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Structure and Thermomechanical Properties of Polyurethane Block Copolymers with Shape Memory Effect

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ABSTRACT: Shape memory polyurethane (PU) block copolymers composed of 4,4′-methylenebis-(phenylisocyanate), poly(tetramethylene glycol), and 1,4-butanediol as a chain extender were synthesized by a two-step process. FT-IR spectra showed that carbonyl peak appearing at 1700 cm^{-1} increased with higher hard segment content, whereas another carbonyl peak at 1730 cm^{-1} decreased. It suggests that hard segments get more aggregated to form domains in the PU block copolymer as hard segment content increases. Such domain formation has a significant influence on the mechanical and thermomechanical properties of PU, such as maximum stress, tensile modulus, and elongation at break. Especially, maximum stress, tensile modulus, and elongation at break increased significantly at 30 wt % of hard segment content, and the highest loss tangent was observed at the same composition. Heat of crystallization as measured by differential scanning calorimetry is also dependent on the hard segment content. Finally, 80−95% of shape recovery was obtained at 30−45 wt % of hard segment content, and the control of hard segment content in PU block copolymers is very important in determining their physical properties.

Introduction

In general, conventional polymer becomes brittle at temperatures below the glass transition temperature (T_g) since it is in the glassy state, but easy deformation at temperature above T_g is observed because it becomes rubbery. In some cases, modulus change with respect to T_g by more than 1000 times is known, when the polymer is deformed at a temperature above T_g and quickly cooled to a temperature below T_g. The deformed shape becomes frozen, and ordinary polymer is hard to restore its original shape even though temperature is raised above T_g. But shape memory polymer is known to recover the original shape after it is warmed above T_g and has drawn wide attention from various fields for the past decade.

Table 1. Composition and Characterization of Polyurethane Block Copolymers

mol %			wt % of hard seg	M_w[a]	T_g (°C)[b]	ΔH_{hc} (J/g)[c]	ΔH_{sc} (J/g)[c]
MDI	PTMG	BD					
5.5	1.0	4.5	50	55 000	1.5	103.9	16.4
5.0	1.0	4.0	45	74 000	0.3	66.9	29.7
4.0	1.0	3.0	40	113 000	−2.4	59.2	34.6
3.5	1.0	2.5	35	81 000	−2.5	29.0	35.1
3.0	1.0	2.0	30	105 000	−3.6	20.9	90.9
2.0	1.0	1.0	25	102 000	−8.5	0	147.4
1.5	1.0	0.5	20	130 000	−15.0	0	324.2

[a] Average molecular weights were found by gel permeation chromatography. [b] T_g was determined by the loss tangent experiment (see Figure 9). [c] ΔH_{hc} and ΔH_{sc} means heat of crystallization of hard segments and soft segments, respectively (see Figure 2).

Especially, shape memory polyurethane (PU) composed of hard segment and soft segment has been extensively researched since its discovery by Mitsubishi in 1988.[1,2] The PU was synthesized from diphenylmethane diisocyanate and polyol using 1,4-butanediol as chain extender and phase-separated structures consisting of hard domain and soft domain due to the thermodynamic immiscibility was microscopically observed. Hard segments can bind themselves via hydrogen bonding and crystallization, making the PU very solid below melting temperature. Reversible phase transformation of soft segment is reported to be responsible for the shape memory effect. Thus, the shape memory effect can be controlled via molecular weight of soft segment, mole ratio between hard segment and soft segment, and polymerization process[3,4] and observed at the range of temperatures around T_g. In addition, the PU can be easily processed by a conventional method, showing excellent resistance to chemicals such as water or gasoline. In the future, the shape memory effect can be applied to the areas like smart fabrics that can control moisture permeability or smart materials with damping capability. In this report, shape memory PU block copolymers with various hard segment ratios were prepared, and their structures and thermomechanical properties were compared to find the optimum combination.

Experimental Section

Polymer Synthesis. 4,4′-Methylenebis(phenylisocyanate) (MDI, Junsei Chemical) and poly(tetramethylene glycol) (PTMG, MW = 1800 g/mol) were dried in a vacuum oven before use, and 1,4-butanediol (BD, Duksan Chemical) was stored on 4 Å molecular sieve. Typically, synthesis of PU was done by the following procedure, and the moles of the added reagents for the various PUs were shown in Table 1. In a 500 mL four-neck cylindrical vessel equipped with a mechanical stirrer, an appropriate amount of MDI and PTMG in 100 mL of dimethylacetamide (DMAC) which was freshly distilled before use were stirred under nitrogen at 80 °C for 3 h to make prepolymer. 1,4-Butanediol was added dropwise to the reaction mixture according to the MDI/PTMG ratios, and the remaining isocy-

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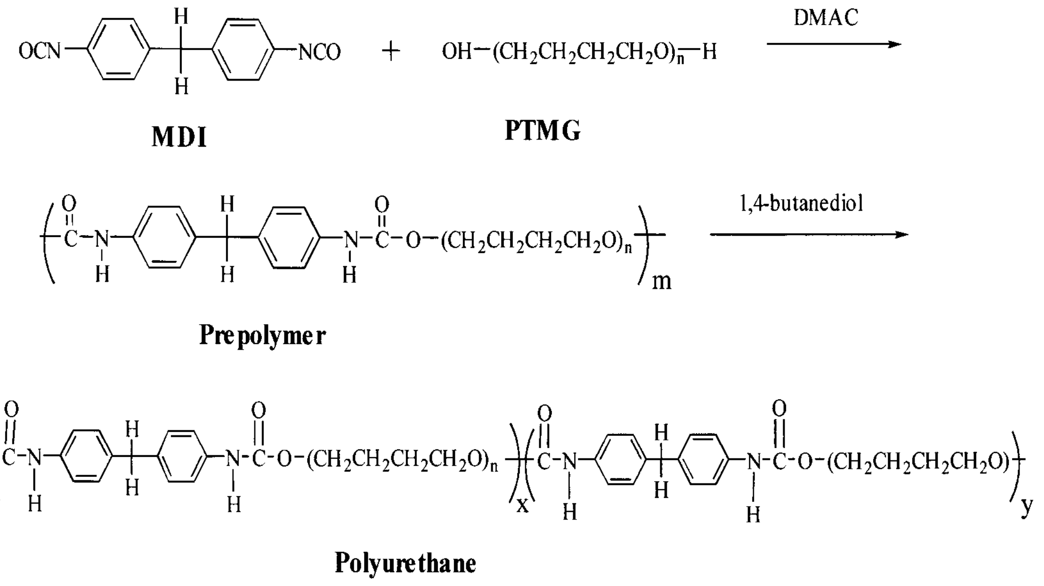
Scheme 1. Synthetic Scheme of Polyurethane Block Copolymer



anate group was intermittently checked by di-*n*-butylamine back-titration during polymerization to determine the progress of polymerization.[5] The reaction mixture became very sticky with polymerization, and it was carried out until the unreacted isocyanate group was not observed. After the polymerization was over, PU was removed of solvent under vacuum and further solidified by storing in an oven (100 °C) for 24 h. Molecular weight of PU block copolymer was determined by gel permeation chromatography (GPC, Younglin, model M930) eluting with THF, and mole ratios of monomers and their molecular weights are summarized in Table 1. FT-IR spectra were taken by a Bomem MB FT-IR spectrometer with a thin film of the PU. NMR spectra were taken by a Bruker 600 MHz NMR spectrometer. ^{1}H NMR (CF_3COOH): δ 2.0 (CH_2 of PTMG), δ 2.1 (CH_2 of MDI), δ 2.3 (CH_2 of BD), δ 4.1 (OCH_2 of PTMG), δ 4.4 (OCH_2 of BD), δ 4.6 (NHCO), δ 7.3 (phenyl of MDI).

DSC. In the first scan, the PU sample was heated to 250 °C (10 °C/min), kept at the temperature for 5 min, and quickly cooled to −50 °C in a differential scanning calorimeter (DSC, TA 2000). In the second scan, the sample was heated again to 250 °C with a heating rate of 10 °C/min, and the second scan was used to find glass transition temperature (T_g) and melting temperature (T_m). A second cooling scan was also recorded to find the heat of crystallization by cooling from 250 °C at a cooling rate of 10 °C/min.

Mechanical Property. The PU block copolymers were molded into tensile specimens with 3 mm thickness at 160−230 °C depending on the hard/soft segment content, and the freshly prepared PU specimens were immediately used for tensile test. A tensile test was performed using a Universal testing machine (UTM, Lloyd LR50K) with a dumbbell-type specimen according to ASTM D-638, and the gauge length and crosshead speed were 25 mm and 10 mm/min, respectively. At least five specimens were tested, and the average was plotted. A dynamic mechanical property of the PU was measured by a dynamic mechanical analyzer (DMTA, Rheometric Scientific Mark IV, UK). Storage modulus, loss modulus, and loss tangent (tan δ) were scanned between −50 and 50 °C at a heating rate of 3 °C/min.

Thermomechanical Property Analysis. To check the shape memory effect of the PU, the relationship between stress and strain at various temperatures was analyzed by a UTM equipped with a controlled thermal chamber. The engaged thermomechanical test was carried out in the following order: (i) apply deformation (ϵ_m) to the sample with a constant crosshead speed of 10 mm/min at T_k, (ii) cool sample to T_l with the same ϵ_m, (iii) maintain at T_l for 5 min with removal of the load, and (iv) raise the temperature from T_l to T_k and keep at T_k for 5 min. Under the conditions, shape retention and shape recovery are defined as follows.

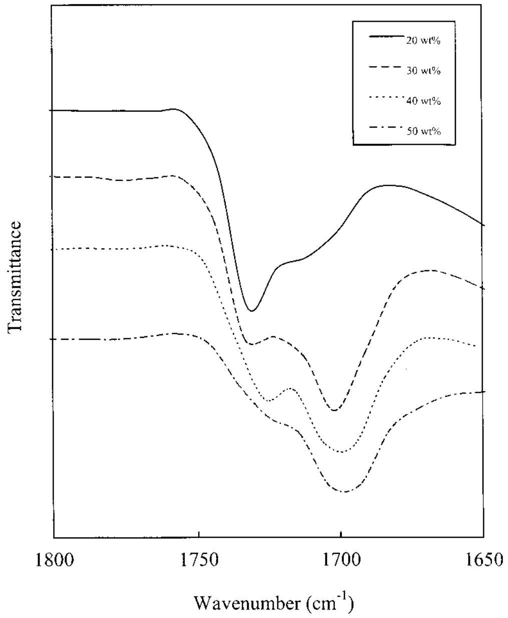


Figure 1. Infrared spectra of polyurethane block copolymer with various wt % of hard segment.

$$\text{shape retention (\%)} = \epsilon_u \times 100/\epsilon_m \qquad (1)$$

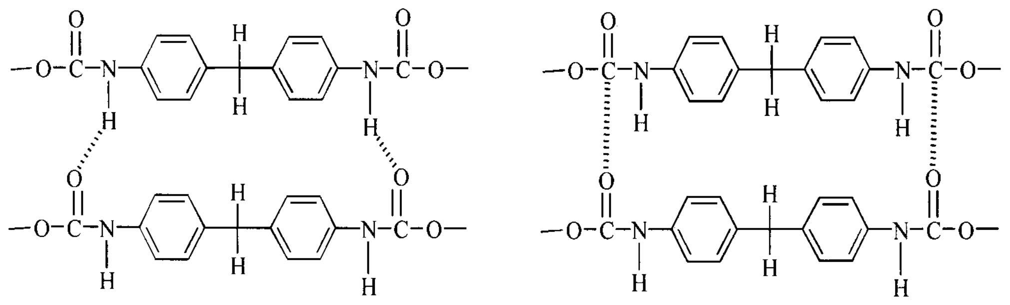
$$\text{shape recovery (\%)} = (\epsilon_m - \epsilon_p) \times 100\,/\epsilon_m \qquad (2)$$

where $T_k = T_g + 20$ °C, $T_l = T_g - 20$ °C, ϵ_m = strain at 50% elongation, ϵ_u = retention strain at $T_g - 20$ °C, and ϵ_p = recovery strain at $T_g + 20$ °C.

Results and Discussion

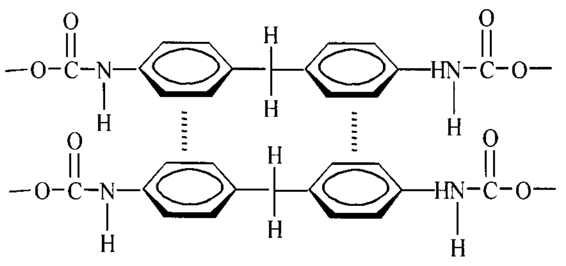
The synthesis of polyurethane is straightforward as shown in Scheme 1. The reaction mixture was getting sticky as polymerization went on, and the polymerization method was quite reproducible under strict moisture and purity control of reactants. NMR spectra showed that the ratio of peak areas of [MDI]/[PTMG] was getting higher with more inclusion of MDI.

Scheme 2. Interactions among Polymeric Chains



(1) hydrogen bonding

(2) dipole-dipole interaction



(3) induced dipole-dipole

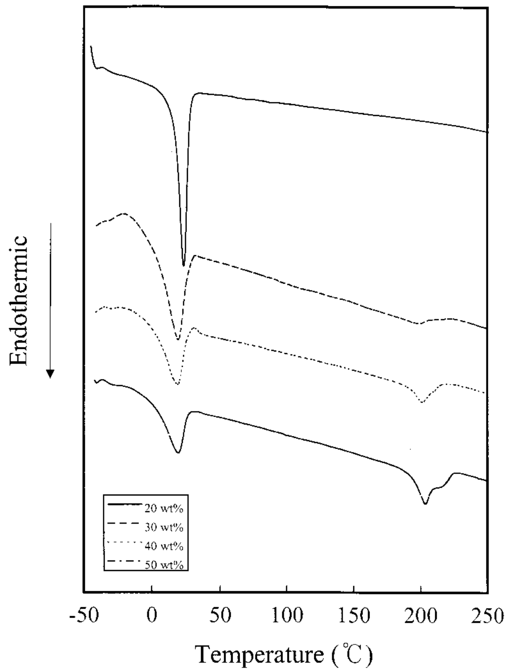


Figure 2. DSC heating scans of polyurethane block copolymers with various wt % of hard segment.

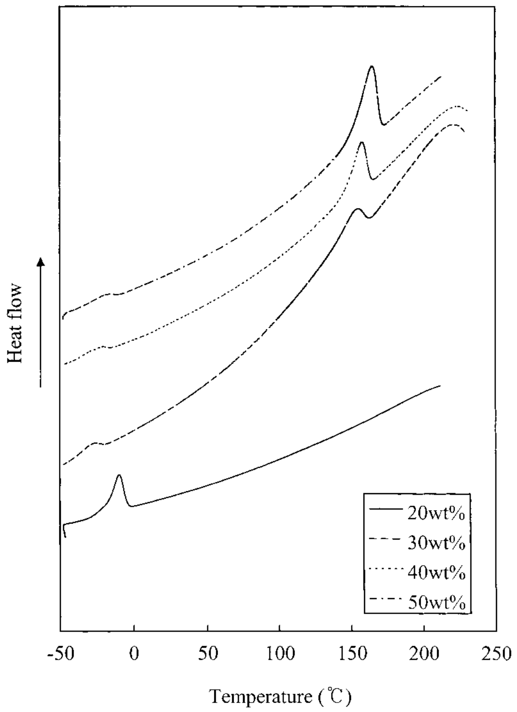


Figure 3. DSC cooling scans of polyurethane block copolymers with various wt % of hard segment.

For convenience, we designate the hard segment and soft segment in the PU as the diphenylmethylene moiety and poly(tetramethylene glycol), respectively. The FT-IR spectrum of the PU in Figure 1 shows that the transmittance peak at 1700 cm^{-1} is growing bigger with the increase of hard segment while the transmittance at 1730 cm^{-1} is getting smaller. A few interactions among the polymeric chains are responsible for the shift of transmittance peak with the inclusion of more hard segment: (1) hydrogen bonding between carbamoyl group and carbony group of hard segment; (2) dipole–dipole interaction between carbonyl groups of hard segments; (3) induced dipole–dipole interaction between aromatic rings of hard segment. The hydrogen bonding among hard segments plus dipole–dipole interaction between carbonyl groups will primarily affect C=O stretching vibration, and the shift of carbonyl stretch peak suggests that more extensive interactions are made with the increase of hard segment content.[6] Thus, the peak observed at 1730 cm^{-1} is for the carbonyl of isolated hard segments that are less influenced by the inter- or intrachain interactions. Strong interaction among hard segments will probably lead to phase

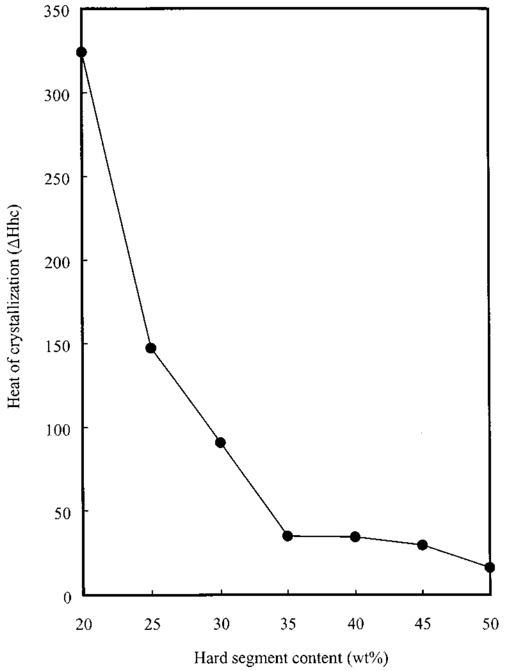


Figure 4. Heat of crystallization of polyurethane block copolymers with various wt % of hard segment.

separation or domain formation,[7,8] which is quite desirable in the point of shape memory effect. Based on FT-IR data, the PU polymer can be endowed with shape memory effect by adjusting the percentage of hard segment content.

Figure 2 shows the heating scans of PU block copolymers with various hard segment contents and cooling scans for the same copolymers are shown in Figure 3. In Figure 2, when the main endothermic transitions at 25 °C were compared, the highest heat of transition was observed at 20 wt % of hard segment. But another endothermic transition at 200 °C was growing bigger with increased hard segment content. It suggested that peaks at 25 and 200 °C were from the transition of soft segment and hard segment, respectively. The PU with higher percentage of hard segment showed rather smaller heat of transition at 25 °C, suggesting that more ordered polymer packaging was obtained at low percentage of hard segment. In Figure 3 and Figure 4, the highest heat of crystallization at −10 °C was found with 20 wt % of hard segment, and PU with higher hard segment also showed smaller heat of crystallization at −10 °C, which was similar to the heating scan. DSC data supports that excess percentage of hard segment do not always provide well ordered structure and proper ratio of hard segment is necessary for ordered structure. More ordered structure would be expected at low wt % of hard segment because hard segments are mainly connected by the long and flexible PTMG as soft segment contains more PTMG than BD. But hindered or restricted alignment of hard segments would be made at higher wt % of hard segment because the short and less flexible butanediol is the major component of the soft segment. Therefore, higher heat of transition is needed for the PU with low wt % of hard segment than the one with high wt % of hard segment. An opposite trend was observed for another peak around 200 °C for the hard segment transition, because more interactions among hard segments were formed with higher hard segment content.

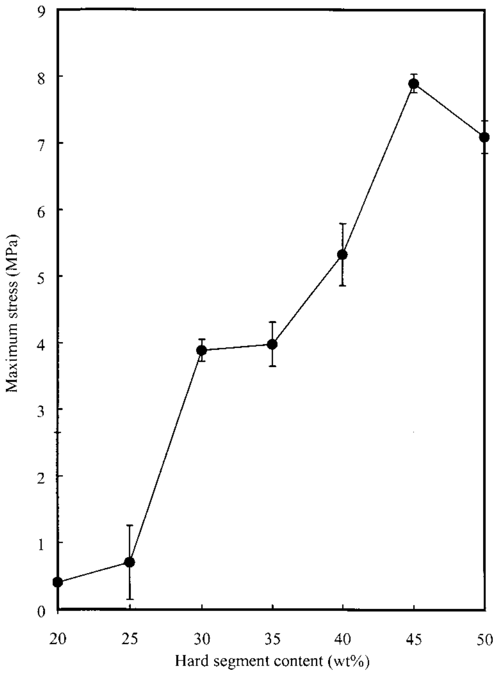


Figure 5. Maximum stress of polyurethane block copolymers with various wt % of hard segment (bar indicates 95% confidence limit).

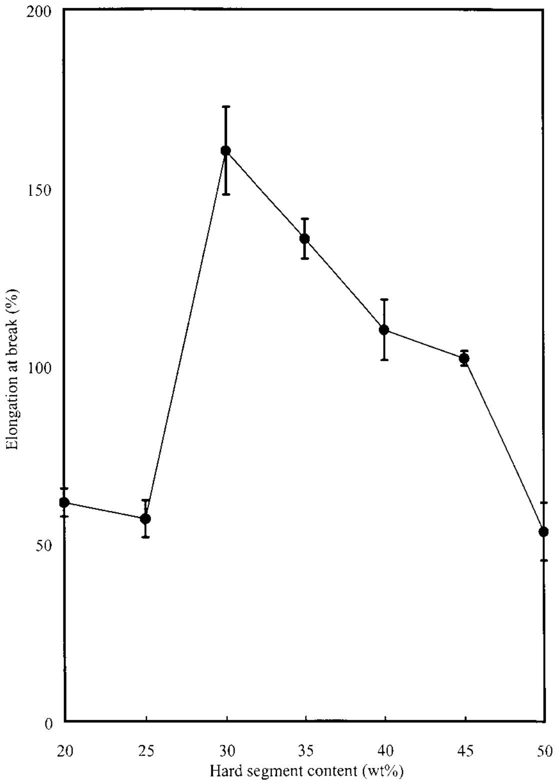


Figure 6. Percent strain at break of polyurethane block copolymers with various wt % of hard segment (bar indicates 95% confidence limit).

Tensile properties of PU block copolymers with various hard segment contents are shown in Figure 5 and Figure 6. In Figure 5, maximum stress increases gradually up to 50 wt %, which is due to the fact that the rigid diphenylmethylene moiety coupled with hydrogen bonding and dipole−dipole interaction make the PU very difficult to stretch as higher percentage of hard segment is incorporated. In addition, physical cross-

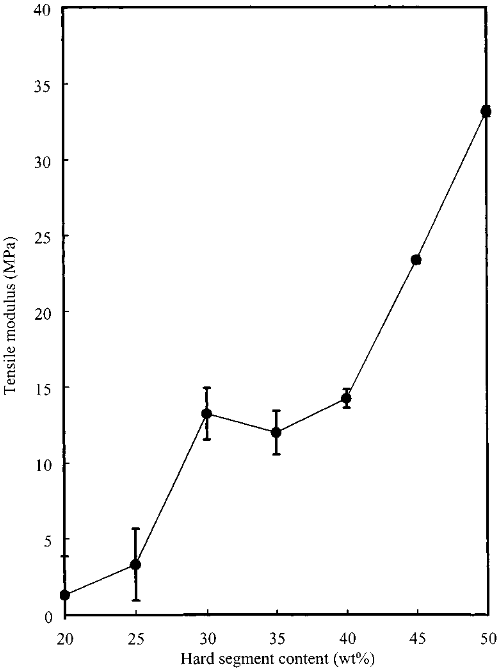


Figure 7. Modulus of elasticity of polyurethane block copolymers with various wt % of hard segment (bar indicates 95% confidence limit).

linking made by the rigid diphenylmethylene moieties also contributes to the high maximum stress with the increase of hard segment. Strain at break of PU block copolymers is shown in Figure 6, where strain at break was the highest at 30 wt % of hard segment and gradually decreased with the increase of hard segment content. At high hard segment content, the rigidity of the PU would not allow it to stretch long, and the very low degree of physical cross-linking at low percentage of hard segment is responsible for the PU break up at short elongation. Yielding is not observed at 20−25 wt % of hard segment, but at more than 30 wt % of hard segment, the PU showed both yielding and necking.

Generally, when the deformation is applied to the physically cross-linked PU, soft segment having low modulus will be extended in the first stage of deformation, and as the strain increases, stress will be transferred to the hard domain. When the stress transferred to the hard domain is increased, chain slippage between the hard segment and the resultant plastic deformation of hard domain will occur.[9−12] While necking, a contraction phenomenon of cross-sectional area, polymer chains will align to the extension direction, and show strain hardening. Such deformation with alignment and strain hardening cannot be corrected after removal of stress for ordinary polymers, but the original shape can be restored by just heating for shape memory polymers. To maximize shape memory effect such factors as stress, deformation, and temperature, together with yielding and necking should be extensively considered.

The tensile modulus change of PU block copolymers with various hard segment contents is shown in Figure 7. In general, modulus increases almost linearly with hard segment content, which is due to the stiffness of polymer chain resulting from the previously mentioned polymeric interactions, showing similar trend as the maximum stress result in Figure 5. Thus, from the tensile behavior of PU block copolymer, it is found that maximum stress, elongation at break, and modulus were all significantly influenced by the hard segment content.

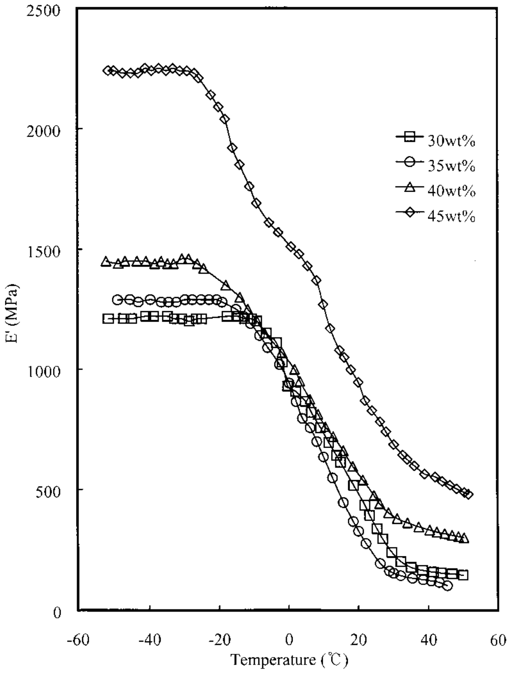


Figure 8. Tensile storage modulus vs temperature of polyurethane block copolymers with various wt % of hard segment.

Figure 8 shows the storage modulus of PU block copolymers having 30, 35, 40, and 45 wt % of hard segment. Storage modulus increases with the hard segment content, which is similar to the tensile results shown in Figure 7, and sharply changes at the T_g region, together with the slight shift of T_g to higher temperature with more hard segment content. Such a shift of T_g in PU is not uncommon. For example, it is known that, if the mole ratio of [hard segement]/[soft segment] is larger than 1, T_g increases slightly due to the strong allophanate interaction by excess hard segment in prepolymer.[6] T_g could be also increased with the number of benzene rings in hard segment at a constant mole ratio of [hard segment]/[soft segment].

In Figure 9 is compared the loss tangent of PU block copolymers, where higher loss tangent values mean that the material is viscous. Some shape memory polymers used for vibration control has a loss tangent value as high as 1.0 at T_g region, so that impact energy can be effectively absorbed.[1−4] Loss tangent for the PUs decreased with the increasing hard segment, and the highest loss tangent value of 0.35 was obtained at 30 wt % of hard segment. Damping effect at T_g is known to be dependent heavily on the hard segment content and crystallization of soft segment.[13−15] The best damping effect of PU could be expected at 30 wt % of hard segment content.

In Figure 10, the shape retention of the PUs with 30, 35, 40, and 45 wt % of hard segment was measured after it was deformed by 50%, kept for 5 min at 20 °C below T_g, and the load was removed. All of the PUs tested show more than 90% of shape retention at each hard segment contents. Shape recovery was measured after the PU was kept for 5 min at 20 °C above T_g with the load removed and ranged from 80 to 95% depending on the hard segments as in Figure 11. But shape recovery was not observed at 20, 25, and 50 wt % of hard segment content. Shape of the PU is well preserved as judged

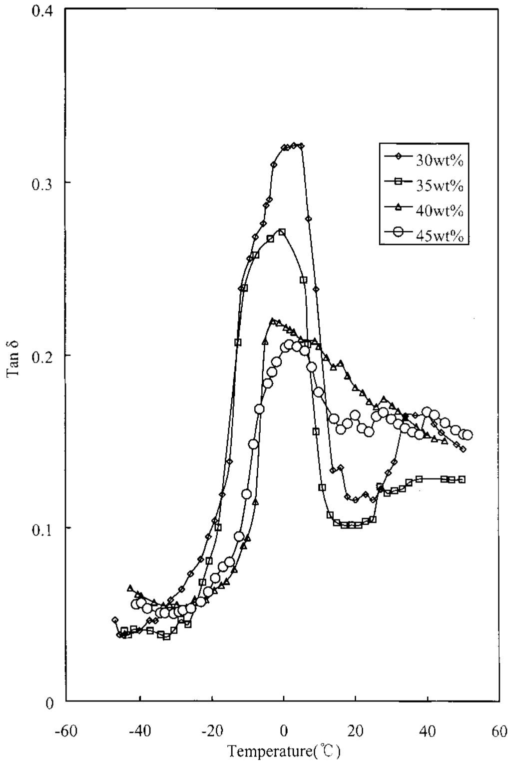


Figure 9. Tan δ vs temperature of polyurethane block copolymers with various wt % of hard segment.

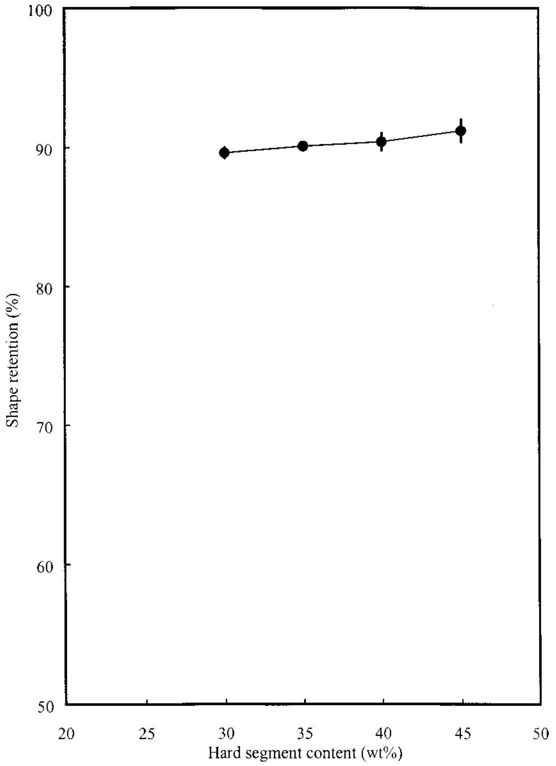


Figure 10. Shape retention of polyurethane block copolymers with various wt % of hard segment (bar indicates 95% confidence limit).

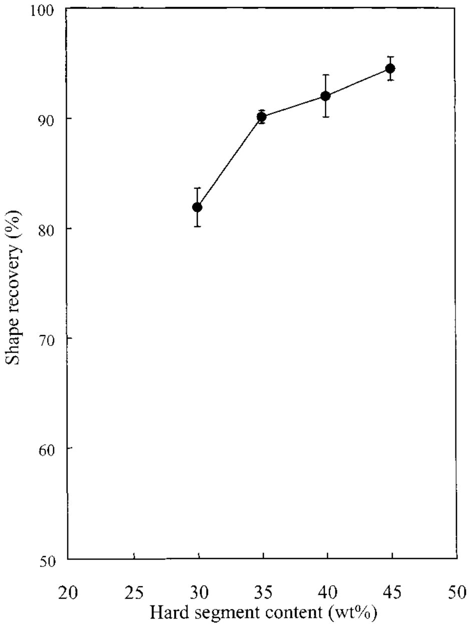


Figure 11. Shape recovery of polyurethane block copolymers with various wt % of hard segment (bar indicates 95% confidence limit).

by shape retention result, because deformation of the chain is restricted at below T_g. In contrast, original shape is almost fully recovered at above T_g, which is due to the strong interactions among the hard segment components. When stress is applied to the PU, soft segment will be preferentially extended to the stress direction rather than hard segment due to the fact that hard segment is close to glassy state and soft segment is rubbery at above T_g. Stabilization of the PU through dipole–dipole interaction, hydrogen bonding, and induced dipole–dipole interaction of the hard segments is responsible for the high shape recovery at above T_g. PU with 20 or 25 wt % of hard segment cannot have strong interaction or physical cross-link due to the low percentage of hard segment, resulting in the loss of shape memory effect. The PU with 50 wt % of hard segment did not show shape recovery due to the excess interaction among the hard segments and the resulting rigid structure.

Thus, from the above observation, it can be concluded that 80–95% of shape recovery was obtained at the 30–45 wt % of hard segment content where PU copolymers can make strong interaction among hard segments enough to restore the polymer back to the original shape. In the long run, we would like to use the shape memory PU for the development of smart fabric that can control moisture and/or smart fiber-reinforced composite with damping capability.

Conclusion

From FT-IR spectra, PU block copolymer could become gradually more intra- or interconnected through dipole–dipole interaction, hydrogen bonding, and induced dipole–dipole interaction as the hard segment content increases. Mechanical properties of PU block copolymers were also influenced by the hard segment content and phase separation, and high degree of crystallinity would be followed with the inclusion of more hard segment. The highest loss tangent was obtained at 30 wt % of hard segment, suggesting the importance of the combination of hard segment and soft segment. The shape recovery of 80–95% was obtained at the hard segment content of 30–45 wt %, but shape recovery property was not observed with excess or shortage of hard segment. Consequently, control of hard segment content in PU is very important in preparing ideal shape memory PU, and further work including modification of PU content is underway in our laboratory.

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