

The Effect of Soft Segment Content and Linker Length on Shape Recovery and Mechanical Properties of Laterally Linked Polyurethane Copolymer

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ABSTRACT: Lateral flexible linking of shape memory polyurethane (SMPU) by a polyethyleneglycol (PEG) linker through the allophanate linking method was studied, while adjusting the soft segment content and PEG length. The SMPU was composed of 4,4'-methylenebis(phenylisocyanate) (MDI), poly(tetramethyleneglycol) (PTMG), 1,4-butanediol (BD), and PEG-200 as a linker. A second MDI was used to connect the carbamate group of the SMPU chain and PEG. The impact of soft segment content and PEG length on the mechanical properties and shape recovery of two series of SMPU were compared. In the best case, a 545% increase in maximum stress compared to a

linear polymer was attained. The flexibly crosslinked SMPUs behave similarly to natural rubber in their stress-strain curve, but their tensile mechanical properties surpassed those of natural rubber. Shape recovery went up to 96%, which is among the best SMPUs tested so far, and shape recovery remained above 90% after four cyclic tests. The extraordinary shape memory results are analyzed and discussed together with DSC and IR data. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2063–2073, 2011

Key words: flexible linking; polyurethane; spacer; shape memory; allophanate

INTRODUCTION

Shape memory polyurethane (SMPU) has been intensively researched due to its exceptional properties, such as a practical and adjustable phase transition temperature range, high and reproducible shape recovery, chemical resistance, mild reaction conditions, easy and simple processing, and ample references for comparison.^{1–11} The characteristics of SMPU were explained by a peculiar structure in which a hard domain and a soft domain were formed due to the difference in intermolecular attraction of hard and soft segments. Hydrogen bonding and dipole-dipole interactions were responsible for binding hard segments to form the hard domain, and the hard domain was important in shape recovery. Meanwhile, the soft segment absorbed external stress or impact and kept the polymer resilient, even at low temperature. Because shape recovery of the linear SMPU significantly decreased after repeated shape recovery

test cycles, a crosslinked SMPU was suggested as an alternative to the failure problem.^{12–15} The crosslinked SMPU was successful in raising tensile stress and maintaining high shape recovery during cyclic tests, but strain was substantially decreased after crosslinking and hardening of SMPU was observed at high crosslinking content. A new crosslinking design was tested by us to gain both high mechanical strength and reliable shape recovery under severe conditions. The new design adopted polyethyleneglycol (PEG) as both spacer and crosslinker between SMPU chains and resolved the problem of low strain after crosslinking, while maintaining high tensile stress and shape recovery. The flexible PEG that was responsible for deterring stiffening of the SMPU after crosslinking connected SMPU chains through the hydroxyl group of glycerol on the polymer chain via MDI.^{16,17} The hydroxyl group content of the SMPU chain had to be detected by a time-consuming titration method and was used for deciding the amount of PEG and MDI necessary for linking.¹⁸ The allophanate linking of carbamate bonding was tested for coupling PEG and MDI in this investigation because of its higher reactivity and more available reactive sites (Fig. 1). The flexibly linked SMPUs, while varying PEG length and soft segment content, were compared with the previous SMPUs in terms of mechanical properties and shape recovery.

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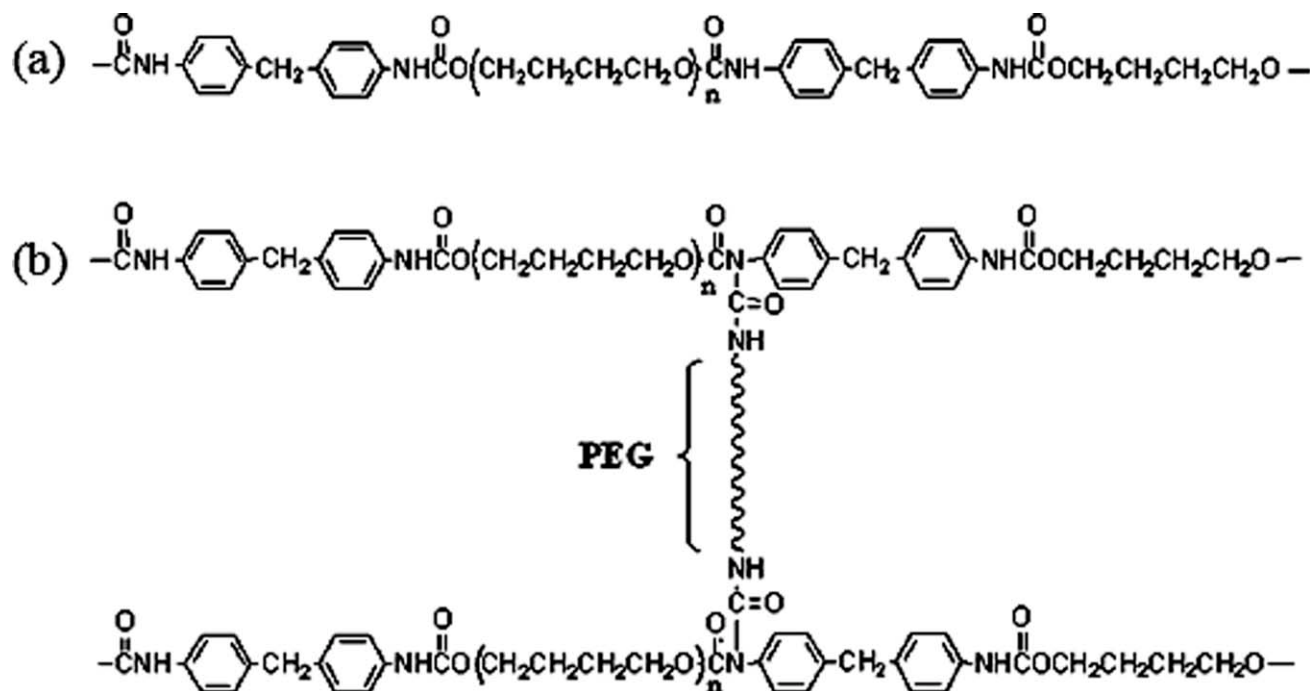


Figure 1 Structures of (a) linear SMPU, and (b) flex-linked SMPU connected at the carbamate group.

EXPERIMENTAL

Materials

Poly(tetramethyleneglycol) (PTMG, $M_w = 2000$ g/mol, Aldrich Chemical, USA), 4,4'-methylenebis(phenylisocyanate) (MDI, Tokyo Kasei, Japan), 1,4-butanediol (BD, Junsei Chemical, Japan), and polyethyleneglycol (PEG-200, or PEG-1000, Duksan Chemical, Korea) were dried under high vacuum (0.1 Torr) for 12 h before use. Dimethylformamide (DMF, Duksan Chemical) and dimethylacetamide (DMAC, Duksan Chemical) were distilled over CaH_2 before use.

Polymer synthesis

The mixture of MDI and PTMG at the ratio specified in Table I was placed in a 500-mL four-necked beaker type flask equipped with a mechanical stirrer, condenser, nitrogen purge, and oil bath, and it was allowed to react for 3 h at 50°C to prepare the prepolymer. BD as a chain extender was added into reaction mixture after dissolving the prepolymer with 100 mL of DMF, and the reaction continued for 1 h. Subsequently, a second MDI was added to the above reaction mixture, and the reaction went on at 50°C for 1 h. Finally, PEG-200 or PEG-1000 equivalent to a half mole of the second MDI was added with an additional 100 mL of DMF and the mixture was stirred under the same conditions for 2 h. As a control, linear PU without PEG was prepared for comparison. After polymerization was over, the polyurethane product was excessively washed in

distilled water, methanol, and chloroform, and then dried to remove residual solvent in a 60°C oven for 3 days. The SMPU structures are shown in Figure 1. The specimen for the mechanical test was prepared by the solvent casting method: DMF in PU solution was slowly evaporated at 70°C for 60 h to get a 0.7- to 0.9-mm thick PU sheet and the specimen was prepared from the sheet according to ASTM D638.

Characterization

An FTIR spectrometer (JASCO 300E) equipped with ATR was used to measure the IR spectrum of the SMPU sample under the conditions of 4-cm^{-1}

TABLE I
Composition of Flexibly Linked SMPU

Sample code	Reactant (mmole)				
	MDI-1	PTMG	BD	MDI-2	PEG ^a
FC1-1			35	–	–
FC1-2			35	5	2.5
FC1-3	50	15	35	10	5
FC1-4			35	15	7.5
FC1-5			35	20	10
FC2-1			30	–	–
FC2-2			30	2	1
FC2-3	50	20	30	4	2
FC2-4			30	6	3
FC2-5			30	10	5

^a PEG-200 for FC1 series and PEG-1000 for FC2 series were used.

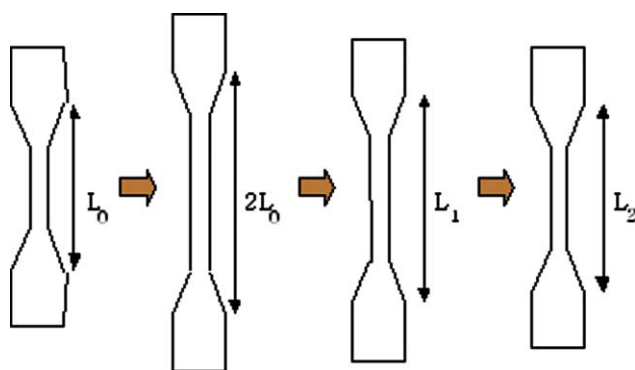


Figure 2 Test specimen for shape retention and shape recovery (L_0 : initial specimen length, $2L_0$: length of L_0 strained 100% above T_m , L_1 : deformed length at below T_m after load removal, L_2 : final specimen length above T_m). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resolution, 25 scans, and 2-mm/s scan speed. A differential scanning calorimeter (Diamond DSC, Perkin–Elmer) was used for the heating and cooling scan at a rate of 10°C/min between –50 and 250°C. A specimen (10 mg), after melting at 250°C for 5 min and quick cooling to –50°C, was warmed to 250°C at 10°C/min, while monitoring the phase transition. A second heating scan was selected for a comparison of the transition temperature range. Tensile mechanical properties were measured by a Universal Testing Machine (LR50K, Lloyd instrument, UK) according to ASTM D638 under the conditions of 25-mm gauge length, 10-mm/min

crosshead speed, and 2.5-kN load cell. The intrinsic viscosity, based on an average of five experiments, was obtained by extrapolation of the viscosity data measured by an Ubbelohde viscometer for SMPU dissolved in DMAC at four different concentrations (0.125, 0.25, 0.5, and 1 g/dL) at 25°C. The solvation of SMPU for intrinsic viscosity measurement was slow and took 3–4 days with heating and vigorous stirring for complete dissolution due to the cross-linked structure of SMPU. The crosslink density was calculated according to the Flory–Rehner equation for a specimen ($0.025 \times 0.025 \times 0.001 \text{ m}^3$) swelled in toluene, a process for which further explanation will appear in the results section. The $^1\text{H-NMR}$ (CF_3COOD) spectrum of FC1-2 was taken by a Varian–Unity Inova 500 NB spectrometer (500 MHz): 1.7 ppm ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$) $_n$, 2.0 ppm $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$, 3.7 ppm ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$) $_n$, 3.9–4.0 ppm $\text{CH}_2\text{CH}_2\text{C}$ $\text{H}_2\text{CH}_2\text{O}$ and ($\text{CH}_2\text{CH}_2\text{O}$) $_n$, 4.3 ppm (PhCH_2Ph), and 7.1 ppm (aromatic). Other SMPU series NMR spectra also showed a similar shape to the above spectra.

Shape memory test

A UTM equipped with a temperature-controlled chamber was also used for the cyclic shape memory test, and the shape memory test method is shown in Figure 2. A specimen with a length L_0 in a temperature-controlled chamber was drawn 100% to $2L_0$ at 45°C for 2 min and stayed at 45°C for 5 min. After the specimen in the chamber was cooled to –25°C with liquid nitrogen for 10 min, the upper grip was

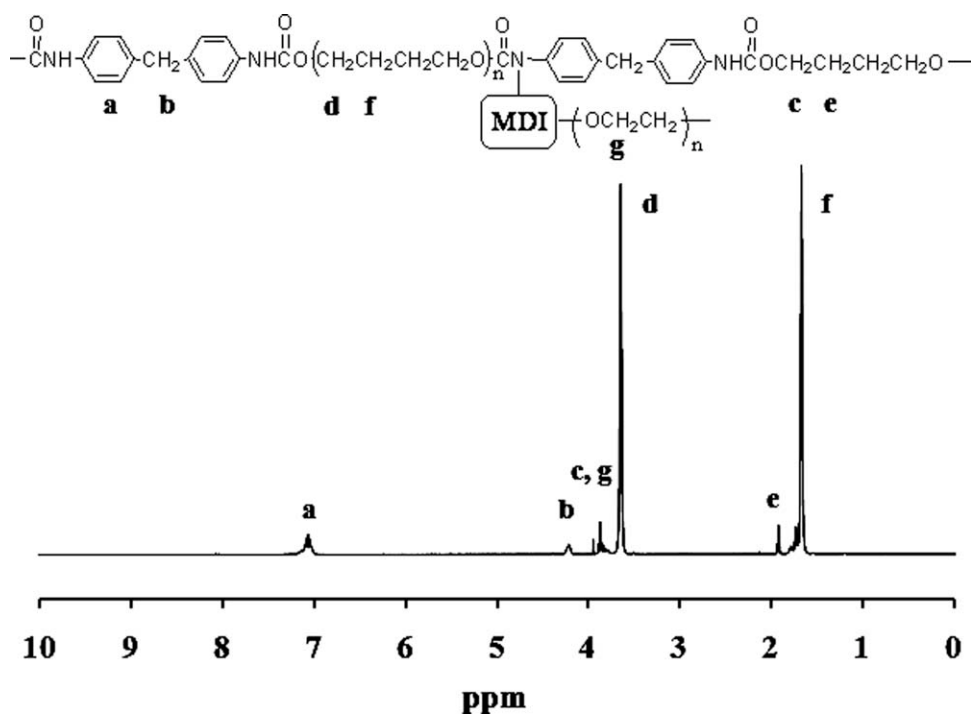


Figure 3 $^1\text{H-NMR}$ spectra of FC1-2.

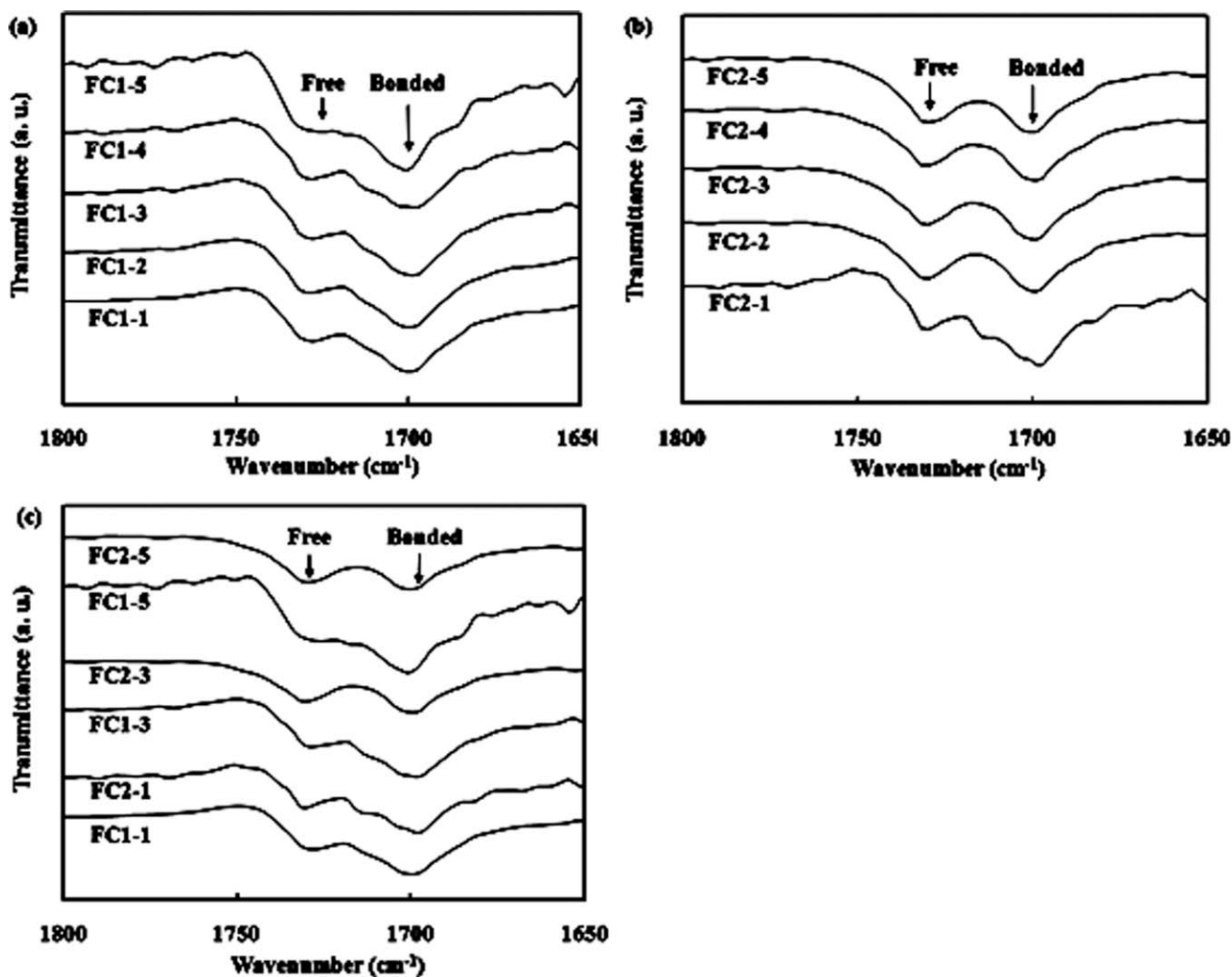


Figure 4 IR spectra of (a) FC1 and (b) FC2 series.

released and the shrunk length (L_1) was measured after 20 min at -25°C . Shape retention (%) was calculated with eq. (1) using L_0 and L_1 . The specimen in the chamber was heated to 45°C for 5 min, and the length (L_2) was measured after 10 min at 45°C . Shape recovery (%) was calculated with eq. (2) using $2L_0$ and L_2 . The shape memory test was repeated three times for the same specimen.

$$\text{Shape retention} = (L_1 - L_0) \times 100/L_0(\%) \quad (1)$$

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

RESULTS AND DISCUSSION

Synthesis

The adoption of crosslinking with a three-way or four-way linker was successful in improving the mechanical and shape memory properties of SMPU, but the rigid structure after crosslinking resulted in

low strain and poor shape recovery.^{13,15} To overcome this problem, polymer chains were connected by a flexible PEG and the crosslink density was controlled, demonstrating a surprising increase in mechanical and shape memory properties together with very high strain.^{16,17} The flexible linking was responsible for the high strain coupled with high stress and shape recovery. In the previous flexible linking method, some of the chain extender, BD, was replaced with glycerol and the extra hydroxyl group of glycerol was used as a crosslinking point. In this investigation, PEG was connected by an allophanate link for the following reasons: (1) the titration process necessary for finding the free hydroxyl group could be obviated, (2) a more reactive amino group was used as a linking site instead of the hydroxyl group of glycerol, (3) the carbamate group was far more evenly distributed along the SMPU chain than the limited glycerol hydroxyl groups, and (4) grafting of the PU chain by an allophanate linking was already well established.¹⁹⁻²⁷ The second MDI

anchored on the carbamate group of one SMPU chain connected PEG that was linked to another SMPU chain so that the SMPU chains were linked by PEG (Fig. 1). A representative NMR spectrum of FC1-2 (Fig. 3) agreed well with the proposed SMPU structure, and other SMPU series also showed similar spectra. Allophanate linking reaction was also tested at higher temperature (80, 100, or 120°C) and with catalysts like dibutyl tin laurate (DBTDL) or triethylamine following literature method,^{25,26} but the fact that any improvement in mechanical properties compared to the reaction at low temperature (50°C) without catalyst was not observed and the incompleteness of allophanate linking due to aggregation problem of reaction mixture at high temperature or with catalyst led us to choose the low temperature without catalyst as the reaction conditions. Shown in Table I, PEG-200 content increased gradually from FC1-1 to FC1-5 at constant soft segment (PTMG) content, and the PEG-1000 was used in FC2-1 through FC2-5 together with the increase in PEG-1000 content. In this investigation, the impact of PEG length and soft segment content on the shape recovery and mechanical properties was assessed.

IR analysis

Molecular interactions between SMPU chains were investigated by comparing the stretching vibration mode of the hydrogen bonded carbonyl group (1699–1706 cm^{-1}) with that of the free carbonyl group (1731–1733 cm^{-1}).^{28–30} The stretching vibration of the carbonyl group could also be affected by dipole-dipole interactions between SMPU chains. The relative shapes of two peaks around 1700 cm^{-1} and 1730 cm^{-1} were not changed with the increase in PEG content for the FC1 series [Fig. 4(a)]. In the FC2 series, the relative shapes remained the same, although PEG content was increased [Fig. 4(b)]. The IR results suggest that a significant change in the molecular interaction between carbonyl groups was not made as the PEG content increased for both the FC1 and FC2 series. However, peak shift from free carbonyl to bonded carbonyl group was observed when three sets of FC1 and FC2 series were compared [Fig. 4(c)]. The FC1 series containing less PTMG (soft segment) than FC2 series had stronger molecular interaction and the bonded carbonyl peak relative to free carbonyl increased. Based on the IR results, the shift between free carbonyl to bonded carbonyl group of FC1 and FC2 series was more dependent on soft segment (PTMG) content of each series and less on PEG content. Therefore, flexible linking by PEG did not affect molecular interactions such as hydrogen bonding and dipole-dipole interactions, and the interaction between hard segments was not disrupted.

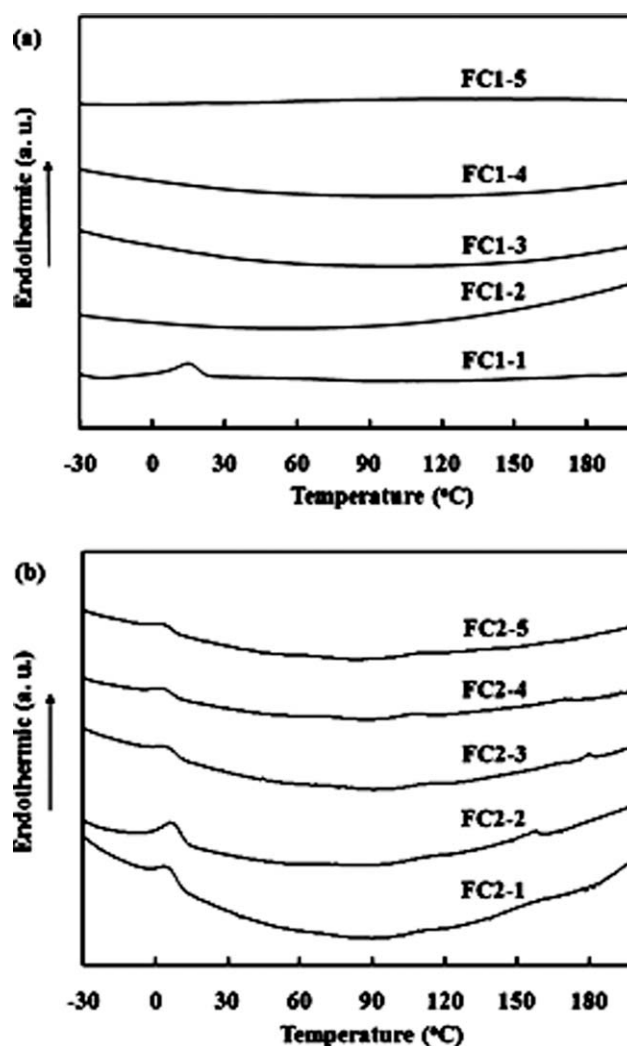


Figure 5 DSC thermograms of (a) FC1 and (b) FC2 series.

Thermal analysis

The soft segment T_m of the FC1 and FC2 series was compared instead of the T_g , which was too low to be detected by DSC. The T_m of the soft segment was very elusive to detect, as shown in Figure 5, in which FC1 series except FC1-1 did not show any transition around 20°C, although FC2 series did show the weak transition peaks. The disappearance of the melting transition peak and the weak transition peak signal were unusual, considering that every SMPU researched by us, whether crosslinked or not, showed very clear and sharp transition peaks between 10 and 20°C. The reason could be that free movement of the soft segment was restricted by the lateral flexible linking so that the melting transition was minimized or almost removed, resulting in weak transition signals. The DSC result was not unexpected, considering that the shrinkage of the transition peak signal after crosslinking of SMPU was already observed in our previous investigation.^{12,15} The disappearance of the soft segment T_m

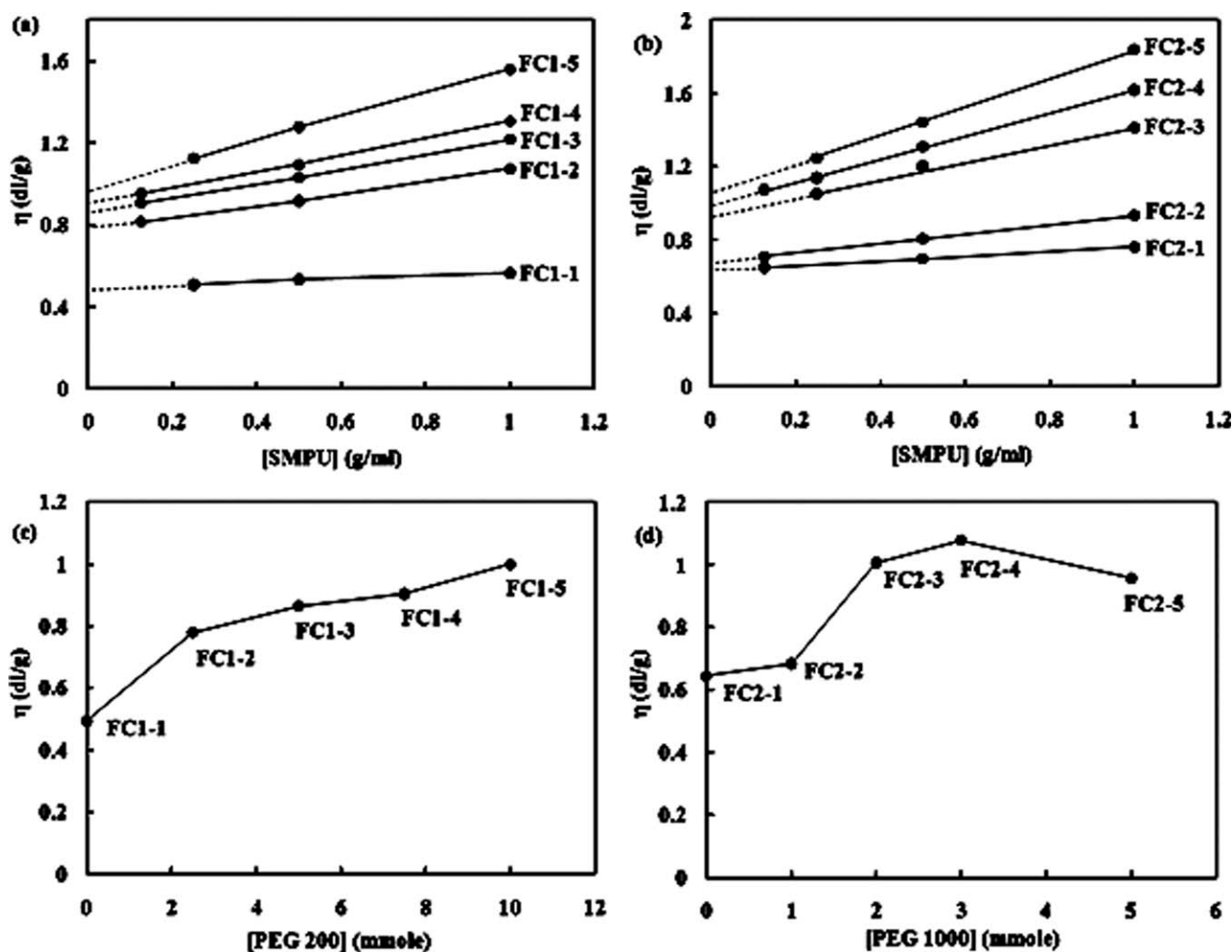


Figure 6 Viscosity versus SMPU concentration profile of (a) FC1 and (b) FC2 series, and viscosity versus PEG content profile of (c) FC1 and (d) FC2 series.

in FC1 series might cause a serious problem in executing the shape memory test because it was used as the critical temperature in the shape recovery experiment. In this investigation, the shape recovery temperature was not changed because the shape recovery results should be compared with those of previous SMPUs, and FC2 series showed the transition peak in the expected temperature range.

Viscosity

The flexibly linked structure of SMPU could be differentiated from the linear one in its intrinsic viscosity because the flex linked SMPU drag each other more than the linear one and thus should have increased viscosity. Intrinsic viscosity was obtained from the intercept of Figure 6(a,b) in which an excellent proportionality was observed between the reduced viscosity and FC1 or FC2 concentration. The intrinsic viscosity of the FC1 and FC2 series increased with an increase in PEG content [Figs. 6(c,d)]. Molecular weight was not calculated

from the intrinsic viscosity data because the deviation of parameters in the case of the crosslinked SMPU made molecular weight determination obsolete. The increase in the intrinsic viscosity of the FC1 series was gradual, while that of the FC2 series abruptly increased to the maximum. It seems that the FC2 series linked with a five times longer PEG could be more easily intermingled than the FC1 series and thus showed a higher intrinsic viscosity. The growth of viscosity with an increase in PEG content suggested that flex-linking was formed as expected, as judged from the fact that the intrinsic viscosity was related to chain length and polymer size.

Crosslink density

The crosslink density of the flex-linked SMPU was estimated by the polymer swelling method. First, the interaction parameter (χ) between solvent and polymer could be found from eq. (3).³¹

$$\chi = (\delta_1 - \delta_2)^2 V_1 / RT \quad (3)$$

TABLE II
Cross-Link Density of SMPU by the Swelling Experiment

Sample code	ρ^a (g/cm ³)	V_p^b (cm ³)	V_2^c	$10^3 n^d$
FC1-1	–	–	–	–
FC1-2	1.035	0.349	0.445	1.720
FC1-3	1.032	0.397	0.469	1.975
FC1-4	1.051	0.225	0.476	2.056
FC1-5	1.068	0.466	0.488	2.211
FC2-1	–	–	–	–
FC2-2	1.026	0.277	0.369	1.071
FC2-3	1.039	0.291	0.396	1.273
FC2-4	1.059	0.323	0.400	1.308
FC2-5	1.071	0.251	0.373	1.098

^a ρ is density.

^b V_p is polymer volume.

^c V_2 is volume fraction of polymer.

^d n is cross-link density.

δ_1 and δ_2 = solubility parameter of solvent and polymer

V_1 = molar volume of solvent

R = gas constant

T = absolute temperature

Solubility parameters were from the reference, and those of toluene (δ_1) and PU (δ_2) were 18.2 and 20.5 (MPa)^{1/2}, respectively.^{26,32} Next, the crosslink density was calculated by the Flory-Rehner eq. (4).

$$-\ln(1 - v_2) + v_2 + \chi v_2^2 = V_1 n [v_2^{1/3} - 1/2v_2] \quad (4)$$

v_2 = volume fraction of polymer in the swollen mass

χ = interaction parameter

n = crosslink density

The crosslink density data, as measured by the swelling method, showed a gradual increase in crosslink density with the increase of PEG content, which demonstrated that PEG was involved in the flex-linking (Table II).

Tensile mechanical properties

The maximum stress of the FC1 series remarkably increased from 11 MPa (FC1-1) to 41 MPa (FC1-2) and 60 MPa (FC1-5), and the FC2 series also showed a similar increase from 16 MPa (FC2-1) to 30 MPa (FC2-2) and 48 MPa (FC2-5) [Fig. 7(a)]. The percent increase in maximum stress compared to a linear SMPU (FC1-1 or FC2-1) is equal to 545% for FC1-5 and 300% for FC2-5. The highest maximum stress of the previous crosslinked SMPU was below 20 MPa, which demonstrated that a better maximum stress could be attained by adopting a flex-linking method. The strain at break of the FC1 series increased from 1470% (FC1-1) to 2040% (FC1-2) and decreased gradually to 1920% (FC1-3) and 1630% (FC1-5). The strain at break of the FC2 series also showed similar

shape: an initial increase from 1770% (FC2-1) to 2175% (FC2-2), followed by a gradual decrease to 1980% (FC2-3) and 1870% (FC2-5) [Fig. 7(b)]. The strain at breaks of some candidates (FC1-2 and FC2-2) were not reduced compared to linear ones (FC1-1 and FC2-1) under the flex-linking condition, and those of other candidates (FC1-5 and FC2-5) remained almost the same as those of the linear ones (FC1-1 and FC2-1) at the highest PEG content. The strain at break of over 2000% (FC1-2 and FC2-2) was quite high compared to that of the previous flex-linked SMPU (1290%). When the FC1 and FC2 series were compared, the maximum stress for both series increased proportionally to the PEG content and reached over 50 MPa. The strain at break of both series was not significantly reduced as the PEG content increased. The tensile mechanical test results are summarized in Table III. The tensile mechanical behavior is also compared in a stress–strain curve (Fig. 8). Both the FC1 and FC2 series showed a similar slope up to 500% strain, but a sudden increase in slope was observed at higher strains for both series.

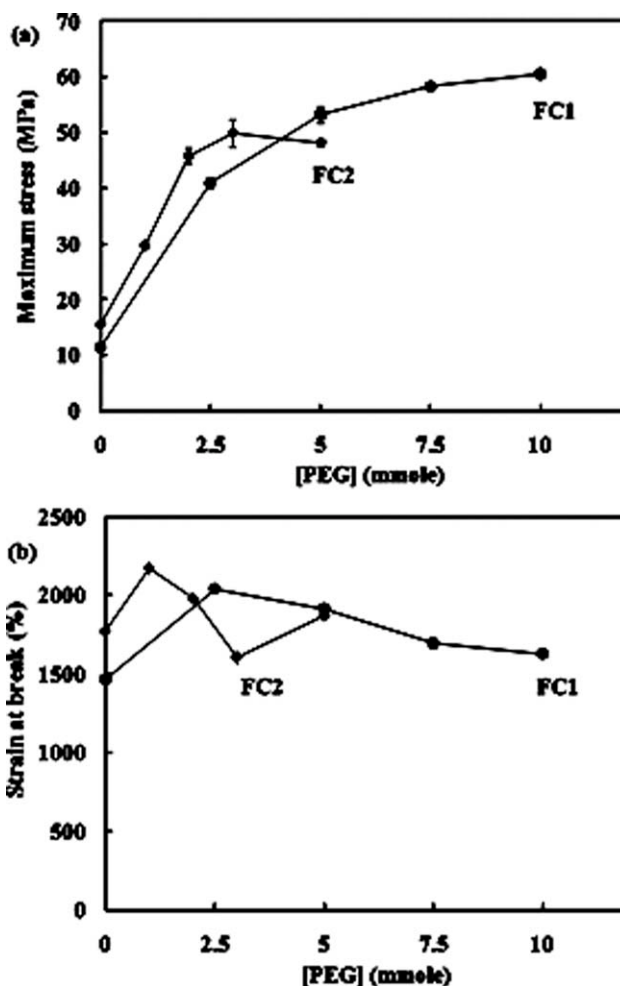


Figure 7 (a) Maximum stress and (b) strain at break of FC1 and FC2 series.

TABLE III
Tensile Mechanical Properties

Sample code	Maximum stress (MPa)	Strain at break (%)
FC1-1	11	1470
FC1-2	41	2040
FC1-3	53	1920
FC1-4	58	1700
FC1-5	60	1630
FC2-1	15	1770
FC2-2	30	2180
FC2-3	46	1980
FC2-4	50	1600
FC2-5	48	1870

Because the behavior of both series is similar to that of natural rubber, the two selected polymers (FC1-5 and FC2-5) and natural rubber (NR) are compared in Figure 8(c). The flexibly linked SMPUs (FC1-5 and FC2-5) are different from the linear SMPUs (FC1-1 and FC2-1) but are close to natural rubber in overall shape except for the higher stress and strain. The steep rise of stress in natural rubber originates from strain-induced crystallization, and the same reason-

ing can be applied to the explanation of flexibly linked SMPU. The FC2 series showed a higher strain than the FC1 series because of the higher soft segment (PTMG) content and linking by a longer PEG (PEG-1000). Structurally, flex-linked SMPUs were laterally connected by PEG, and they became stronger when stretched due to strain-induced crystallization. Conventional crosslinking of SMPU could increase the maximum stress with a significant decrease in strain, but the adoption of a flexible linker and lateral linking along the SMPU chain allowed a remarkable increase in maximum stress without a decrease in strain. The highly flex-linked SMPUs (FC1-5 and FC2-5) are exceptional in having the maximum stress and strain at break, which was not attainable in the previous SMPUs.^{4,9}

Shape memory effect

The cyclic shape memory test was carried out in 20°C above and below T_m range to investigate shape recovery and shape retention of the FC-1 and FC2 series (Figs. 9 and 10). The melting temperature of

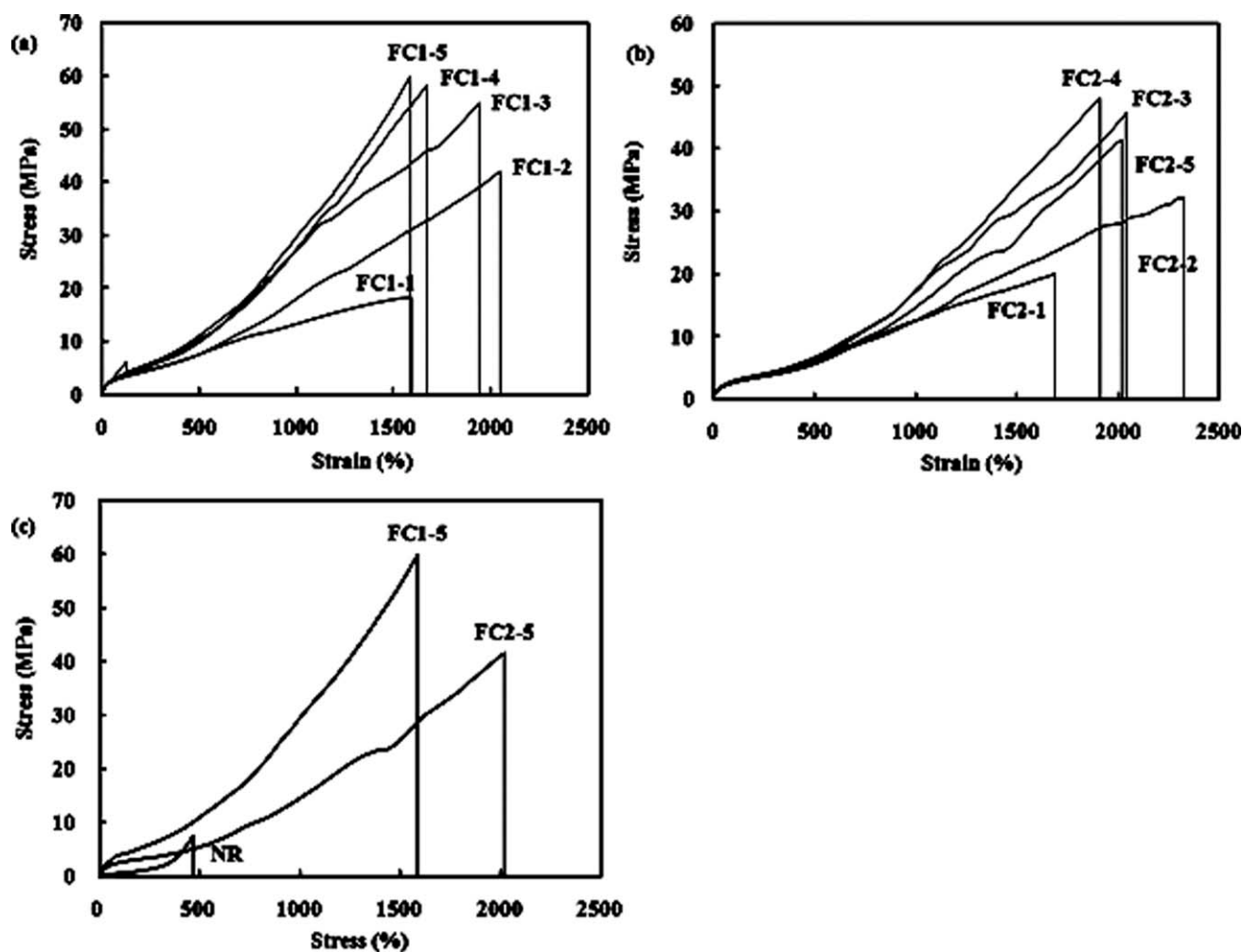


Figure 8 Stress-strain curve of (a) FC1, and (b) FC2 series, and (c) comparison of FC1-5 and FC2-5 with natural rubber (NR).

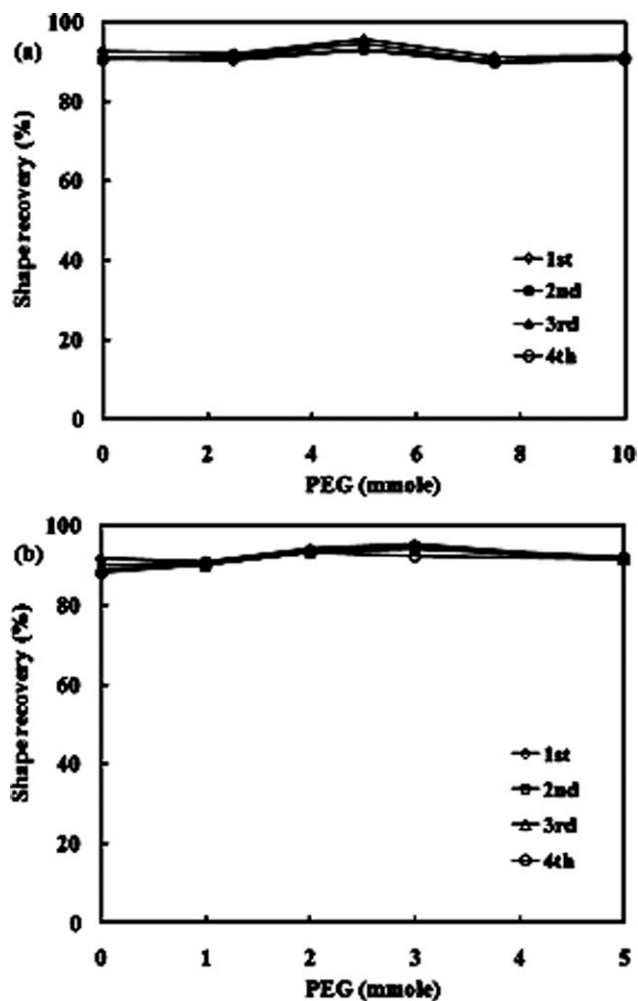


Figure 9 Cyclic shape recovery of (a) FC1 and (b) FC2 series.

the soft segment (T_m) was selected as the critical temperature for the shape memory test instead of the glass transition temperature of the soft segment (T_g), which was too low to control the temperature and not practical for application. Shape recovery of the FC1 series increased from 93% for FC1-1 to 96% for FC1-3 and decreased to 92% for FC1-5 and that of the C2 series also increased from 92% for FC2-1 to 95% for FC2-4 and decreased to 91% for FC2-5. Shape recovery of both series for all values of PEG content was over 90% and remained above 90% after four cyclic tests. Therefore, the shape of SMPU could be fully recovered to the original shape after repetitive distortions. In addition, shape recovery did not diminish after repetitive cyclic tests in both the FC1 and FC2 series and remained above 90% for the entire PEG content range. Shape retention of the FC1 series decreased from 95% for FC1-1 to 56% for FC1-3 and then increased to 79% for FC1-5 and that of the FC2 series decreased from 95% for FC2-1 to 77% for FC2-3 and 73% for FC2-5. Shape retention of both the FC1 and FC2 series fell compared to the lin-

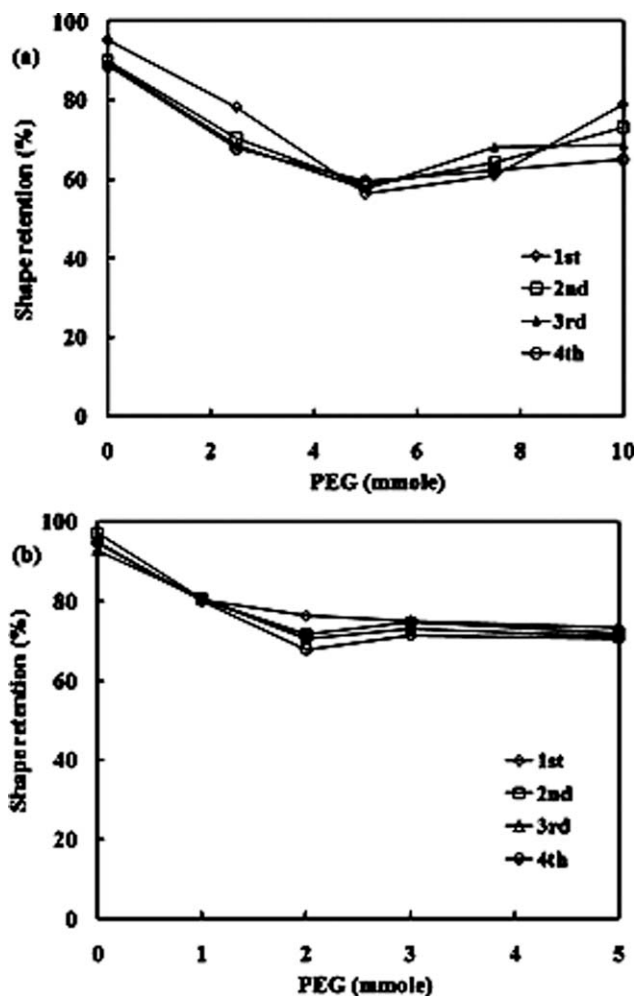


Figure 10 Cyclic shape retention of (a) FC1 and (b) FC2 series.

ear SMPUs as the PEG content increased. The cyclic shape retention test also demonstrated that the first shape retention of both the FC1 and FC2 series remained almost the same after four cyclic tests: for example, the first shape retention of FC1-3 (56%)

TABLE IV
Shape Memory Properties

Sample code	Shape memory (%) ^a	
	Recovery	Retention
FC1-1	93	95
FC1-2	92	78
FC1-3	96	56
FC1-4	91	61
FC1-5	92	78
FC2-1	92	95
FC2-2	91	80
FC2-3	94	77
FC2-4	95	75
FC2-5	91	73

^a First cycle shape memory results.

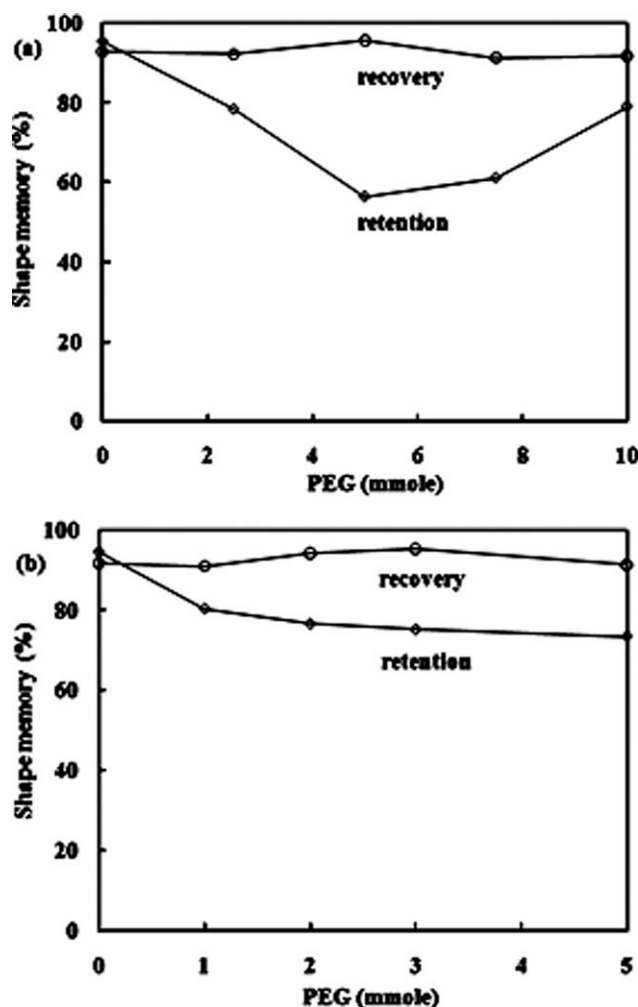


Figure 11 Comparison of shape recovery and shape retention of (a) FC1 and (b) FC2 series.

was changed to 59% after cycle four and that of FC2-3 (77%) became 71% after cycle four. The shape memory test results are summarized in Table IV. Shape recovery and shape retention of the FC1 and FC2 series are compared in Figure 11. A decrease in shape retention of the FC1 series with an increase in PEG content is obvious compared to the FC2 series, although shape recovery was similar for both series. Adoption of a longer PEG as a linker and higher content of soft segment enabled the FC2 series to stay in shape better than the FC1 series at the shape retention test temperature (-20°C). When shape recovery and shape retention of the two series are comprehensively compared, the FC2 series seems to be more competitive than the FC1 series. Considering shape recovery and shape retention plus tensile mechanical test results, flex-linking significantly improved mechanical properties while maintaining high shape memory properties. The lateral flexible linking of SMPU chains with a flexible spacer provided a significant improvement in shape recovery

and mechanical properties compared to the conventional crosslinked and linear SMPU.

CONCLUSIONS

SMPUs that were flexibly linked by PEG were characterized and tested in terms of tensile mechanical and shape memory properties. Two SMPU series, FC1 and FC2, were differentiated by having different soft segment content and linker length. The maximum stress of both series exponentially increased with an increase in PEG content and reached as high as 60 MPa in the best case. The strain at break of both series remained similar to those of linear SMPU although the PEG content was raised. The behavior of both series in stress-strain curves was very similar to natural rubber, but stress and strain were improved more than 400% over those of natural rubber. The shape recovery of both series was over 90%, and shape retention of the FC1 series decreased more than that of the FC2 series as PEG content increased. The shape recovery and shape retention remained almost the same after four cyclic tests. The outstanding mechanical and shape memory properties of flex-linked SMPU originated from the lateral linking SMPU chains with flexible PEG.

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