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Comparison of thermal/mechanical properties and shape memory effect of polyurethane block-copolymers with planar or bent shape of hard segment

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Abstract

A series of shape memory polyurethane copolymers synthesized from 1,4-phenyldiisocyanate (PDI) and poly(tetramethyleneglycol) (PTMG) plus 1,4-butanediol as chain extender were compared with similar ones from 4,4′-methylene-bis-phenyldiisocyanate (MDI) and PTMG in various shape memory tests at temperature ranges of ±20 °C around glass transition temperature (T_g). Similarity and some differences between two series were found in other characterization methods such as IR spectra, phase transition, and mechanical properties. Especially, T_g increased with the content of hard segment (PDI or MDI) and both copolymers generally showed similar T_g at the same content of hard segment. In addition, vibration and shock absorption ability was investigated by measuring both loss tan δ and storage modulus with dynamic mechanical analyzer.

Keywords: Polyurethane; Hard segment; Shape memory

1. Introduction

Shape memory polymer, having a lot of advantages over shape memory alloy or inorganic material like low density (1.0–1.3 g/cm^3), high shape recovery (maximum shape recovery ratio more than 400%), low manufacturing cost, and easy processing, has drawn wide attention these days [1–5]. Since its introduction as a polynorborane type by Nippon Zeon company in 1984, various forms of shape memory polymers including poly(isoprene–butadiene–styrene), polyurethane, and polystyrene series were followed [6–13]. Specifically, shape memory polyurethane, developed by Nagoya Research and Development Center of Mitsubishi Company in 1988 [3,7], was composed of hard and soft segment and could recover the original shape in the temperature range of −30 to 65 °C. Hard segment (diphenylmethanediisocyanate) and soft segment (polyol) were alternatively polymerized, and various interactions among hard segments leaded to domain formation; hard segment worked as pivoting point for shape recovery and soft segment could mainly absorb external stress applied to the polymer. As polyurethane is already well known to have distinct properties such as (1) easy preparation method, (2) high resistance to organic solvent and aqueous solution, (3) long-term stability against exposure to sunlight, (4) consistent elastic property, and (5) possible biocompatibility, control of hard segment structure and chain length of soft segment is very important in obtaining better characteristics of shape memory polyurethane. In our investigation, the hard segment, core component of shape memory polymer, was replaced with 1,6-diphenyldiisocyanate (PDI) for 4,4′-diphenylmethyldiisocyante (MDI), because PDI's planar shape could be advantageous to MDI's bent form in getting tighter interactions among hard segments (see Fig. 1), thus leading to the development of high-performance shape recovery polyurethane. Our eventual goal of this study is to develop smart shape memory polyurethane that can sense the change of surrounding temperature and reversibly change the physical properties: possible applications of the smart polyurethane include moisture-controlling fabric and mechanical parts under severe vibrational and thermal stress. Comparison in thermal/mechanical properties of the polyurethane made from either PDI or

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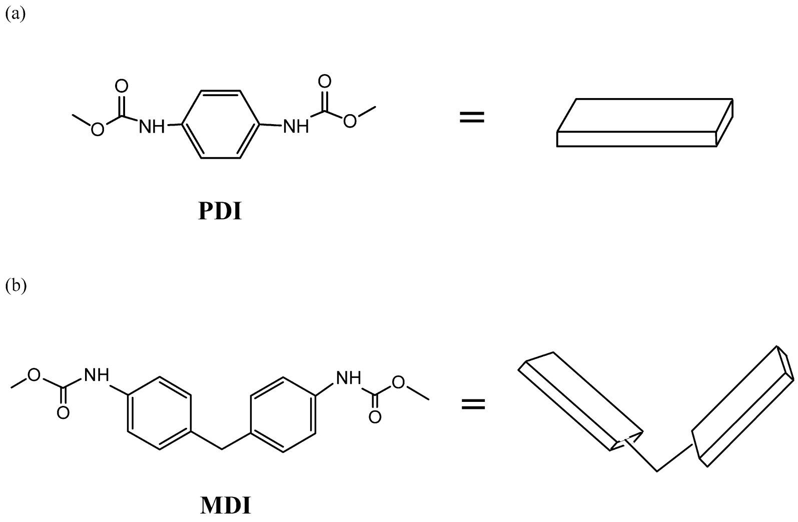

Fig. 1. (a) Linear shape of PDI, and (b) bent shape of MDI.

MDI was made [11], together with discussion about the origin of their differences.

2. Experimental

2.1. Materials and methods

PDI (Aldrich Chemical), MDI (Junsei Chemical), and PTMG ($M_w = 2000$ g/mol, gift from Cheil Chemical) were dried under high vacuum (0.1 Torr) overnight before use, and 1,4-butanediol (BD, Duksan Chemical) was dried by distillation and stored over 4 Å molecular sieve. FT-IR spectrometer (Jasco 300 E) equipped with ATR was used to take IR spectrum of the polyurethane sample at a resolution of 4 cm^{-1} (50 scans). Wide angle X-ray diffractometer (Rigaku Rint 2000) was operated at the conditions of $2\theta = 10-30°$, 5 °/min, Cu Kα, 40 kV, and 30 mA.

2.2. Polymerization

In a four-necked reaction vessel equipped with stirrer, nitrogen purge, and oil bath was placed MDI and PTMG at the specified equivalent ratio in Table 1, allowed to react for 3 h at 65 °C, and then the prepolymer was dissolved in dimethylacetamide (DMAC), followed by addition of BD as a chain extender depending on the mole ratio of NCO/OH. Polymerization further went on until the remaining isocyanate group disappeared as detected by separate amine titration method (usually three more additional hours). After polymerization was over, the sticky polyurethane was further dried in an oven for a day.

2.3. Preparation of test specimen

Synthesized polyurethane after additional drying at 100 °C for 24 h was used for preparing mechanical test specimens by a mini-max molder (Bautech model BA-915); molding temperature was adjusted between 160 and 230 °C depending on the composition of hard and soft segment according to ASTM D-638. Molecular weight of the polyurethane was determined by GPC (Younglin M930) with THF as eluting solvent.

Table 1
Composition of polyurethane block copolymers

Composition (relative mole ratio)			Hard segment content (wt%)	Molecular weight (M_w)	T_g (°C)[a]
MDI (PDI)	PTMG	1,4-BD			
5.0 (4.5)	1.0	4.0 (3.5)	45 (35)	74,000 (78,000)	0.3 (−1.3)
4.0 (3.5)	1.0	3.0 (2.5)	40 (30)	113,000 (105,000)	−2.4 (−2.6)
3.5 (3.0)	1.0	2.5 (2.0)	35 (25)	81,000 (103,000)	−2.5 (−7.8)
3.0 (2.5)	1.0	2.0 (1.5)	30 (20)	105,000 (153,000)	−3.6 (−12.3)
2.0 (1.5)	1.0	1.0 (0.5)	25 (15)	102,000 (184,000)	−8.5 (−16.8)
1.5 (1.0)	1.0	0.5 (0)	20 (10)	130,000 (164,000)	−15.0 (NA)[b]

M_w of PTMG was 2000 g/mol, and M_w of PDI and MDI were 160.13 and 250.26 g/mol, respectively. Values in parenthesis belong to PDI-based polyurethane.

[a] T_g data are obtained from DMA results in Fig. 12.

[b] NA means that the data are not available.

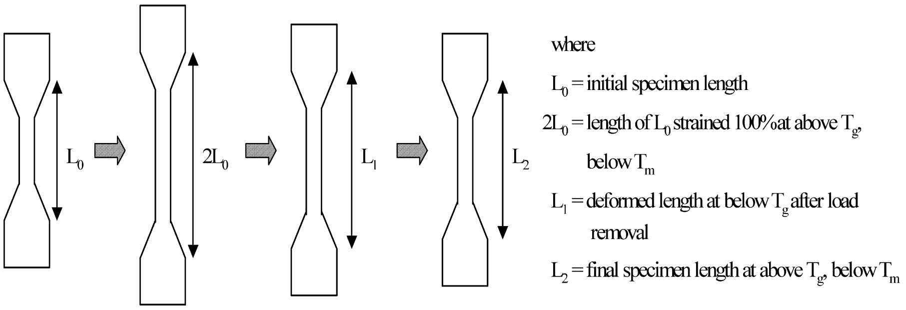

Fig. 2. Method for testing shape retention and shape recovery rate.

2.4. Thermal analysis

Glass transition temperature (T_g) and melting temperature (T_m) were detected by DSC (Du Pont DSC-2000). After melting at 250 °C for 5 min and quick cooling to −50 °C, the specimen (20 mg) was warmed to 250 °C at 10 °C/min, while monitoring phase transition.

2.5. Mechanical analysis

Tensile strength was measured according to ASTM D638 by UTM (Lloyd Instrument, Model LR50K) with a dumbbell type specimen under the conditions: gauge length = 25 mm; crosshead speed = 10 mm/min; load cell = 2.5 kN. Shear test was also measured by UTM for the specimen

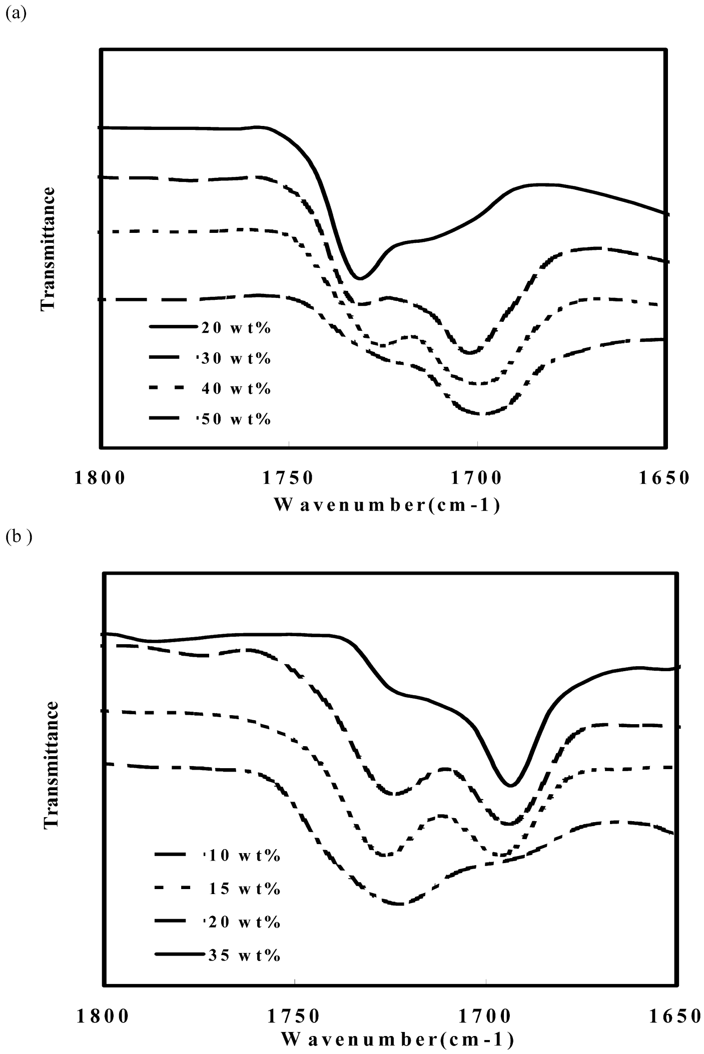

Fig. 3. Infrared spectrum of (a) MDI-based, or (b) PDI-based polyurethane block copolymer with various hard segment contents.

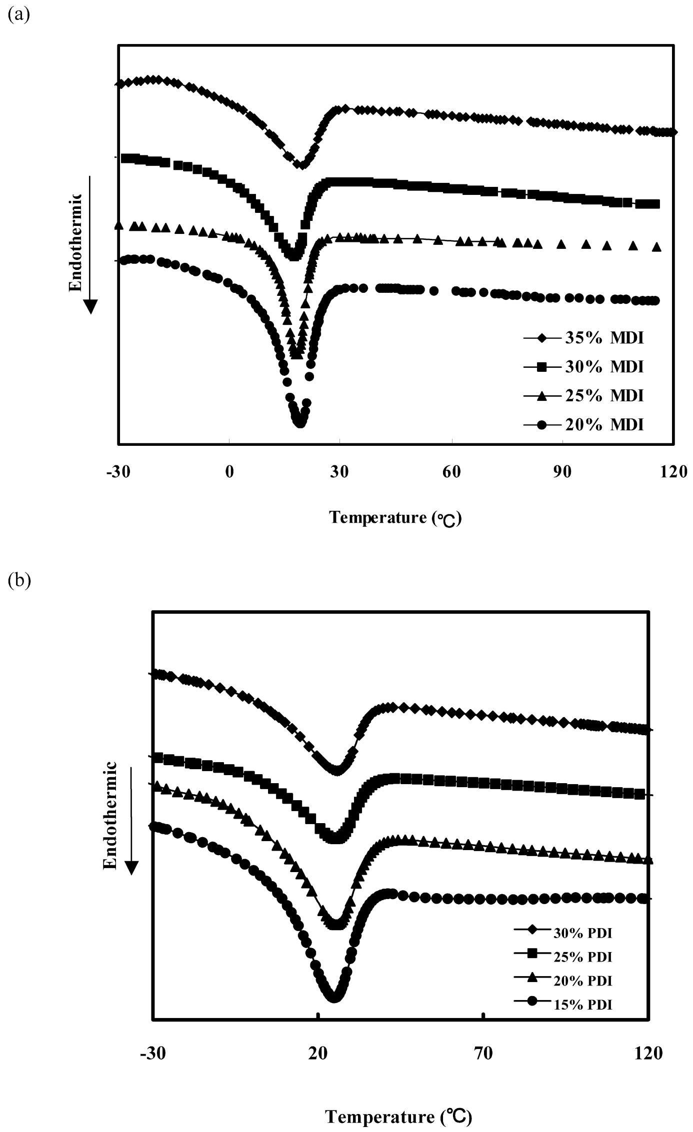

Fig. 4. DSC heating scans of (a) MDI-based, or (b) PDI-based polyurethane block copolymers with various hard segment contents.

shaped like the one in Fig. 2, and the conditions were 1 mm/min of crosshead speed and 2.5 kN of load cell. Impact strength was measured by Impact Tester (Testing Machine Inc., Model TMI 43-02, pendulum 75 kg/cm) by unnotched Charpy method.

2.6. Thermomechanical analysis

The above-mentioned UTM equipped with a temperature-controlled chamber was used to measure stress and strain at various temperatures for the investigation of shape memory: 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 rate and shape recovery rate could be calculated with L_1 and L_2 from the following equations

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

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

2.7. Dynamic mechanical analysis

Vibration control and damping effect were investigated by dynamic mechanical analyzer (DMA) (Rheometric Scientific, Mark IV, UK), and loss tan δ for the specimen sized $5 \times 8 \times 1$ mm^3 ($l \times w \times d$) was tested at a heating rate of 3 °C/min between −60 and 65 °C.

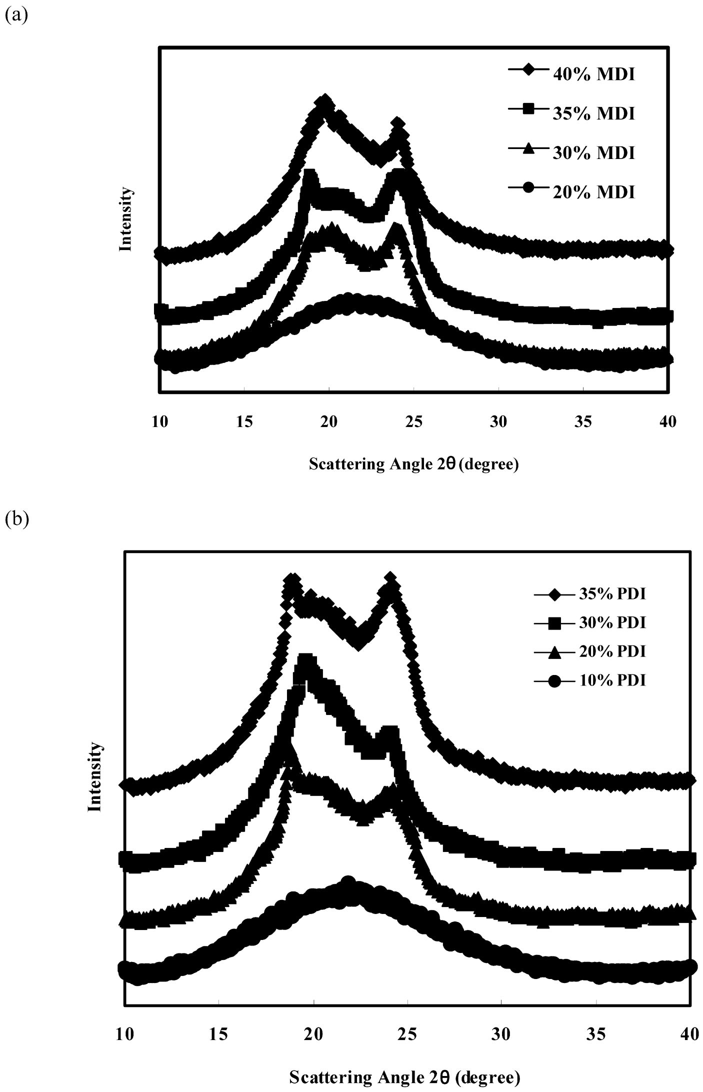

Fig. 5. X-ray diffraction patterns of (a) MDI-based, or (b) PDI-based polyurethane block copolymer with various hard segment contents.

3. Results and discussion

3.1. FT-IR spectrum

Infrared spectra of polyurethane copolymer with various hard segments were compared in Fig. 3. The absorption peak around 1730 cm^{-1}, corresponding to stretching vibration of carbonyl group, shifted to 1700 cm^{-1} as hard segment content increased, which could originate from the fact that interactions among hard segments (MDI or PDI part), through hydrogen bonding and dipole–dipole interaction of carbamoyl group plus induced dipole–dipole interaction of phenyl ring, were weakened because long and flexible PTMG was replaced with relatively short and rigid butanediol at high hard segment content. Specifically, more stable and undistorted interactions could be formed, if the intervened segment (PTMG or BD) was long and flexible enough to allow perfect topographical position of hard segment for interaction. The shift of vibrational absorption region from 1730 to 1700 cm^{-1} testified that vibrational energy band gap was narrowed with increase in hard segment and thus inter-chain interaction was weakened as expected. Overall physical properties of the polyurethane copolymer are heavily dependent on the composition of hard and soft segment and the exact composition should be decided depending on the usage of copolymers.

3.2. Thermal analysis (DSC)

Phase transition behavior of two polyurethane series were investigated with DSC (Fig. 4): transition peak temperature slightly increased with hard segment content, but increase in transition area, endothermic energy for phase transition, and sharpening of peak shapes were observed for both polyurethane series as hard segment content decreased. As explained in IR data, hard segment interaction among polymeric chains were strengthened at low hard segment content because of more well-oriented position of hard segment and the resulting better interaction among chains; accordingly, more heat energy was consumed for phase transition of the ones with lower hard segment content. The almost constant position of peak transition temperatures for entire hard segment contents signified that phase transition mainly originated from the interactions of hard segments of polymeric chain: energy required for phase transition was to be used for rotation of each components in polymeric chains, and hard segment content do not affect peak transition temperature but the total energy necessary for transition of whole polymeric chains would be higher with lower hard segment contents due to the reasons mentioned above.

3.3. X-ray analysis

Crystalline structures of the two series of polyurethane were compared in Fig. 5. For both polyurethane series, typical reflection peak at $2\theta = 19.5°$ was observed, and the peak resolution and intensity increased with hard segment content. But PDI-based polyurethanes showed comparatively sharper peaks and larger peak areas than corresponding MDI-based ones (Fig. 6). At high hard segment content, well-aligned structure originating from interactions among hard segments contributed to the high reflection peak, but inclusion of relatively flexible structure by intervention of PTMG at low hard segment content rendered the overall polymeric structure dynamic and fluid, thus resulting in low reflection peak. Linear shape of PDI seems to have some advantage over bent-shaped MDI in getting more crystalline structure when stacked in polymeric chains.

3.4. Mechanical analysis

Figs. 7–9 show tensile results of polyurethane block copolymers at various hard segment contents: maximum stress and modulus increase with hard segment content (Figs. 7 and 8), but elongation at break decreased at higher hard segment inclusion (Fig. 9). As weight percentage of hard segment went up, stronger interactions among polymeric chains led to crystallinity of the hard segment, high tensile strength, and high modulus, but elongation at break decreased due to the interactions. As expected, linear PDI-based polyurethanes showed superior mechanical properties to MDI-based ones due to reasons delineated above.

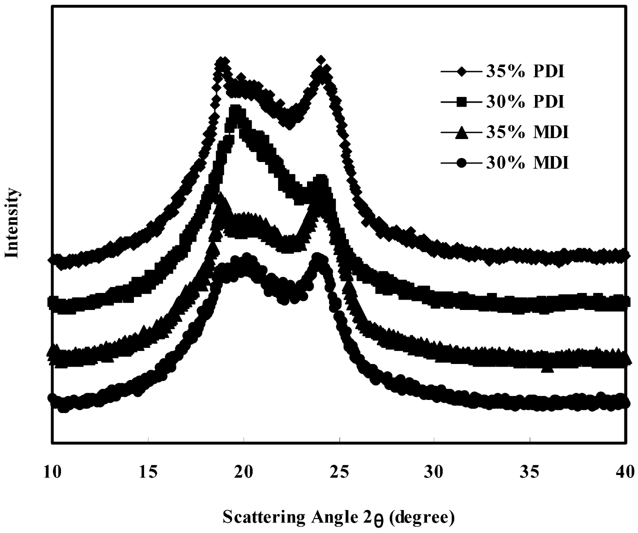

Fig. 6. Comparison of X-ray diffraction patterns of MDI-based and PDI-based polyurethane block copolymers.

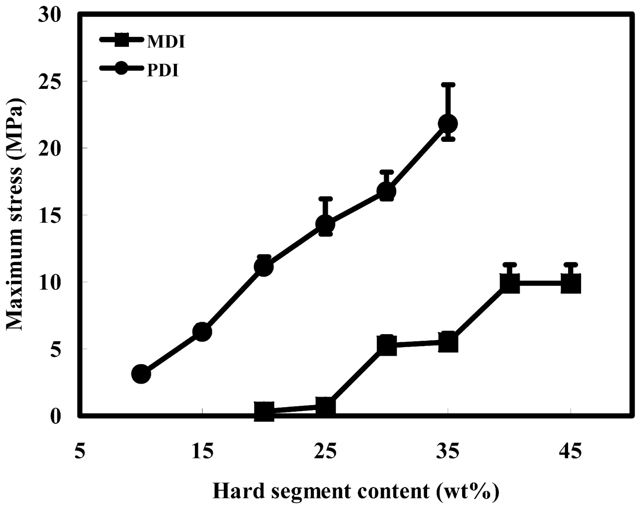

Fig. 7. Maximum stress of polyurethane block copolymer with various hard segment contents.

3.5. Thermomechanical analysis

Shape recovery and retention from three independent experiments were shown in Figs. 10 and 11. In order for the shape memory polymer to work, glassy hard segments should maintain its shape through inter or intra-polymeric chain attractions such as hydrogen bonding or dipole–dipole interaction, together with the physical crosslinking, but soft

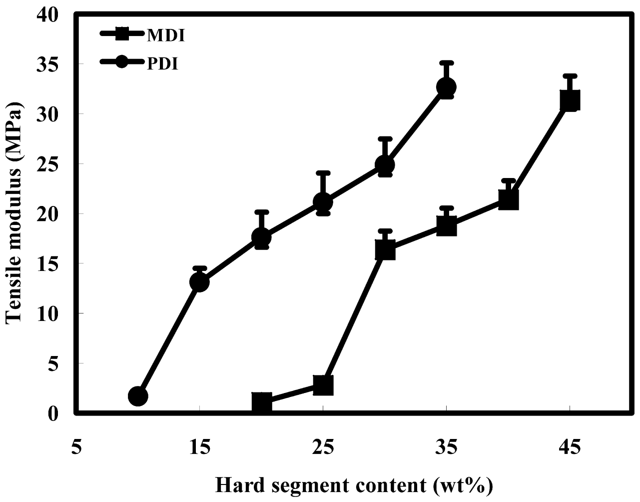

Fig. 8. Modulus of elasticity of polyurethane block copolymer with various hard segment contents.

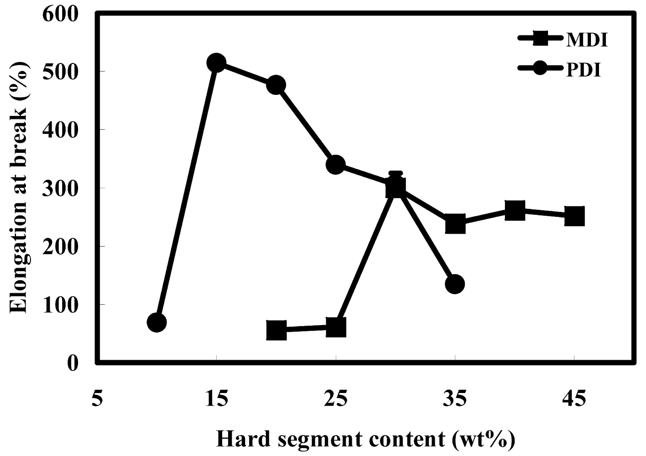

Fig. 9. Percent strain at break of polyurethane block copolymer with various hard segment contents.

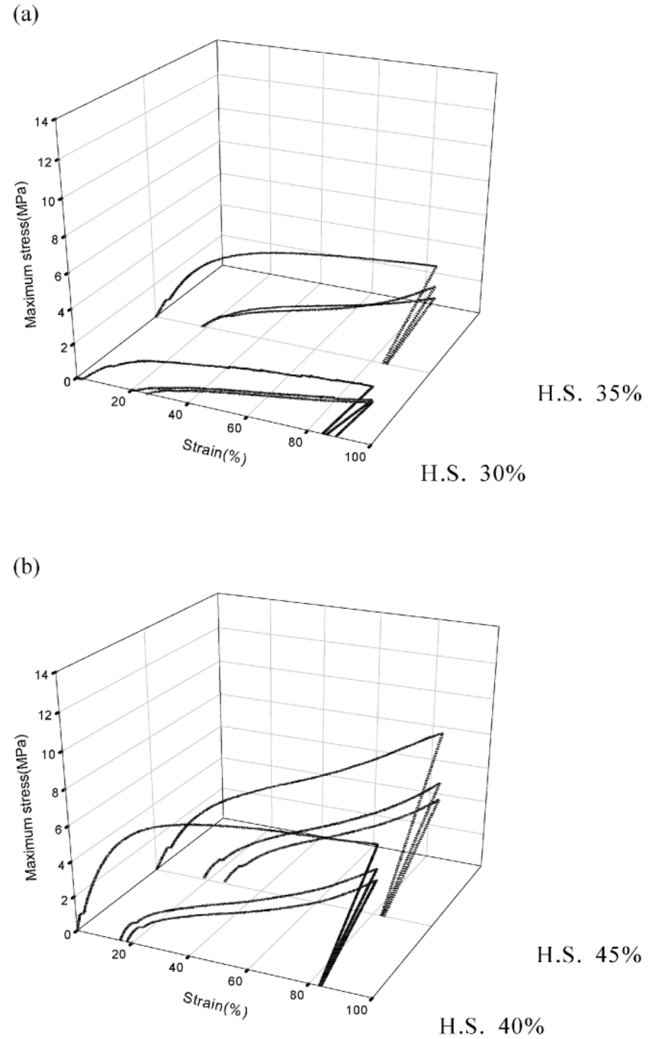

Fig. 10. Cyclic shape memory effect of MDI-based polyurethane block copolymer with (a) 30 and 35 wt%, or (b) 40 and 45 wt% of hard segment.

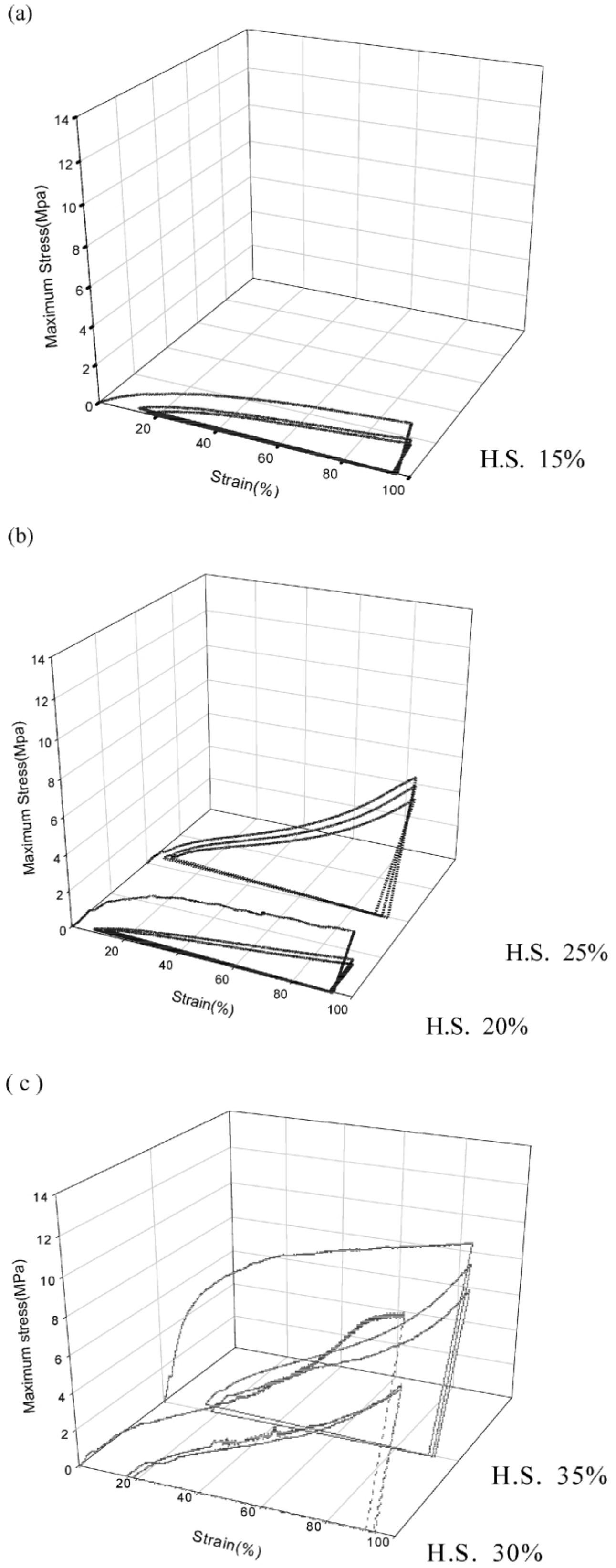

Fig. 11. Cyclic shape memory effect of PDI-based polyurethane block copolymer with (a) 15 wt%, (b) 20 and 25 wt%, or (c) 30 and 35 wt% of hard segment content.

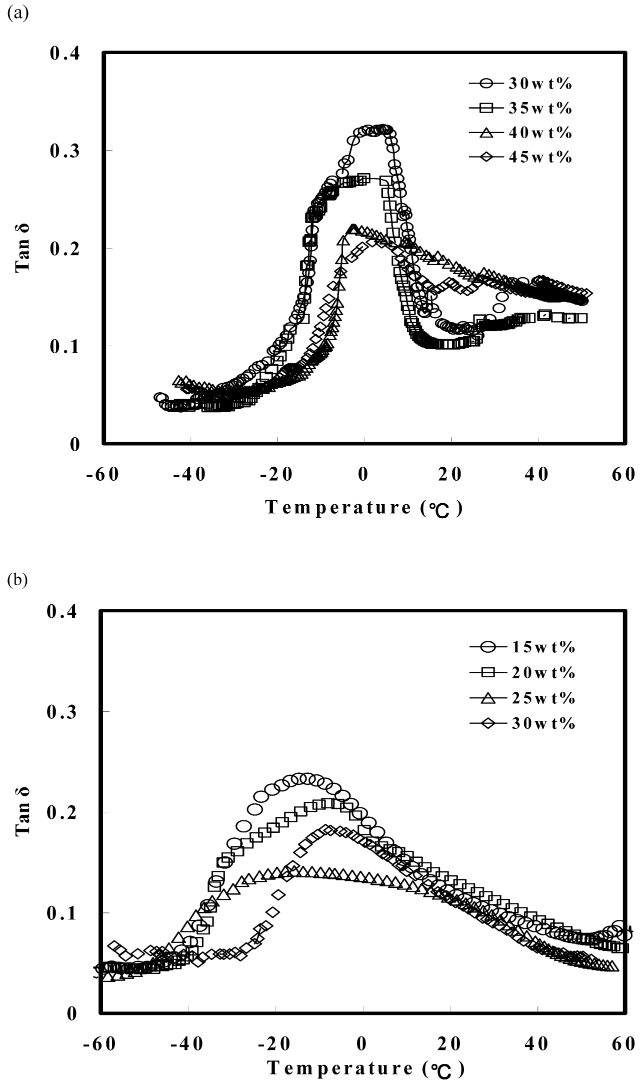

Fig. 12. Loss tan δ vs. temperature of (a) MDI-based or (b) PDI-based polyurethane block copolymer with various hard segment contents.

segments could freely absorb external stress by unfolding or extending their molecular chains. If stress exceeds and breaks the interactions among hard segments, shape memory will be lost and original shape cannot be restored. Therefore, precise control of the composition and structure of hard and soft segments is very important to satisfy the conditions required for various smart materials. Polyurethane with 15–35 wt% of PDI or 30–45 wt% of MDI recovered more than 80% of initial shape after first elongation-recovery cycle, but recovery ratio became a little reduced as more cyclic tests were tried, suggesting that hard segments were well oriented for shape recovery even after repeated deformation cycles. Shape recovery was better for the ones with higher hard segment content, and shape retention could be maintained at higher than 85%. PDI-based polyurethane showed better shape recovery than MDI-based one by ca. 10% for the entire range of hard segment content and the planar shape of PDI seemed to be responsible for its distinct and superior properties compared to bent shape of MDI.

3.6. Dynamic mechanical analysis

In Fig. 12 where the plot of loss tan δ vs. temperature for the polyurethanes with 15–30% of PDI or 30–45% of MDI was shown, loss tan δ decreased with hard segment content because additional interactions among hard segments due to the above-mentioned intermolecular forces resulted in interchain attraction and crystallization, thus losing its elasticity and getting low tan δ. Highest loss tan δ was observed at 15% of PDI or 30% of MDI, and significant change in loss tan δ was observed around glass transition temperature, which depended on the chain rearrangement of hard and soft segments, and crystallization of soft segments.

4. Conclusion

Two series of shape memory polyurethane copolymers (PDI and MDI series) with various hard segment contents between 15 and 45% were synthesized in two steps and were characterized and tested in the points of thermal transition, X-ray diffraction pattern, mechanical properties, and shape recovery. As hard segment content in polyurethane increased, higher shape recovery was observed, and especially shape retention was more than 80% for all of the polyurethanes tested. In general, PDI-based polyurethane showed superior properties to MDI-based one for all of tests and the difference was thought to be originating from the planar shape of PDI in comparison to the bent shape of MDI. There are still a lot of rooms to be developed for the smart shape memory polymers and fine-tuning of the polymeric structure will fulfill the requirements for developing highly vibration-controllable material or moisture-controlling fabric.

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