

The crosslink density was calculated from the polymer swelling experiment. The interaction parameter (χ) between the solvent and polymer could be found from the following expression.[13]

$$\chi = (\delta_1 - \delta_2)^2 V_1/RT \quad (5)$$

where, δ_1 and δ_2, solubility parameter of solvent and polymer; V_1, molar volume of solvent; R, gas constant; T, absolute temperature.

The solubility parameters of toluene (δ_1) and PU (δ_2) were 18.2 and 20.5 $(MPa)^{1/2}$, respectively.[14] The degree of cross-linking was calculated from the Flory-Rehner eq. (6).

$$-[\ln(1 - v_2) + v_2 + \chi v_2^2] = V_1 n[v_2^{1/3} - 1/2v_2] \quad (6)$$

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

The cross-link density was found to increase with an increase of pentaerythritol content, which suggested that the added pentaerythritol was included for cross-linking (Table II).

IR analysis

Usually, the IR peak of the hydrogen-bonded urethane carbonyl group appears at 1699–1706 cm^{-1}, a little lower than the free urethane carbonyl group (1731–1733 cm^{-1}).[15] The stretching vibration of the carbonyl group is also affected by dipole–dipole interactions between the PU chains.[9] The peak around 1700 cm^{-1} relatively decreased with the increase of pentaerythritol content, whereas the one

TABLE II
Cross-Link Density of SMPU Obtained by a Swelling Experiment

Sample code	[a]ρ (g/cm^3)	[b]Q	[c]v_2	[d]10^3n
P-0	0.932		–	
P-5	1.09	2.33	0.300	0.649
P-10	1.00	1.98	0.336	0.852
P-12.5	0.862	1.90	0.344	0.903
P-15	0.867	1.67	0.374	1.10
P-17.5	0.875	1.65	0.377	1.12
P-20	0.833	1.61	0.382	1.15

[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.

around 1730 cm^{-1} remained the same (Fig. 3). Based on the IR result, the shift from bonded carbonyl to free carbonyl continued as the pentaerythritol content increased. Therefore, cross-linking reduced the hydrogen bonding and disrupted the hard segment interaction. From the IR result, it can be proposed that the chemical cross-linking by pentaerythritol changed the polymer chain alignment, and resulted in a reduction of the interaction between chains.

The shift phenomena can be quantified by the following equation. The phase separation of hard and soft segments can also be calculated from the IR spectra by comparing the peak intensity ratios of the carbonyl groups at 1703 cm^{-1} and 1733 cm^{-1}.[16] The parameter indicating phase separation, the hydrogen bonding index (R), is calculated by the following equation.

$$-\frac{C_{bonded}\varepsilon_{bonded}}{C_{free}\varepsilon_{free}} = \frac{A_{1703}}{A_{1733}} \quad (7)$$

In eq. (7), A is absorbance, C is concentration, ε_{bonded} is the extinction coefficient of the peak at

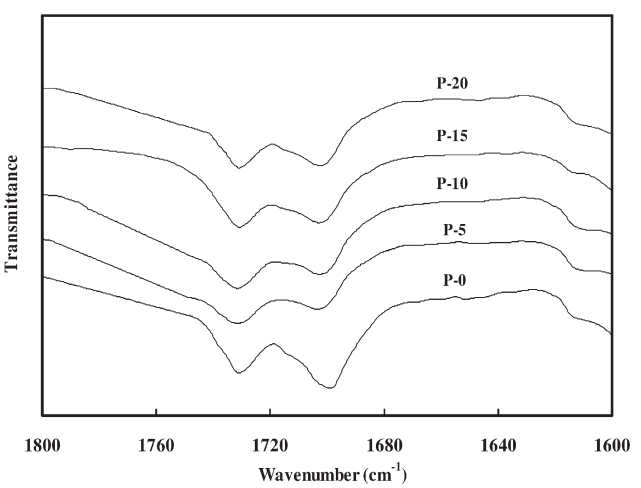

Figure 3 Infrared spectra of PU with various pentaerythritol contents.

TABLE III
Comparison of Hydrogen Bonding Index (R) and DPS

Sample code	[a]R (A_{1703}/A_{1733})	[b]DPS
P-0	1.15	53.4
P-5	0.83	45.3
P-10	0.85	45.9
P-12.5	1.02	50.3
P-15	0.99	49.7
P-17.5	1.01	50.2
P-20	1.03	50.8

[a] A_{1703}: absorbance at 1703 cm^{-1} and A_{1733}: absorbance at 1733 cm^{-1}.
[b] Degree of phase separation (DPS) = $R/1 + R$.

1703 cm^{-1}, and ε_{free} is the extinction coefficient of the peak at 1733 cm^{-1}. The ratio, $\varepsilon_{bonded}/\varepsilon_{free}$, is close to 1.0.[17] The degree of phase separation (DPS) is calculated from the following equation using the R value from eq. (7).[17,18] The combined result is summarized in Table III.

$$DPS = \frac{C_{bonded}}{C_{bonded} + C_{free}} = \frac{R}{R+1} \quad (8)$$

As the pentaerythritol content increased, R decreased from 1.15 (P-0) to 0.85 (P-10) and 1.03 (P-20). The hydrogen bonding became weaker as the pentaerythritol content increased. The change in the phase separation becomes clear if the DPS is compared. The DPS decreased from 53.4% (P-0) to 45.9% (P-10) and 50.8% (P-20). It is clear from the IR experiment that the phase separation decreases by pentaerythritol cross-linking.

XRD analysis

The X-ray deflection peak of the PU, irrespective of pentaerythritol content, is observed at $2\ominus = 19.5°$. The linear P-0 showed a low peak intensity compared with the cross-linked PUs, and the peak intensity increased with the increase of pentaerythritol content (Fig. 4). As the cross-linking content increased, the hard segments were forced to stay close to the cross-linking points and the relatively ordered hard segment alignment increased the peak intensity. Although the cross-linking hampered the hydrogen bonding between the hard segments in the IR analysis, the strong covalent bonding by the cross-linking held the hard segments in place, overcoming the adverse hydrogen bonding effect. However, it is not easy to decipher the effect of the pentaerythritol on cross-linking simply by the XRD spectra.

Thermal analysis

The melting temperature (T_m) of the soft segment was detected by DSC, and the thermal analysis data

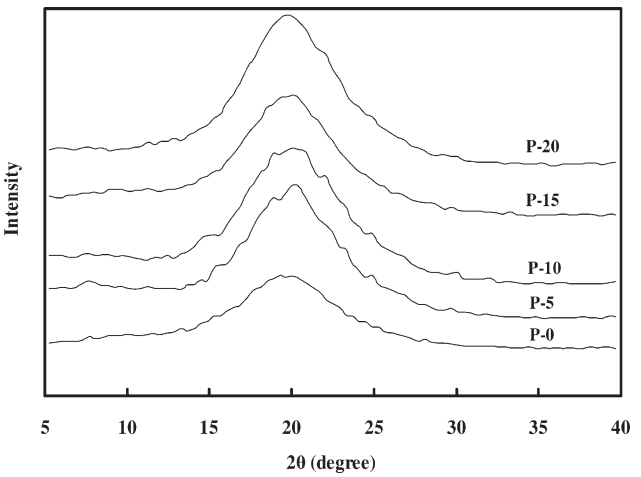

Figure 4 X-ray diffraction spectra of PU with various pentaerythritol contents.

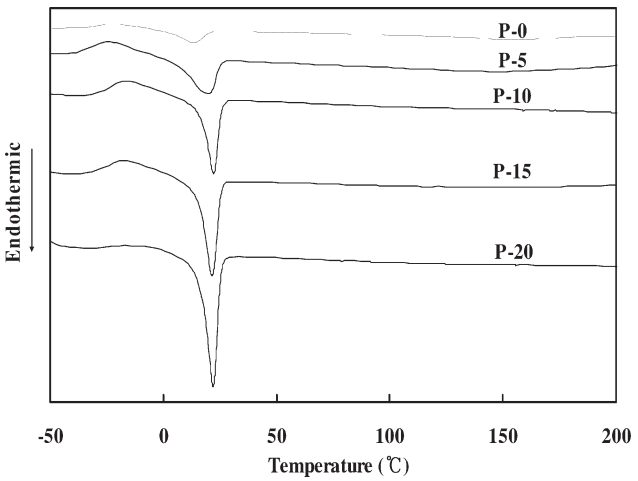

Figure 5 DSC thermogram of SMPU with various pentaerythritol contents.

are summarized in Table IV. The T_m of P-0 (13.7°C) increased with cross-linking: 20.2°C (P-5) and 22.0°C (P-20). The cross-linked network structure raised the T_m. It is very interesting that the T_m did not significantly increase after cross-linking, although the pentaerythritol content was raised. It seems that the cross-linking density of the hard segment does not affect the soft segment melting, because the soft segment acquires enough energy for melting at the T_m. The peak area can be quantitatively compared by the heat of melting (ΔH_m), as seen in Table IV. In accordance with the peak increase with cross-linking shown in Figure 5, ΔH_m increased significantly from 3.47 J/g (P-0) to 11.9 J/g (P-5) and 22.9 J/g (P-20). The restricted soft segment melting by pentaerythritol cross-linking is responsible for the increase of ΔH_m.

Tensile mechanical properties

The tensile mechanical properties averaged from 5 tests are compared in Figure 6. The maximum stress of cross-linked PU (P-20) steeply increased up to 1000% compared with P-0. The strain seen at the break reached as high as 1300%, although it did not change above 5 wt % pentaerythritol content. The

TABLE IV
Thermal Properties of PU with Various Pentaerythritol Contents

Sample code	T_m (°C)	ΔH_m (J/g)
P-0	13.7	3.47
P-5	20.2	11.9
P-10	22.2	12.9
P-12.5	22.4	20.1
P-15	21.6	17.6
P-17.5	22.7	28.0
P-20	22.0	22.9

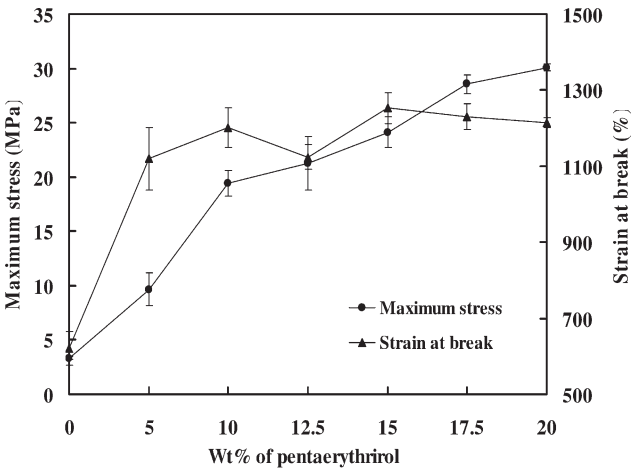

Figure 6 Mechanical properties of cross-linked SMPU versus wt % of pentaerythritol: (a) maximum stress and strain at break and (b) tensile modulus and yield stress.

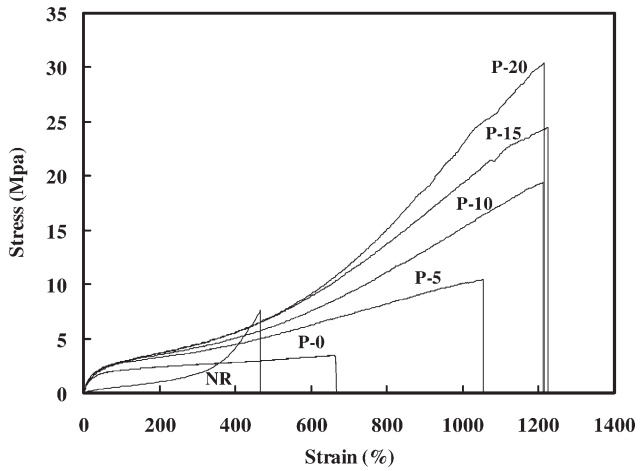

Figure 7 Stress–strain curve of cross-linked SMPU.

tensile modulus showed a maximum at 5 wt % of pentaerythritol and decreased with further increases in pentaerythritol content. The yield stress reached a maximum at 10 wt % of pentaerythritol and decreased at a higher wt % of pentaerythritol. It is remarkable that a high maximum stress was obtained by changing the cross-linking method while maintaining a similar modulus, and that the strain at break increased up to 1300% by cross-linking. The tensile mechanical behavior is also compared in a stress–strain curve (Fig. 7). The PU series showed a similar slope of up to 600% strain, but a sudden increase in slope was observed at higher strain. Because the behavior is similar to that of natural rubber (NR), the polymers are compared with NR in Figure 7. As you can recognize, P-20 is the best PU and is close to NR in overall shape, although it has a higher stress and strain. This steep rise of stress in NR originates from the strain-induced crystallization, and the same reasoning can be applied to the explanation of P-20. The P series polymers aligned along the chain length because each polymer chain was laterally connected by a PEG-200 spacer, and became stronger when stretched due to the strain-induced crystallization. We know from our previous experiments on SMPU that cross-linking at a hard segment can increase the maximum stress, whereas sacrificing strain instead. However, the adoption of a flexible spacer with cross-linking at its side, as is the case in P-20, elevated the maximum stress without any sacrifice of strain. When it comes to the comparison with similarly cross-linked PUs, the maximum stress of P-20 improves 87 and 30% compared with the best results of pentaerythritol cross-linked PU and flexibly cross-linked PU by glycerol, respectively. As noticed in the above analyses and mechanical tests, P-20 was different from the conventional PUs because of the flexible spacer and lateral cross-linking.

TABLE V
Comparison of Shape Recovery Times

	Shape recovery rate (%)			
Sample code	[a]300 s	[b]600 s	Maximum	Time to maximum (s)
P-0	80	83	84	751
P-5	84	89	89	516
P-10	85	89	89	478
P-12.5	86	90	90	351
P-15	86	90	90	354
P-17.5	85	88	88	361
P-20	89	90	90	375

[a] Shape recovery after 300 s.
[b] Shape recovery after 600 s.

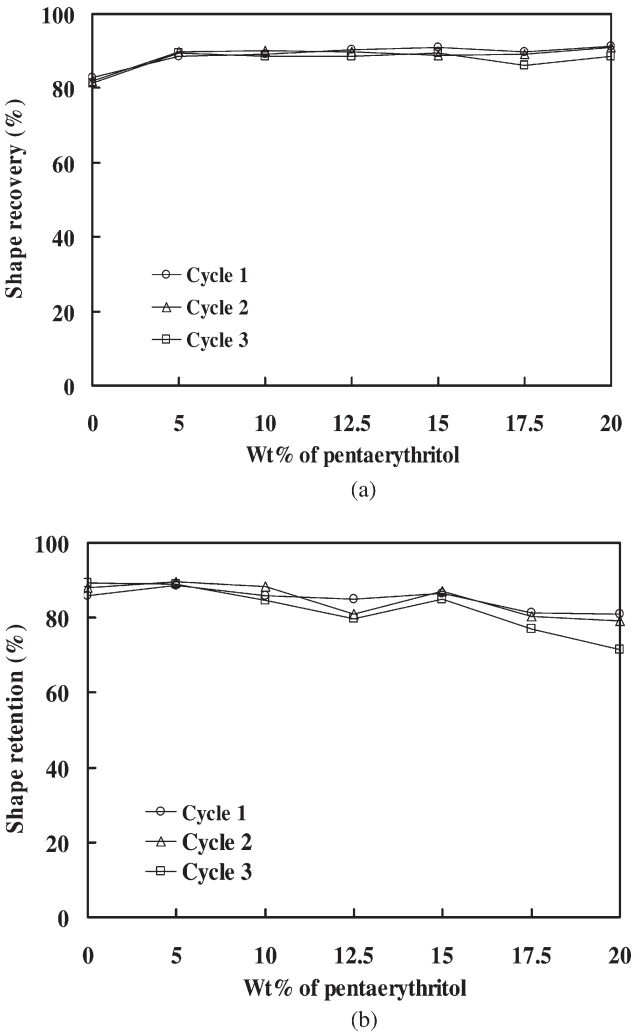

Figure 8 (a) Shape recovery and (b) shape retention versus pentaerythritol content profile.

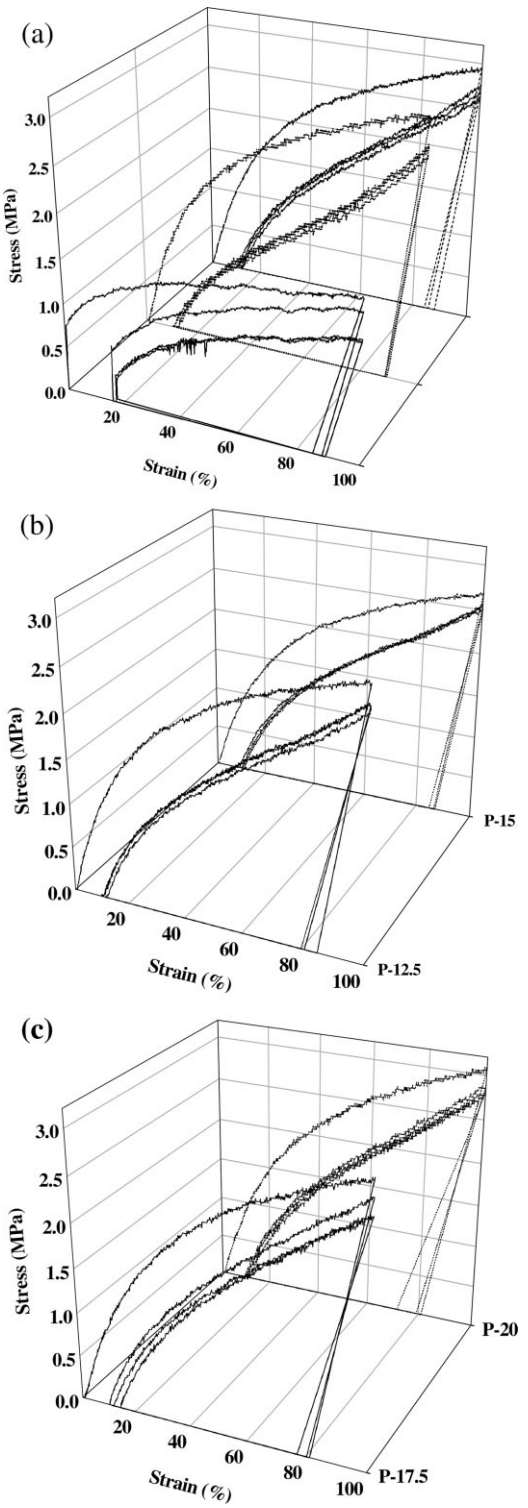

Figure 9 Cyclic shape memory test of (a) P-0, P-5, and P-10, (b) P-12.5 and P-15, and (c) P-17.5 and P-20.

Shape memory effect

The cyclic shape memory test was used to compare the shape recovery rate and shape retention rate at a T_m range of ±20°C. Because the T_g is too low and it is hard to control the temperature around it, the shape memory test was carried out around the T_m of the soft segment.[8,9] As seen in Table V, the shape recovery process, in the best case, was completed in less than 10 min at a T_m of +20°C. The shape recovery increased from 84% of P-0 to 89% of P-5 and 90% of P-20. The shape recovery remained almost the same if pentaerythritol was included, irrespective of its content. The shape recovery speed also increased with the increase in pentaerythritol content and was almost the same at pentaerythritol content higher than 12.5%. After three cyclic tests, the shape recovery was not reduced for all of the pentaerythritol contents, but the shape retention slowly decreased with increased pentaerythritol content. Because shape recovery and retention are opposite properties, shape retention is sacrificed as shape recovery increases. As an ideal example, P-10 maintained both good shape recovery and retention even after cycle three. It is remarkable that the shape recovery of some PUs increases up to 90% and the similar shape recovery is maintained after three test cycles, based on our experience from the previous shape memory polymers covering both polyester and PU. Generally, the shape recovering force of the P series as the pentaerythritol content increased became so strong that shape retention decreased compared to the uncross-linked one (Fig. 8). The three-dimensional cyclic shape memory test, shown in Figure 9, also demonstrates that the shape recovery significantly improved, if P-0 is compared with other P-series, after the inclusion of pentaerythritol. In line with all the above analytical and mechanical data, the shape memory test results demonstrate that lateral cross-linking with a flexible spacer plays a decisive role in improving the overall properties compared with linear P-0. Therefore, the application of a flexible cross-linking method to PU is very encouraging and intriguing, and suggests that challenging goals, such as developing a highly effective shape memory polymer with high stress and strain, are attainable by optimizing PU structure.

CONCLUSIONS

A series of PU cross-linked with pentaerythritol using a PEG-200 spacer were compared with PU without cross-linking. With an increase in pentaerythritol content, the cross-link density increased, whereas the DPS decreased. The structure of the hard segment was disrupted by the cross-linking based on the IR analysis. The enthalpy of transition and the T_m increased compared with P-0 with increased pentaerythritol content. The maximum stress of P-20 increased up to 1000% and the strain also improved 200% compared with P-0. The behavior of the P-series in stress–strain curves was very

similar to that of NR, but both stress (400%) and strain (300%) in the best case were higher than for NR. The shape recovery of most P-series went up to an amazing 90% and did not decrease below 85% after cycle four while showing no significant drop in the shape recovery speed. All of the outstanding mechanical shape memory properties of the P series originate from the flexible cross-linking of PU chains with a PEG-200 spacer. Many candidate structures in our archive remain to be tested.

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