Shape memory polyurethane containing amorphous reversible phase

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Segmented thermoplastic polyurethanes (TPUs), which consist of an amorphous soft segment from 1,3-butanediol and hexamethylene diisocyanate (HDI) and a crystalline hard segment from 4,4′-bis-(6-hydroxy hexoxy)biphenyl and tolylene 2,4-diisocyanate were synthesized. Their thermal and mechanical properties, shape memory effect, utilizing amorphous soft segment domain as reversible phase and crystalline hard segment domain as frozen phase, were examined. The reversibility observed on repeated deformation was improved as the magnitude of deformation was reduced and the hard segment content was increased, or by crosslinking with excess HDI. © *2000 Kluwer Academic Publishers*

1. Introduction

Thermal-responsive shape memory polymers are functional polymers which can be applied usefully in temperature-sensing elements. These polymers basically consist of two phases, a frozen phase and a thermally reversible phase [1–3]. Crystal, glassy state, entanglement network, or crosslinking network can be used as a fixed structure memorizing original shape. The thermally reversible phase is generally designed to have a large drop in elastic modulus on heating through the shape recovery temperature (T_s). The melting temperature of a crystalline phase or the glass transition temperature of an amorphous phase can be used as a T_s.

Segmented polyurethanes can have a separated microphase structure due to the incompatibility of the constituent segments [4]. In our previous article [5], we synthesized segmented thermoplastic polyurethanes (TPUs) from diol-terminated poly(caprolactone) (PCL diol) as a soft segment, 4,4′-diphenylmethane diisocyanate (MDI) as a diisocyanate, and mesogenic 4,4′-bis-(2-hydroxy ethoxy)biphenyl or 4,4′-bis-(6-hydroxy hexoxy)biphenyl as chain extenders. Their mechanical and thermal properties, and the shape memory effect were examined and compared with those of PCL diol/MDI/1,4-butanediol based TPUs [5, 6]. In these TPUs, the melting temperature of the soft (PCL) segment was used as a T_s, because a large drop in elastic modulus occurs on heating through the melting temperature of the soft segment, and the crystalline hard segment (MDI + chain extender) can perform its role as a frozen phase. Rubber elasticity was observed within the temperature range between the melting temperature of the soft segment (T_{ms}) and the melting temperature of the hard segment (T_{mh}) because of the micro-Brownian motion of the soft segment and the restricted

molecular motion due to the crystalline frozen phase. When they were deformed in the temperature range between T_{ms} and T_{mh} and subsequently cooled below T_{ms} under constant strain, the deformed shape was fixed because the micro-Brownian movement was frozen. When they were reheated to the temperature range between T_{ms} and T_{mh}, the original shape was recovered again by the elastic force generated during the deformation.

The glass transition temperature of the polyurethane segment can be designed variously because a wide range of monomeric materials is commercially available. The polyurethane segment with appropriate T_g (i.e. T_s) can also be used properly as a reversible phase, as commercialized by Mitsubishi Heavy Industries, Ltd. [3, 7]. However, literatures about the chemical structure-property relationship of these kinds of shape memory polyurethanes are not accessible easily. Besides the hard segment with mesogenic moiety can enhance the modulus of TPU [5, 8, 9]. So, in this study, we synthesized high modulus shape memory TPUs with an amorphous polyurethane segment whose T_s (i.e. T_g) lies in the temperature range 10–35°C as a reversible phase, and with a crystalline hard segment from tolylene 2,4-diisocyanate and mesogenic 4,4′-bis-(6-hydroxy hexoxy)biphenyl as a frozen phase. The thermal and mechanical properties, including the shape memory effect were examined.

2. Experimental procedures
2.1. Materials

N,N-Dimethylacetamide (DMAc, from Junsei) was used after dehydration with a 0.4 nm molecular sieve for 2 days. 4,4′-Bis-(6-hydroxy hexoxy)biphenyl (BHBP)

was synthesized by the reaction of 4,4′-dihydroxy biphenyl (from Tokyo Kasei) with 6-chloro-1-hexanol (from Fluka) [10]. Tolylene 2,4-diisocyanate (2,4-TDI, from Aldrich), 1,3-butanediol (1,3-BD, from Fluka), hexamethylene diisocyanate (HDI, from Aldrich), and dibutyltindilaurate (DBTDL, from Aldrich) were used as received.

A thermoplastic polyurethane elastomer, TPU630 was synthesized from PCL diol ($Mn = 4000$), 4,4′-diphenylmethane diisocyanate (MDI), and BHBP. The content of hard segment (MDI + BHBP) in TPU630 was 30 wt%, and the detailed synthetic method was described in our previous paper [5].

2.2. Synthesis of TPUs
A 500 millilitre round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube was used as a reactor. TPUs were synthesized by solution polymerization in DMAc under dry N_2 by two steps. That is, BHBP and 2,4-TDI were reacted in the presence of DMAc for 2 h and 70°C, to prepare a hard segment. This hard segment was subsequently chain extended with soft segment by the reaction with 1,3-BD and HDI in the presence of DBTDL for 3 h at 90°C. DMAc was added into the reactor occasionally when the viscosity of the reaction mixture was too high. The final polymer concentration of TPUs in DMAc was about 25 wt%. The mole ratios of 2,4-TDI/BHBP and HDI/1,3-BD of 6TPU series in Table I were kept around 1.05/1.00 and 1.00/1.00 respectively to get linear polymers. The 65TPU series in Table I were synthesized with additional 5 phr of HDI to induce crosslinking by allophanate linkage during casting at 120°C for 24 h. The intrinsic viscosity, $[\eta]$ and the hard segment content in polymer of the 6TPU series are shown in Table I.

2.3. Characterization
The viscosity of TPU solution in dimethyl sulfoxide was measured with a Cannon-Fenske Routine Viscometer at 30 °C.

^{1}H n.m.r. spectra were obtained in DMF-d_6 on a Varian Gemini-2000.

Differential scanning calorimetry (d.s.c.) was carried out with TA Instruments DSC-2910 at a heating and cooling rate of 10 °C/min. All runs were carried out with a sample of ca. 5 mg. After melting for 3 min at 20 °C above the melting temperature of the hard segment (T_{mh}) in the d.s.c. device, the crystallization temperature on cooling (T_{mc}) and the heat of crystallization (ΔH_{mc}) of hard segment were measured using a cooling scan to −50 °C. The glass transition temperature of the soft segment (T_{gs}), the glass transition temperature of the hard segment (T_{gh}), the crystallization temperature on heating (T_{cc}) of the hard segment, T_{mh}, and the heat of fusion at T_{mh} (ΔH_{mh}) were measured using a heating scan from −50 °C with samples quenched in liquid nitrogen after melting for 3 min at 20 °C above the melting temperature of the hard segment.

Films for the measurements of tensile properties and dynamic mechanical properties were prepared by the casting of TPU solution in DMAc on a glass plate. After evaporation of DMAc at 120 °C for 24 h, the films were further dried at 25 °C under vacuum for the next 4 days. Tensile tests were done using a tensile tester (Tinius Olsen Series 1000), to which was attached a constant temperature heating chamber. The microtensile test specimen had the dimensions of 30 mm length, 5 mm width, and 0.5 mm thickness. Dynamic mechanical properties were determined with a dynamic mechanical thermal analyzer (Rheometric Scientific DMTA MK-III), using a bending mode at a heating rate of 3 °C/min and 2 Hz.

3. Results and discussion
In Fig. 1d, we can see that 6TPU4 has a sharp T_{gs} at 13.4 °C, a broad T_{gh} around 60 °C, a small exothermic crystallization peak of the hard segment at 100.9 °C, and endothermic T_{mh} at 154.8 °C. These results show that the 6TPU4 is phase separated into an amorphous soft segment domain and a partially crystalline hard segment domain. Other thermograms shown in Fig. 1 and data shown in Table II suggest similar phase separation behavior of all the TPUs used in this study.

In Fig. 1 and Table II, we can see that T_{gs}, T_{gh} generally decrease as the hard segment content in TPU is increased (glass transition temperature of 2,4-TDI/BHBP

TABLE I Characteristics of TPUs prepared

Sample designation	Composition of hard segment in feed (wt%)		Composition of soft segment in feed (wt%)		Content of hard segment in polymer[a] (wt%)	$[\eta]$ (m^3/kg)
	BHBP	2,4-TDI	1,3-BD	HDI		
6TPU series						
6TPU1	5.7	4.3	31.9	58.1	9.7	4.2
6TPU2	12.6	7.4	28.4	51.6	21.5	3.8
6TPU3	19.5	10.5	24.8	45.2	32.2	4.7
6TPU4	26.4	13.6	21.3	38.7	41.6	5.0
65TPU series						
65TPU1	5.7	4.3	31.9	63.1	—	—
65TPU2	12.6	7.4	28.4	56.6	—	—
65TPU3	19.5	10.5	24.8	50.2	—	—
65TPU4	26.4	13.6	21.3	43.7	—	—

[a]Determined by ^{1}H n.m.r. analysis.

TABLE II Thermal properties of TPUs

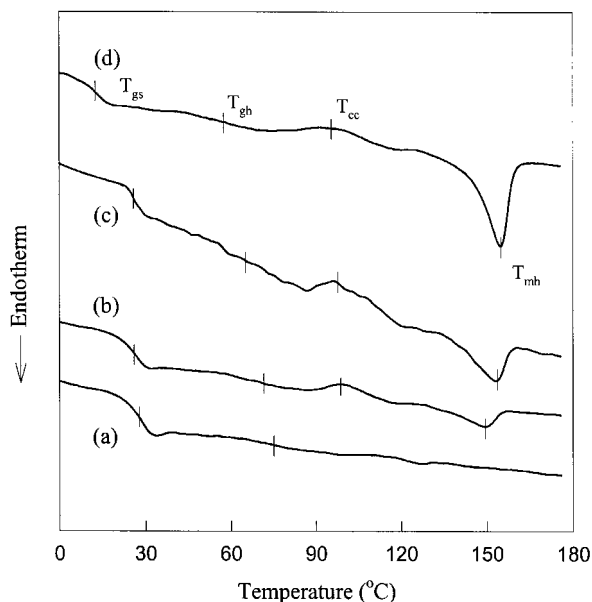| Sample	T_{gs} (°C)	T_{gh} (°C)	T_{mh} (°C)	(ΔH_{mh} (J/g-hard segment)	T_{mc} (°C)	ΔH_{mc} (J/g-hard segment)
6TPU series						
6TPU1	29.2	75.3	—	—	—	—
6TPU2	26.3	72.5	149.5	20.0	101.3	22.3
6TPU3	25.7	59.8	153.6	21.9	102.5	23.7
6TPU4	13.4	57.5	154.8	30.6	100.9	28.4
65TPU series						
65TPU1	31.4	78.5	—	—	—	—
65TPU2	32.2	75.4	152.7	20.1	102.6	22.9
65TPU3	28.3	66.7	153.7	19.6	101.5	23.3
65TPU4	28.6	66.9	160.4	28.5	112.7	28.3

Figure 1 DSC thermogram obtained on heating of TPU: (a) 6TPU1, (b) 6TPU2, (c) 6TPU3, (d) 6TPU4.
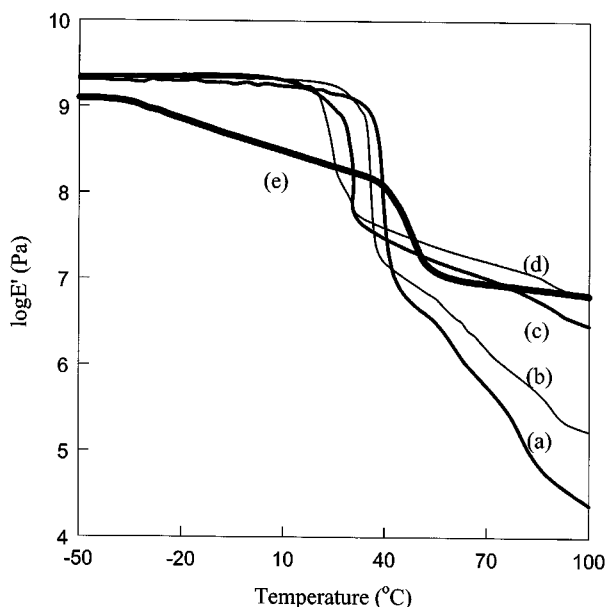

Figure 2 Tensile storage modulus of TPU: (a) 6TPU1, (b) 6TPU2, (c) 6TPU3, (d) 6TPU4, (e) TPU630.

based polyurethane was reported to be 87 °C or 95 °C) [11, 12]. These results suggest that the dissolution of hard segment into the soft segment domain is enhanced with accompanying T_{gs} increase as the content of soft segment in TPU is increased, and conversely that the dissolution of soft segment into the hard segment domain is enhanced with accompanying T_{gh} decrease as the content of hard segment in TPU is increased.

The thermal properties of the 65TPU series (Table II) are similar with those of the 6TPU series except that the T_{gs}s are somewhat higher than those for the 6TPU series, probably due to crosslinking by excess HDI.

It has been reported that the crystalline phase of 2,4-TDI/BHBP based polyurethane is thermodynamically more stable than the mesophase at room temperature [13]. Because it was not easy to estimate the exact natures of crystal or mesophase of our TPUs at soft segment-rich compositions, we gave only the peak temperatures and total heat values of exothermic or endothermic peaks in Table II, where we can see that ΔH_{mh} and ΔH_{mc} generally increase as the hard segment content in TPU is increased.

The changes of tensile storage modulus, E' in the 6TPU series on heating are shown in Fig. 2. Fig. 2 shows

that sharp drop of E' at T_{gs} occurs and this transition occurs at lower temperature as the content of hard segment is increased, as anticipated from T_{gs} measured by d.s.c. (Table II). The sharp transition at T_{gs} and the minor variation of E' below T_{gs}, compared with TPU630 (Fig. 2) in our previous article, suggest the availability of 6TPU series as a keen temperature sensing material [5].

The tensile modulus increases and the elongation at break decreases as the hard segment content in TPU is increased (Table III), and the 65TPU series generally

TABLE III Tensile properties of TPUs

Sample	5% secant modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
6TPU series			
6TPU1	23.6	12.1	390.6
6TPU2	41.1	11.2	261.9
6TPU3	97.6	8.4	190.5
6TPU4	263.7	14.9	13.3
65TPU series			
65TPU1	155.5	17.1	367.6
65TPU2	221.8	17.0	340.5
65TPU3	253.4	15.6	25.6

have higher values of modulus than the 6TPU series, probably due to crosslinking by allophanate linkage.

The results of cyclic tests to examine the shape memory effect of TPUs that can sustain 100% strain at 10 °C
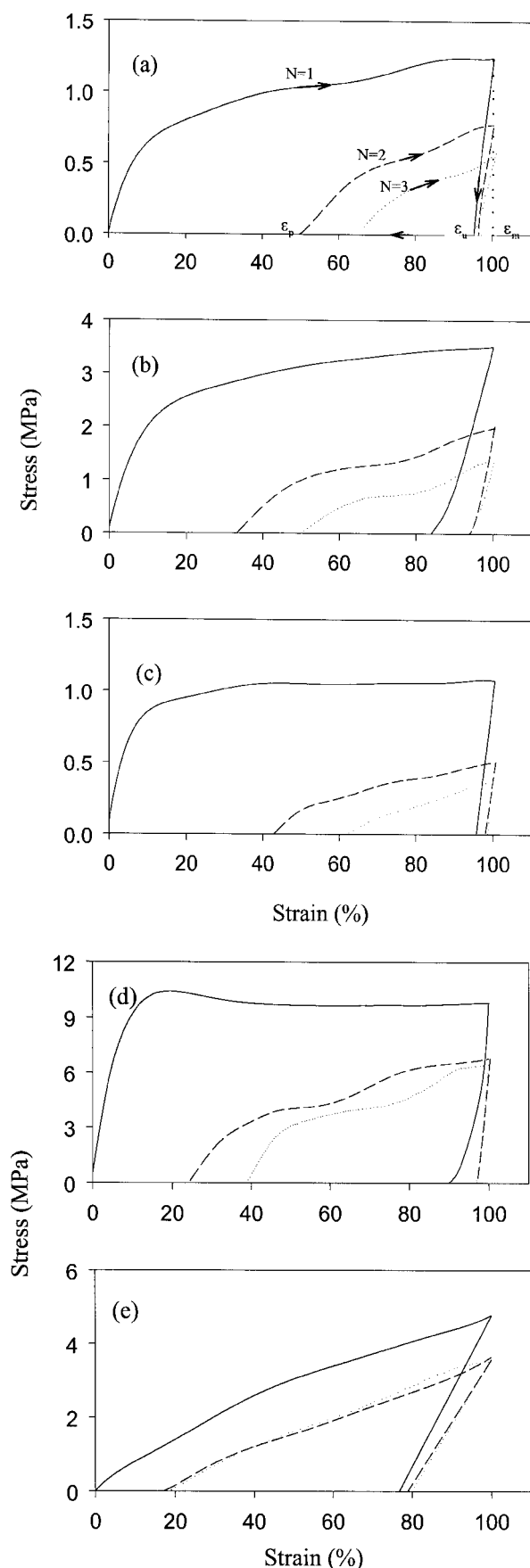

Figure 3 Cyclic tensile behavior of TPU: (a) 6TPU1, (b) 6TPU2, (c) 65TPU1, (d) 65TPU2, (e) TPU630.

TABLE IV Residual strains after cyclic tensile test ($\varepsilon_m = 50\%$)

Sample	ε_p (%) after			
	$N = 1$	$N = 2$	$N = 3$	$N = 4$
6TPU series				
6TPU1	10.8	20.3	27.1	32.5
6TPU2	10.0	18.1	24.4	25.5
6TPU3	5.5	12.7	12.8	13.3
65TPU series				
65TPU1	5.8	10.9	18.0	21.8
65TPU2	4.8	8.8	9.6	9.6
65TPU3	4.9	4.8	5.7	5.6

above T_{gs} are shown in Fig. 3. Samples were elongated at 10 °C above T_{gs} to 100% strain (ε_m) at a constant elongation rate of 10 mm/min. While maintaining the strain at ε_m the sample was cooled to 20 °C and unloaded. Upon removing the constraint at 20 °C a small recovery of strain to ε_u occurred. The sample was subsequently heated again to 10 °C above T_{gs} in 3 min, and held at that temperature for the next 10 min, allowing recovery of strain. This completes one thermomechanical cycle ($N = 1$) leaving a residual strain, ε_p where the next cycle ($N = 2$) starts. Compared with TPU630 (Fig. 3e), Fig. 3a–d show larger ε_p values, and these values increase with repeated deformation. Because fatigue by repeated deformations in TPUs comes from soft-hard phase mixing and orientation [14, 15], these results show that changes due to phase mixing or segmental orientation by repeated deformations are more evident when both soft and hard segments have urethane linkage or the soft segment has higher T_{gs}. In Fig. 3, we can also see that ε_p decreases as the content of hard segment and crosslinking by excess HDI are increased.

Table IV shows the variation of ε_p in the cyclic tensile test when ε_m was adjusted to 50% and liquid nitrogen instead of air (20 °C) was used as a cooling medium. The fact that ε_p values of 6TPU3, 65TPU2, and 65TPU3 do not vary so much after the first tempering cycle, suggests their suitability as shape memory materials at low deformation.

4. Conclusions
1) Segmented thermoplastic polyurethanes, having the amorphous soft segment from 1,3-BD and HDI, and the crystalline segment from BHBP and 2,4-TDI, showed phase separation behavior.

2) The shape memory behavior of these TPUs, utilizing amorphous soft segment domain as reversible phase and crystalline hard segment domain as frozen phase, showed fatigue behavior when the strain was 100% and the hard segment content was 10–20 wt%.

3) The fatigue behavior was reduced when the strain was 50% and hard segment content was 30 wt%, or when crosslinked with excess HDI.

Acknowledgements

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