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Effect of glycerol cross-linking and hard segment content on the shape memory property of polyurethane block copolymer

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Abstract Effect of glycerol cross-linking and hard segment content on the shape memory property of polyurethane block copolymer is comprehensively investigated. Phase separation of hard and soft segment is dependent on glycerol cross-linking and hard segment content as judged from FT-IR and DSC data. Hydrogen bonding and dipole–dipole interaction between hard segments provides strong interaction between copolymer chains in addition to chemical cross-linking by glycerol. As the hard segment content increases, the copolymer shows better tensile mechanical properties and higher melting temperature of soft segment (T_m). Effect of glycerol cross-linking on mechanical properties and T_m of soft segment is low compared to hard segment effect. Although XRD peak at $2\theta = 19.5°$ is observed, clear difference between the copolymers with various hard segment and cross-linking content is not observed. Significant increase in shape recovery rate in the case of 30 wt% hard segment copolymer is observed after glycerol cross-linking. The drastic change of the properties of polyurethane block copolymer is discussed in the point of copolymer chain interaction.

Introduction

Shape memory polymer (SMP), one of smart materials, has been widely researched in such areas as thermo-chromic polymer, smart textile fiber, thermo-sensitive polymer, vibration-control composite material, and medical stent [1–4]. Polyurethane is favored due to the excellent shape recovering property compared to other SMP candidates. In addition, polyurethane has many unparalleled characteristics such as easy processing under ordinary processing conditions, high solvent resistance, and constant modulus after 300 h of sunlight exposure. Generally, SMP is composed of hard and soft segment where soft segment plays a role as an absorber of external stress and hard segment contributes in recovering original shape, and able to achieve high shape recovery after repetitive distortion and recovery cycles [5]. However, problems such as low shape recovery rate and stiffening of SMP after cyclic shape memory tests remain to be solved. The rigid hard segment has T_m much higher than room temperature, whereas T_m of the flexible soft segment is usually below 0 °C. Due to the thermodynamic incompatibility of these two segments, phase-separated domains are formed. Shape memory effect works by the mechanism that soft segment in rubbery state is extended under external stress, and hard segment in glassy state remains unchanged; the stretched and unstable soft segment tends to return to original length and hard segment guides the shape recovery process. Therefore, it is very important to control the ratio of hard and soft segment in designing SMP. Because phase separation plays an important role in the elasticity and shape memory property of polyurethane, influence of hard segment and glycerol cross-linking on phase separation and shape recovery is discussed in this paper.

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Experimental

Materials and methods

4,4′-diphenylmethane diisocyanate (MDI) and poly(tetramethylene glycol) (PTMG, Mw = 2,000 g/mol) were dried overnight under high vacuum (0.1 Torr) before use. 1,4-butanediol (BD) were stored over 4 Å molecular sieve. *N*,*N*-Dimethylacetamide (DMAC) was distilled over CaH_2 before use.

Synthesis of polyurethane

In a 500 ml four neck flat-bottomed flask equipped with condenser and mechanical stirrer, a mixture of MDI and PTMG was stirred at 50 °C for 3 h to prepare a prepolymer, followed by the addition of 1,4-butanediol dissolved in 10 ml of DMAC as a chain extender. The combined mixture was further stirred at 80 °C for an hour, and the stirring after addition of glycerol was continued for another hour to get final polyurethane product that was dried overnight to remove remaining DMAC. Specific mole ratios of reaction mixture were shown in Table 1.

Specimen preparation

Specimen for the mechanical and shape memory test was prepared by the following method. After complete drying at 120 °C for 24 h, the copolymer was put into a minimax molder (Bau Tech. Model Ba-915) at 160–230 °C depending on the copolymer composition, and the specimen was made according to the specification of ASTM D638.

Table 1 Composition of cross-linked polyurethane block copolymer

Composition (mol%)				Hard segment (wt%)	Cross-linking (mol%)
MDI	PTMG	BD	Glycerol		
5.1	4.0	1.0	0.1	15	2
5.2	4.0	1.0	0.2	15	4
5.3	4.0	1.0	0.3	15	6
5.1	3.0	2.0	0.1	20	2
5.2	3.0	2.0	0.2	20	4
5.3	3.0	2.0	0.3	20	6
5.1	2.0	3.0	0.1	30	2
5.2	2.0	3.0	0.2	30	4
5.3	2.0	3.0	0.3	30	6

Mechanical and shape memory analysis

Tensile mechanical strength was measured according to ASTM D638 by a universal testing machine (UTM) equipped with a temperature-controlled chamber (Lloyd Instrument, Model LR50K) under the conditions: gauge length = 25 mm; crosshead speed = 10 mm/min; load cell = 2.5 kN. The UTM was also used to measure stress and strain at various temperatures for the investigation of shape memory effect: for shape retention, L_1 was measured by drawing the specimen 100% at 20 °C above T_g for 5 min, and letting it to shrink at 20 °C below T_g for 30 min; for 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. The measurements were repeated three times, and shape retention and shape recovery rate could be calculated with L_1 and L_2 from the following equations (Fig. 1) [6].

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

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

General analysis

Glass transition temperature (T_g) and melting temperature (T_m) were detected by a differential scanning calorimeter (DSC, Perkin Elmer Diamond 6) from the second heating scan where the sample was heated up to 200 °C at a fixed rate of 10 °C/min, left at the temperature for 1 min, and quickly cooled to –30 °C. FT-IR spectra were taken by Bomen MB series 104. X-ray diffraction pattern was recorded by wide-angle X-ray diffractometer (Rigaku) under the conditions of 2θ = 10–30°, (CuKα, 40 kV, and 30 mA).

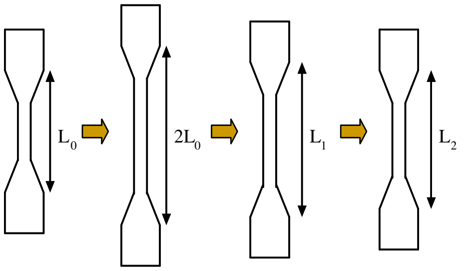

Fig. 1 Method for testing shape retention and shape recovery rate

where

L_0= initial specimen length

$2L_0$= length of L_0 strained 100% at above T_g, below T_m

L_1= deformed length at below T_g after load removal

L_2= final specimen length at above T_g, below T_n

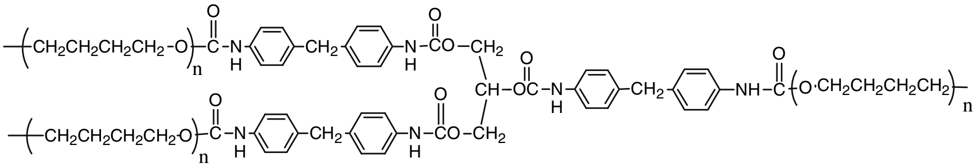

Fig. 2 Structure of cross-linked polyurethane block copolymer

Results and discussion

Synthesis

Synthesis of polyurethane is based on our previous report [6, 7], where MDI and PTMG work as hard and soft segment, respectively, and BD is used as a chain extender. Glycerol with its three hydroxyl groups is selected as a chemical cross-linker, because the hydroxyl group can cross-link hard segment rather than soft segment and hard segment cross-linking is more effective than soft segment cross-linking [8]. Solvent usage is minimized for the entire polyurethane synthesis, because the added solvent results in poor physical properties and lower polymer yield. Hard segment content is adjusted by controlling both PTMG and BD content (Table 1). Glycerol cross-linked structure of the copolymer is shown in Fig. 2.

FT-IR analysis

Polyurethane copolymer is composed of hard and soft segment where hard segment forms a separate microscopic domain from soft segment. Inter-molecular attraction such as hydrogen bonding and dipole–dipole interaction between hard segments segregate themselves from soft segments, thus resulting in phase separation (Fig. 3). FT-IR spectrum is used to analyze phase separation by comparing the peak shift in the range of 1,700–1,750 cm^{-1}. As the hard segment content increases, shift to lower wavenumber is observed (Fig. 4a compared to 4b and c), but the increase of cross-linking content does not change the spectrum.

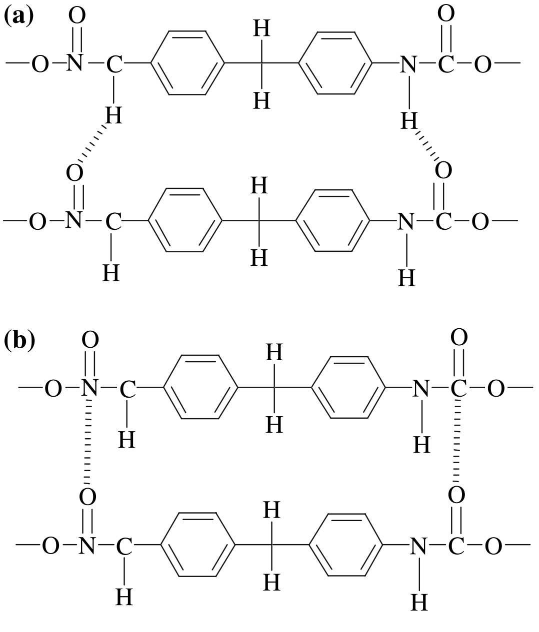

Fig. 3 Interaction between hard segments: (**a**) hydrogen bonding, and (**b**) dipole–dipole interaction

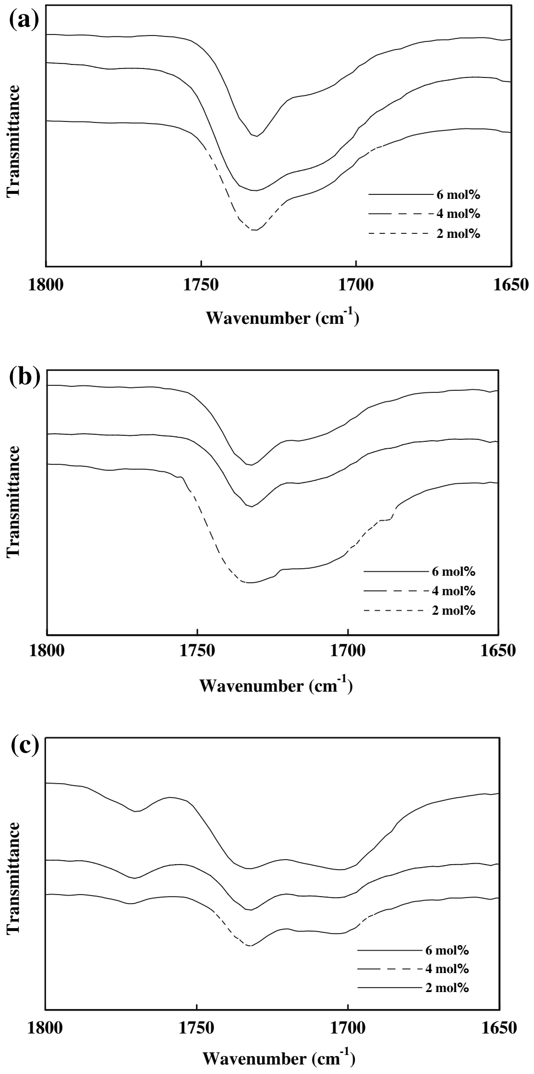

Fig. 4 Comparison of infrared spectra of cross-linked polyurethane block copolymers: (**a**) 15 wt%, (**b**) 20 wt%, and (**c**) 30 wt% hard segment. The mol% in the legend designates cross-linking content in this and following figures

Stretching vibration mode of the carbonyl group is observed at lower energy level, because electron density and the related bond order (measuring bond strength) of carbonyl group are lowered as inter-chain interaction between hard segments increases [6, 7]. Therefore, peak shift to 1,710 cm^{-1} region occurs as hard segment content increases. The strong interaction between hard segments at high hard segment content, together with chemical cross-linking by glycerol, results in phase separation.

Thermal analysis

Glycerol cross-linking substantially increases T_m of the soft segment of copolymer compared to uncross-linked one. In the case of 20 wt% hard segment copolymer, T_m jumps from –15 to 13 °C by adopting 2 wt% glycerol cross-linking. T_m also increases from –3 to 16 °C by adopting 2 wt% glycerol cross-linking for 30 wt% hard segment copolymer. But T_m increase after cross-linking is reduced even though cross-linking content increases (Fig. 5a). Chemical cross-linking by glycerol restricts the melting of soft segment, and thus increases the T_m of copolymer. Once the copolymer is cross-linked, the additional cross-linking does not have as much impact on T_m as the initial cross-linking. As the hard segment content is raised, T_m of the soft segment of cross-linked copolymer increases proportionally to hard segment content. For example, in the case of 6 wt% cross-linked copolymer, T_m increases from 10 to 19 °C as the hard segment increases from 15 to 30 wt%. As for 2 wt% cross-linked copolymer, T_m increases from 7 to 16 °C as the hard segment increases from 15 to 30 wt%. As the hard segment content increases, more hydrogen bonding forms between copolymer chains and T_m increases due to the restricted chain movement. In DSC thermograms, difference in T_m, as the cross-linking and hard segment content increases, can be compared (Fig. 5b–d). The fact that T_m can be raised by the control of cross-linking and hard segment content is very important in the point that copolymer should have T_m around room temperature to be useful as a SMP.

WAXD analysis

Numerous research results on crystalline structure of polyurethane have been reported so far [10–12]. Major diffraction peak is observed at $2\theta = 19.5°$, and glycerol cross-linking and hard segment content does not change the apparent shape of WAXD peaks (Fig. 6). Unlike crystalline structure observed in inorganic material, copolymer chain, especially elastic polyurethane, may show partially crystalline structure originating from hard domains scattered around copolymer chains, but it is very difficult to show clear difference of diffraction peaks because polymeric chains are dynamic and the degree of interactions in hard segment is dependent on the surrounding structure. However, appearance of diffraction peak at $2\theta = 19.5°$ partially supports the presence of hard domain in copolymer chains.

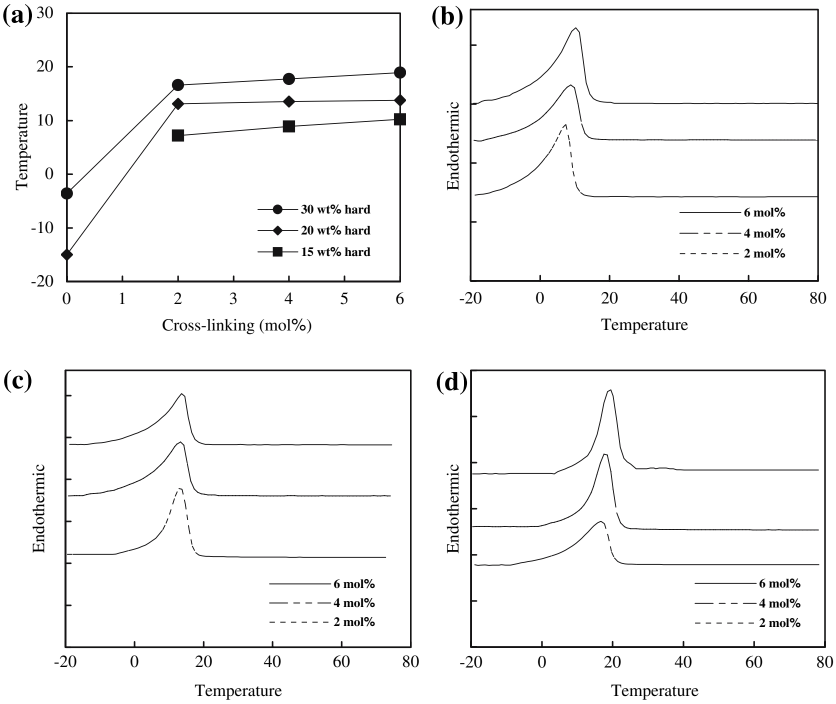

Fig. 5 (**a**) Melting temperature of soft segment (T_m) versus cross-linking content profile of polyurethane block copolymers with various hard-segment contents, and DSC thermogram of the copolymer with (**b**) 15 wt%, (**c**) 20 wt%, and (**d**) 30 wt% hard segment

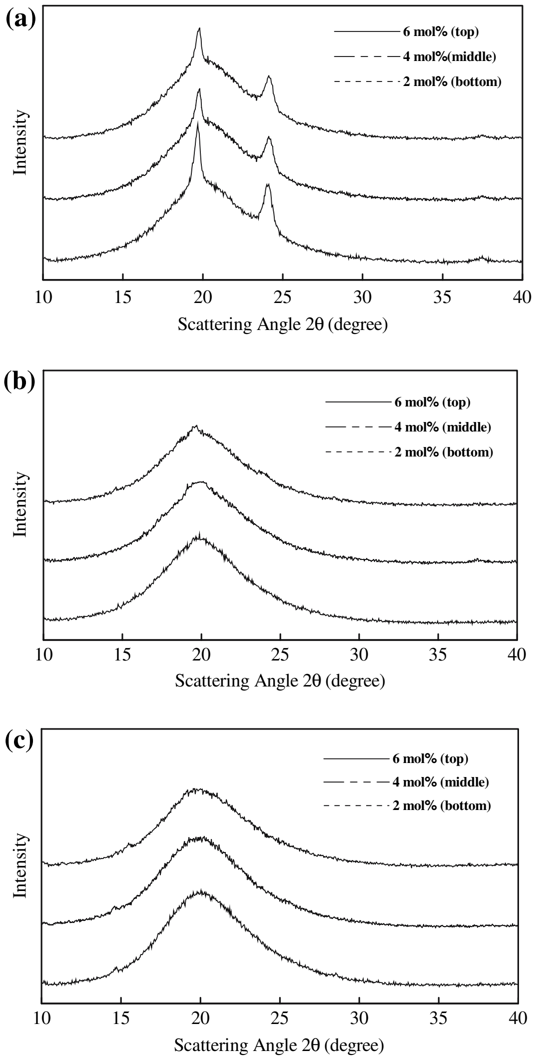

Fig. 6 X-ray diffraction profiles of cross-linked polyurethane block copolymer with various cross-linking contents: (**a**) 15 wt%, (**b**) 20 wt%, and (**c**) 30 wt% hard segment

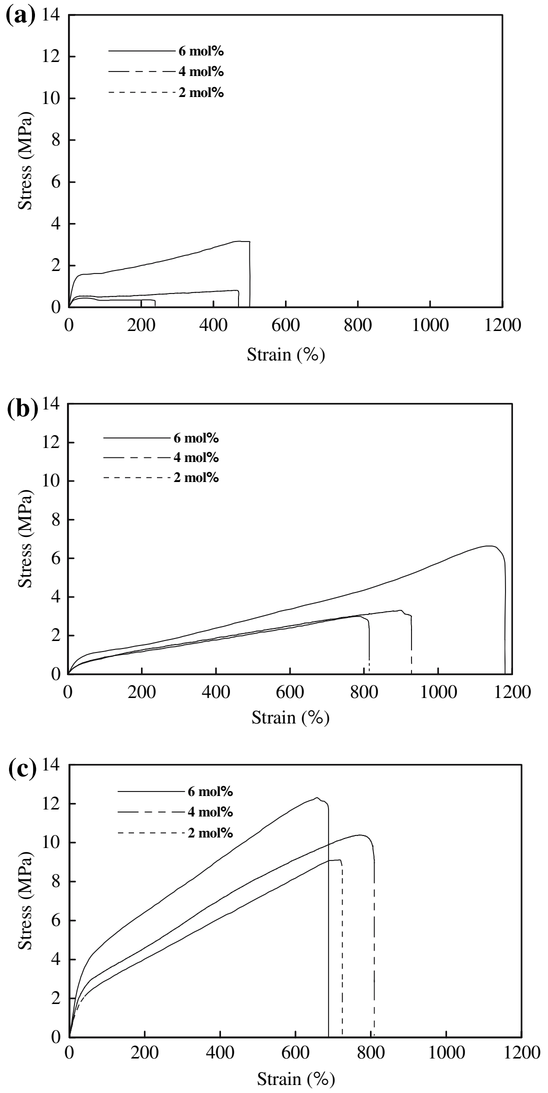

Fig. 7 Stress–strain curve of polyurethane block copolymer with various cross-linking content: (**a**) 15 wt%, (**b**) 20 wt%, and (**c**) 30 wt% hard segment

Mechanical property

Tensile mechanical properties of polyurethane are influenced by hard segment and cross-linking content as in stress–strain curves (Fig. 7). Tensile stress, strain, and modulus slightly increases with the cross-linking content, but significant increase in the tensile mechanical properties is observed at high hard segment content. For example, strain at break increases from 500 to 1,181% by changing

Table 2 Mechanical properties of cross-linked polyurethane block copolymer

Hard seg. (wt%)	Cross-linking (mol%)							
	0		2		4		6	
	Max. stress (MPa)	Strain at break (%)	Max. stress (MPa)	Strain at break (%)	Max. stress (MPa)	Strain at break (%)	Max. stress (MPa)	Strain at break (%)
15	–	–	0.4	238	0.8	470	3.2	500
20	0.3	56	3.0	814	3.3	928	6.6	1181
30	5.2	300	9.1	725	10.4	809	12.3	687

Table 3 Cyclic shape memory test result of cross-linked polyurethane block copolymer

Hard seg. (wt%)	Test cycle	Cross-linking (mol%)							
		0		2		4		6	
		Shape rec.[a]	Shape ret.[a]	Shape rec.	Shape ret.	Shape rec.	Shape ret.	Shape rec.	Shape ret.
20	1	–[b]	–	91	93	92	92	95	90
	2	–	–	85	94	87	93	88	91
	3	–	–	82	95	85	94	85	92
30	1	80	86	90	93	94	94	88	90
	2	76	87	84	93	87	93	86	93
	3	76	90	81	93	86	94	84	93

[a] Shape recovery and shape retention in %

[b] Shape memory test result was unable to acquire

the hard segment content from 15 to 20 wt% at 6 wt% of cross-linking, and maximum stress increases from 3.2 to 12.3 MPa by changing the hard segment content from 15 to 30 wt% at 6 wt% of cross-linking (Table 2). Tensile mechanical properties of uncross-linked 15 wt% copolymer are not included due to the very poor result. Maximum stress increases with hard segment content irrespective of cross-linking content. So the highest maximum stress is observed at 30 wt% hard segment. But the strain at break decreases after the maximum at 20 wt% hard segment. As the hard segment content increases, the copolymer becomes hard to stretch, although its maximum stress increases. Therefore, tensile mechanical properties are more influenced by the hard segment content than chemical cross-linking by glycerol. The mechanical test results are similar to T_m data in the point that hard segment content is more influential than cross-linking. More hydrogen bonding at high hard segment content is responsible for the improved mechanical properties, and the combined control of hard segment and cross-linking content will be helpful in achieving the desired properties.

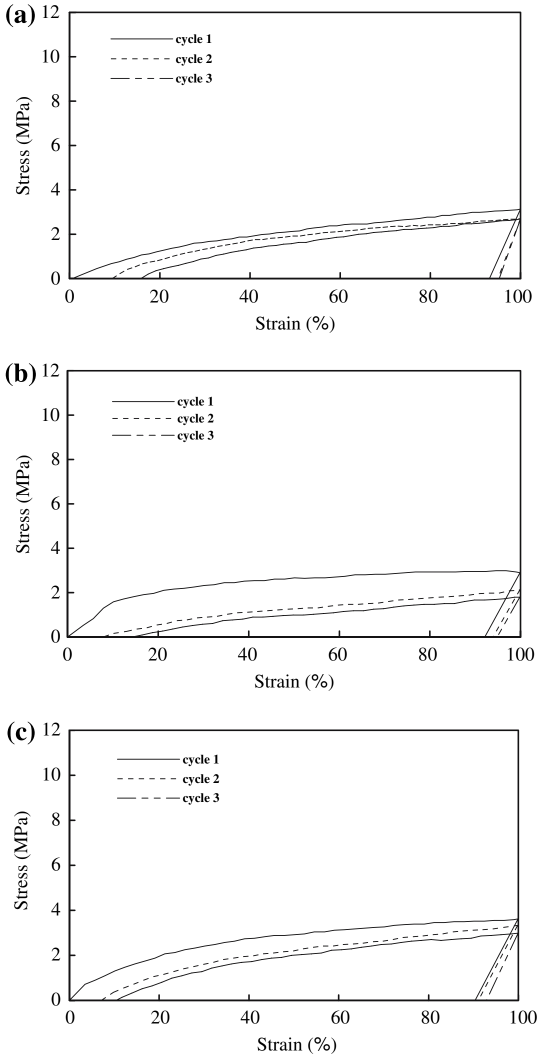

Fig. 8 Cyclic shape memory test of polyurethane block copolymer with 20 wt% hard segment content: (**a**) 2 mol%, (**b**) 4 mol%, and (**c**) 6 mol% cross-linking

Shape memory property

Hard segment domain has glassy state at ambient temperature due to the high T_m of hard segment, whereas soft segment domain is rubbery and shows dynamic movement of molecular chains due to the low T_m of soft segment. Thermodynamic incompatibility of each segment induces phase-separated structures, and the shape recovery process starts at a switching temperature. Hard segment domain plays an important role in retaining the distorted shape below the switching temperature and recovering its shape after distortion at the temperature above the switching temperature, and soft segment domain which decides the switching temperature absorbs the applied tensile stress by unfolding the entangled chains. Original shape can be recovered at above the switching temperature, because the interaction between hard segments such as hydrogen bonding guides the recovery process. Therefore, the shape memory mechanism relies on the stress-absorbing ability of soft segment and shape retention and recovery of hard segment. The difference between ordinary elastic polymer and shape memory polymer comes from whether the switching temperature range is narrow and constant. However, permanent deformation in hard segment domain, by repetitive stress-release cycles, may limit the shape memory effect [13, 14].

Cyclic shape memory test results for 20 and 30 wt% hard segment copolymers are shown in Table 3, and Figs. 8 and 9. The shape memory test result for 15 wt% hard segment copolymer is not included, because the copolymer specimen breaks down during the cyclic test irrespective of cross-linking content. Both copolymers show shape recovery rate higher than 80%, and 30 wt% hard segment copolymer has 3–4 times higher maximum stress than 20 wt% one as expected from the mechanical test results. As for 20 wt% copolymer, one without cross-linking breaks down during cyclic shape memory test. Shape recovery rate increases with the cross-linking content and reaches 95% for 6 mol% cross-linking. But shape recovery rate decreases to below 90% after the third cycle for the entire cross-linking contents. The shape retention rate of 20 wt% hard segment copolymer stays above 90% for the entire cross-linking content (Fig. 8). Similar cross-linking effect on shape recovery rate is found for 30 wt% copolymer: shape recovery rate, after cross-linking, increases from 80% (uncross-linked one) to 94% (4 mol% cross-linked one) and the shape retention rate maintains higher than 90% for the entire cross-linking content. Interestingly, shape recovery rate decreases at 6 mol% cross-linking. Chemical cross-linking by glycerol draws polymeric chains in close proximity so that inter-molecular interaction through hydrogen bonding and dipole–dipole interaction supports the hard domain formation and improves the shape recovery rate. Increase of hard segment content improves maximum stress, but does not change the shape recovery rate. Shape recovery rate generally deteriorates with the repeated cyclic tests resulting from the deformation of hard segment domain, and chemical cross-linking by glycerol helps in reducing the deformation of hard segment domain.

Conclusion

Various polyurethane block copolymers composed of MDI, PTMG, BD, and glycerol as cross-linking agent are prepared. Phase separation of hard and soft segment is dependent on hard segment and cross-linking content. Both glass transition temperature and mechanical properties are more dependent on hard segment content than cross-linking. Shape recovery rate improves with cross-linking, but cross-linking content does not proportionally change the shape recovery rate. Introduction of glycerol as a chemical cross-linker and control of hard segment in polyurethane copolymer are effective in the control of physical properties and shape recovery rate.

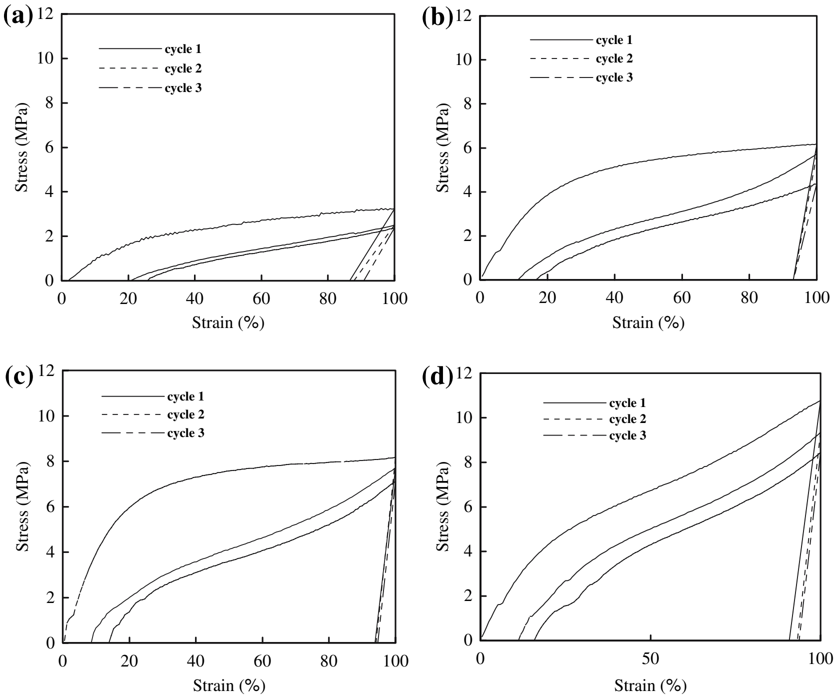

Fig. 9 Cyclic shape memory test of polyurethane block copolymer with 30 wt% hard segment content: (**a**) 0 mol%, (**b**) 2 mol%, (**c**) 4 mol%, and (**d**) 6 mol% cross-linking

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