

Miscibility and shape memory effect of thermoplastic polyurethane blends with phenoxy resin

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Abstract

Segmented thermoplastic polyurethane (TPU) with poly(caprolactone) (PCL) based soft segment and hexamethylene diisocyanate (HDI)/1,4-butane diol (BD)/4,4'-dihydroxy biphenyl (DHBP) based hard segment was blended with phenoxy resin to examine miscibility and shape memory effect. The PCL segment and phenoxy resin made single miscible domain with single glass transition temperature (T_g) which lied between those of PCL segment and phenoxy resin. In the shape memory effect, utilizing this miscible domain as a reversible phase and utilizing phase separated hard segment domain as a fixed structure memorizing the original shape, hysteresis was reduced as the content of hard segment was increased in the blend and the block length of TPU was decreased. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymer blending is an efficient method to obtain new materials with unique or desirable properties. Because it can utilize commercial polymers, it is economically advantageous compared with the synthesis of novel new polymers.

Thermal-responsive shape memory polymers generally consist of two phases, a thermally reversible phase for maintaining transient shape and a fixed structure for memorizing original shape. Crystal, glassy state, entanglement, or crosslinking can be used as a fixed structure memorizing the original shape. Thermally reversible phase is designed to have a large drop in elastic modulus on heating above the shape recovery temperature (T_s). So, the glass transition temperature of amorphous seg-

ment can be used as a T_s [1–3]. When they were deformed at the rubbery plateau above the glass transition temperature (T_g) and subsequently cooled below T_g under constant strain, the deformed shape is fixed because molecular mobilities are frozen. As they were reheated above T_g , the original shape is recovered by the elastic force generated during the deformation. In order to fulfill the various needs on the T_s and the physical properties for shape memory polymers, polymer blend technology can be utilized, because in miscible polymer blend the T_g and physical properties varies smoothly with composition. However, open literatures about the shape memory effect of polymer blends are not so much [4].

It is well known that several aliphatic polyesters are miscible with poly(vinyl chloride) (PVC) [5], poly(styrene-co-acrylonitrile) (SAN) [6], and phenoxy resin [7]. When PVC was blended with segmented thermoplastic polyurethanes (TPUs) based on aliphatic polyester soft segment, we observed that the T_g of miscible PVC/aliphatic polyester segment domain changed smoothly with

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Table 1
Characteristics of TPUs prepared

Sample designation	Feed (mol)						Soft segment content in feed (wt.%)	(η) (dl/g)
	Soft segment		Hard segment					
	PCL2000	PCL4000	HDI	BD	DHBP	M_n^a		
2TPU6	1.0	–	5.2	3.5	0.7	1340	60	0.65
2TPU7	1.0	–	3.4	2.0	0.4	840	70	0.65
4TPU6	–	1.0	10.0	7.6	1.4	2630	60	0.65
4TPU7	–	1.0	6.6	4.7	0.9	1720	70	0.65

^a $M_n = (1+r)/(1-r) \times$ average molecular weight of structural unit of hard segment, where r is the feed mole ratio of hydroxyl group in BD and DHBP/isocyanate group in HDI.

composition and the phase separated hard segment domain acts as a physical crosslinker [8,9]. However, in the blends of TPUs based on aliphatic polyester with SAN or acrylonitrile–butadiene–styrene (ABS) resin, aliphatic polyester segment and SAN were not miscible. They showed two separate T_g s of aliphatic polyester segment and SAN domains, when the content of aliphatic polyester segment in TPU is 20–75 wt.% [10,11].

In this study, we synthesized TPUs with an aliphatic polyester, poly(caprolactone) (PCL) based soft segment and hexamethylene diisocyanate (HDI)/1,4-butane diol (BD)/4,4'-dihydroxy biphenyl (DHBP) based hard segment. The miscibility of these TPUs with phenoxy resin was studied. And the shape memory effect of these blends, utilizing the miscible phenoxy resin/PCL phase as a reversible phase and hard segment domain of TPU as a fixed structure was examined.

2. Experimental procedures

2.1. Materials

The PCL diol (from Daicel) with number average molecular weight (X_n) of 2000 (PCL2000) and 4000 (PCL4000) were dried under vacuum at 80°C for 12 h. Dimethylacetamide (DMAc) was used after dehydration with 4 Å molecular sieve for two days. Phenoxy resin (average molecular weight: 40,000) HDI, BD, DHBP, and dibutyltin dilaurate (DBTDL) (all from Aldrich) were used as received.

2.2. Synthesis of thermoplastic polyurethanes

A 500 ml round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube was used as a reactor. Segmented thermoplastic polyurethanes were synthesized by solution polymerization in DMAc under dry N_2 by one shot method. That is, PCL diol,

BD, DHBP, and HDI were polymerized in the presence of DMAc and catalytic amount of DBTDL for 4 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 was about 25 wt.%. The mole ratio of HDI/(PCL diol + BD + DHBP) was kept at 1/1 to yield linear polymer. The feed ratio, hard segment content, and intrinsic viscosity are shown in Table 1. In the sample designation code, the number preceding TPU means the X_n of soft PCL segment and the number following TPU means the soft segment content. For example, 2TPU6 means that this TPU has the soft PCL segment whose X_n is 2000 and has the soft segment content of 60 wt.%.

2.3. Characterization

The viscosity of TPU solution in DMAc was measured with Ostwald viscometer at 25°C. Blends of phenoxy resin with TPU were prepared by casting the polymer solution in DMAc. DMAc was evaporated at 100°C for 24 h, and the blends were further dried at 25°C under vacuum for the next 24 h. Films for the measurements of thermal and mechanical properties were cast on a glass plate.

Differential scanning calorimeter made by TA Instruments (DSC-2100) was used to study the thermal transitions in blends at a cooling and heating rate of 10°C/min. All runs were carried out with a sample of ≈ 5 mg. After melting for 3 min at 200°C in DSC device, the crystallization temperature (T_{ch}) and the heat of crystallization (ΔH_{ch}) of hard segment, and the crystallization temperature (T_{cs}) and the heat of crystallization (ΔH_{cs}) of PCL segment were measured on cooling scan to -100°C . On the subsequent heating scan after staying 1 min at -100°C , the glass transition temperature (T_g), the melting temperature (T_{ms}) and the heat of fusion (ΔH_{ms}) of PCL segment, the melting temperature (T_{mh}) and the heat of fusion (ΔH_{mh}) of hard segment were measured. The subscripts h and s of above designations

mean that they are the thermal properties of hard segment and soft PCL segment respectively.

Dynamic mechanical properties were determined with a dynamic mechanical thermal analyzer (Rheometry Scientific DMTA MKIII), using a bending mode at a heating rate of 4°C/min and 10 Hz.

Tensile tests were performed using a tensile tester (Tinius Olsen Series 1000), attaching with a constant temperature heating chamber. Microtensile specimens with dimensions of 25 mm length, 5 mm width, and 1 mm thickness were used. The specimens were elongated at the rate of 10 mm/min.

3. Results and discussion

3.1. Thermal properties

The DSC thermograms of 2TPU6/phenoxy resin blends are shown in Fig. 1 and the numerical values from these thermograms are given in Table 2, together with those of other TPU/phenoxy resin blends. All the T_g s of TPUs shown in Table 2 lies in the temperature range -56.2°C to -62.4°C . In TPUs, T_g of soft segment generally increases as some of hard segment is dissolved into soft segment domain due to phase mixing [12]. As the T_g of pure PCL is about -60°C [7], the T_g s of TPUs

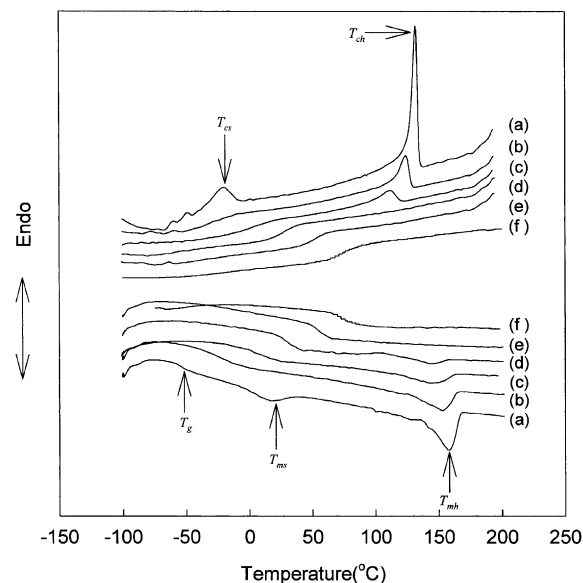


Fig. 1. DSC thermograms of 2TPU6/phenoxy resin blends obtained on cooling (upper thermograms with exothermic peaks) and subsequent heating (lower thermograms with endothermic peaks) scans: (a) 10/0, (b) 8/2, (c) 6/4, (d) 4/6, (e) 2/8 and (f) 0/10 by weight.

in Table 2, show that the dissolution of hard segment into PCL domain is not high.

All the TPU blends with phenoxy resin show a single T_g that varies smoothly with composition. This shows that PCL segment and phenoxy resin are miscible in blends, because a single T_g which lies between the T_g s of pure component is the generally accepted criterion for the blend miscibility. Disappeared crystallization and melting peaks of PCL segment in the blends with phenoxy resin show that the crystallization of PCL segment is severely hindered in the miscible blend [7].

Fig. 1 and Table 2 show that T_{mh} and ΔH_{mh} decrease from those of pure TPUs when phenoxy resin is blended. In the crystalline polymer the decrease in change in free energy by a miscible diluent results in a decreased equilibrium melting temperature [13]. So, the decrease of T_{mh} , although it is not an equilibrium value and may contain kinetic contributions, shows that the partial dissolution of PCL segment or phenoxy resin into hard segment domain is increased by the added phenoxy resin.

3.2. Dynamic mechanical properties

Dynamic mechanical properties of TPU blends with phenoxy resins are shown in Figs. 2–5. In all the thermograms of TPUs, we can see the gradual decrease of tensile storage modulus, E' at the temperature range between T_g and T_{ms} , and another drop of E' at T_{ms} . The rubbery plateau above T_{ms} of TPU extends up to 100–150°C. The $\tan \delta$ peak due to glass transition varies smoothly with composition in the temperature range between those of TPU and phenoxy resin, which shows that PCL segment and phenoxy resin are miscible as in the result of DSC. The glassy moduli below T_g generally increase from those of TPUs when some amount of phenoxy resin is blended with TPUs. However, 4TPU6 and 4TPU7 blends show some decrease of glassy moduli from those of TPUs when the weight ratio of TPU/phenoxy resin is 8/2. This seems to be due to the decreased crystallinity of PCL phase in the presence of phenoxy resin. The value of rubbery plateau modulus and the upper limit temperatures that rubbery plateau can persist generally decrease from those of TPUs as the amount of phenoxy resin in TPU/phenoxy resin blend is increased. The decrease in total amount of hard segment, the decreased ΔH_{mh} and T_{mh} , and the enhanced partial dissolution of hard segment into PCL segment–phenoxy resin domain when the amount of phenoxy resin in blend is increased, seem to be the causes of these variation of rubbery plateau. Because phenoxy resin has only one amorphous domain, it does not have rubbery plateau and flows when heated above T_g . However, TPU/phenoxy resin blends have rubbery plateau even when the blend ratio is 2/8. This shows that hard

Table 2
Thermal properties of TPU/phenoxy resin blends

Blend (by weight)	Cooling scan				Heating scan				
	T_{cs} (°C)	ΔH_{cs} (J/g)	T_{ch} (°C)	ΔH_{ch} (J/g)	T_g (°C)	T_{ms} (°C)	ΔH_{ms} (J/g)	T_{mh} (°C)	ΔH_{mh} (J/g)
<i>2TPU6/phenoxy resin</i>									
10/0	-21.3	8.2	132.0	23.9	-62.4	8.0	5.8	158.4	19.6
8/2	-	-	124.0	12.9	6.5	-	-	152.8	14.9
6/4	-	-	112.2	5.7	36.7	-	-	144.7	9.0
4/6	-	-	-	-	60.6	-	-	128.2	3.9
2/8	-	-	-	-	79.9	-	-	-	-
0/10	-	-	-	-	85.4	-	-	-	-
<i>2TPU7/phenoxy resin</i>									
10/0	-17.6	9.5	118.0	7.0	-56.5	22.6	11.8	143.3	13.0
8/2	-	-	104.6	3.3	-6.3	-	-	123.3	9.0
6/4	-	-	107.8	3.2	25.8	-	-	129.8	4.7
4/6	-	-	-	-	49.6	-	-	-	-
2/8	-	-	-	-	73.5	-	-	-	-
0/10	-	-	-	-	85.4	-	-	-	-
<i>4TPU6/phenoxy resin</i>									
10/0	3.1	21.3	137.7	22.8	-59.2	42.5	21.4	165.1	23.3
8/2	-	-	99.4	6.9	-1.5	-	-	142.3	11.3
6/4	-	-	93.8	2.5	30.9	-	-	137.6	7.3
4/6	-	-	-	-	53.6	-	-	143.5	3.8
2/8	-	-	-	-	70.6	-	-	-	-
0/10	-	-	-	-	85.4	-	-	-	-
<i>4TPU7/phenoxy resin</i>									
10/0	5.6	25.3	132.5	13.5	-57.4	44.4	24.7	159.9	13.4
8/2	-	-	105.4	2.8	8.4	-22.7	2.9	141.4	6.9
6/4	-	-	97.2	1.3	21.4	-	-	135.5	4.5
4/6	-	-	-	-	48.6	-	-	131.2	1.6
2/8	-	-	-	-	64.6	-	-	-	-
0/10	-	-	-	-	85.4	-	-	-	-

T_g is the glass transition temperature, T_{cs} and T_{ms} the crystallization and melting temperatures of soft PCL segment, T_{ch} and T_{mh} the crystallization and melting temperatures of hard segment.

segment domain is phase separated and does its role as a physical crosslinker. These results suggest that TPU/phenoxy resin blend can have a shape memory effect when the miscible PCL segment/phenoxy resin domain is used as a reversible phase and hard segment domain is used as a fixed structure. In this case T_g is used as shape recovery temperature (T_s) and this temperature can be designed variously by the blend ratio and kind of TPU.

3.3. Shape memory effect

In order to examine the shape memory effect of TPU/phenoxy resin blend, utilizing the miscible PCL segment/phenoxy resin phase as a reversible phase and hard segment domain as a fixed structure, cyclic tensile test was carried out. The result for 2TPU6/phenoxy resin (4/6 by

weight) blend is shown in Fig. 6. Sample was elongated at rubbery plateau (75°C, $\approx T_g + 15^\circ\text{C}$) to 100% strain (ϵ_m) at a constant elongation rate of 10 mm/min. While maintaining the strain at ϵ_m , sample was quenched to glassy state (50°C, $\approx T_g - 10^\circ\text{C}$) and unloaded. Upon removing the constraint at 50°C small recovery of strain to ϵ_u occurs. The sample was subsequently heated to 75°C in 5 min, and stayed 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. In Fig. 6, we can see that hysteresis develops, i.e. ϵ_p increases and stress for deformation decreases, as the thermomechanical cycles are repeated. The measured ϵ_p values of TPU/phenoxy resin blends (6/4 and 4/6 by weight) are shown in Table 3. In Table 3, we can see that ϵ_p values generally increase by repeated deformation in the range of 9–27%. However there exist some differences according to the

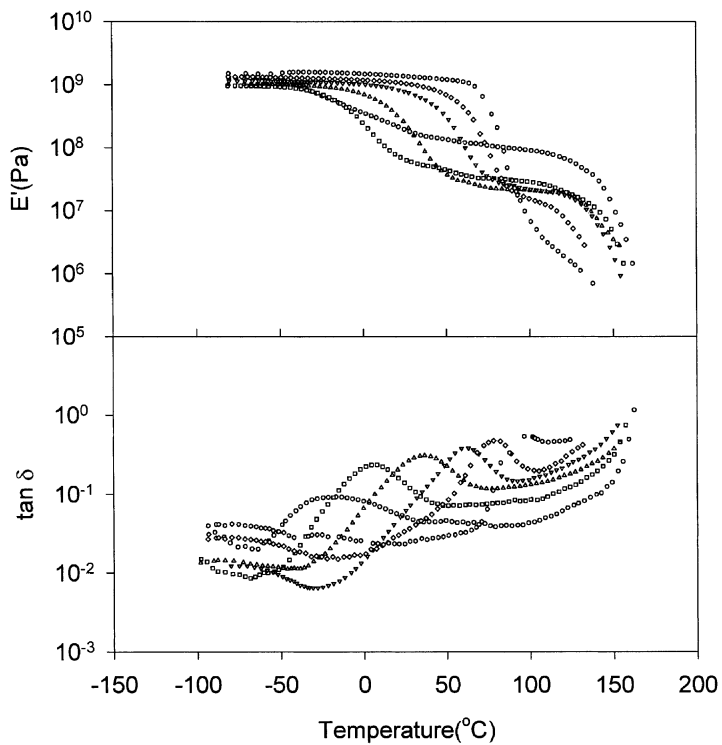


Fig. 2. Storage tensile modulus and $\tan \delta$ of 2TPU6/phenoxy resin blends: (○) 10/0, (□) 8/2, (△) 6/4, (▽) 4/6, (◇) 2/8 and (○) 0/10.

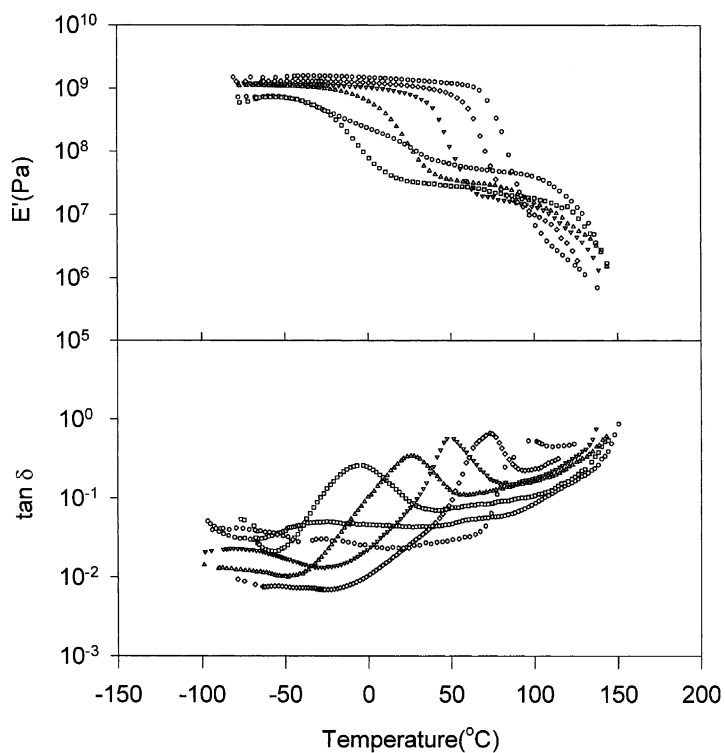


Fig. 3. Storage tensile modulus and $\tan \delta$ of 2TPU7/phenoxy resin blends: (○) 10/0, (□) 8/2, (△) 6/4, (▽) 4/6, (◇) 2/8 and (○) 0/10.

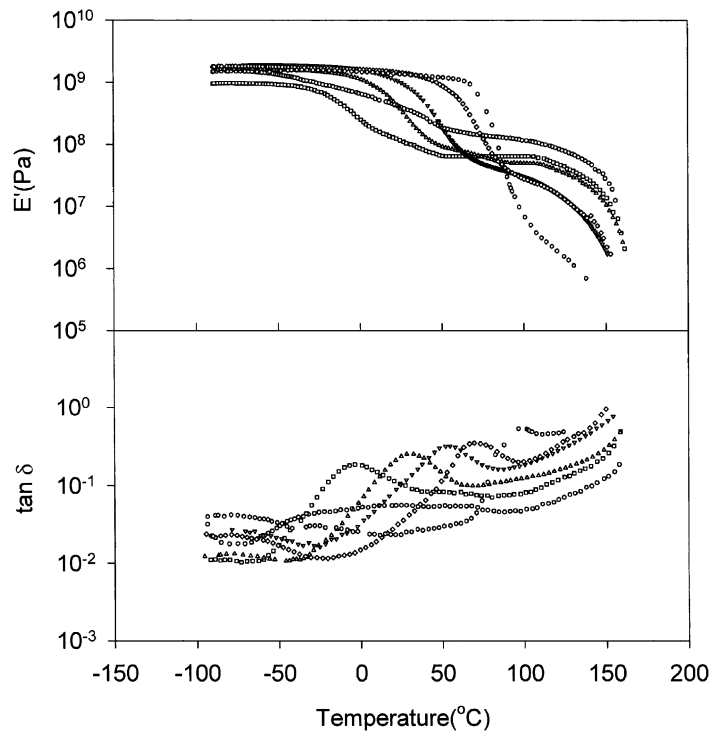


Fig. 4. Storage tensile modulus and $\tan \delta$ of 4TPU6/phenoxy resin blends: (○) 10/0, (□) 8/2, (△) 6/4, (▽) 4/6, (◇) 2/8 and (○) 0/10.

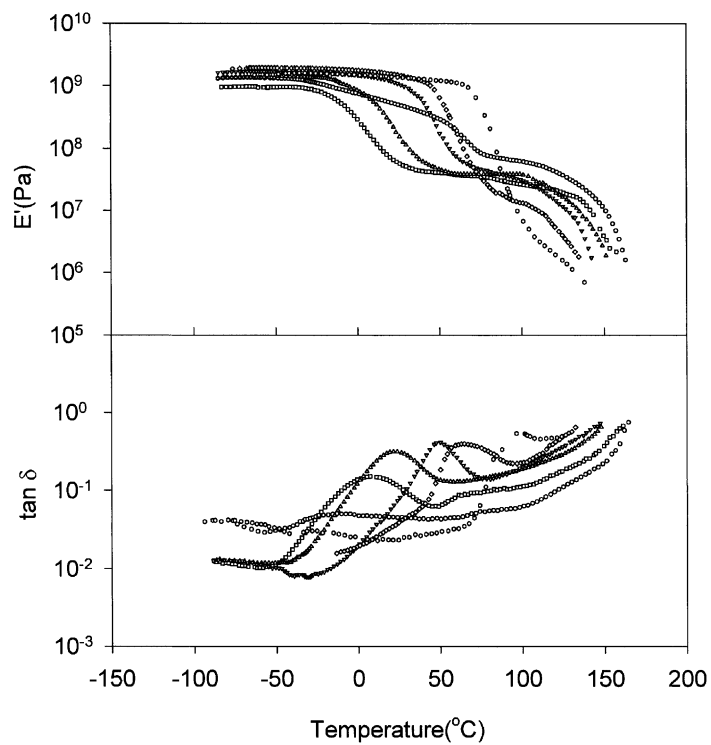


Fig. 5. Storage tensile modulus and $\tan \delta$ of 4TPU7/phenoxy resin blends: (○) 10/0, (□) 8/2, (△) 6/4, (▽) 4/6, (◇) 2/8 and (○) 0/10.

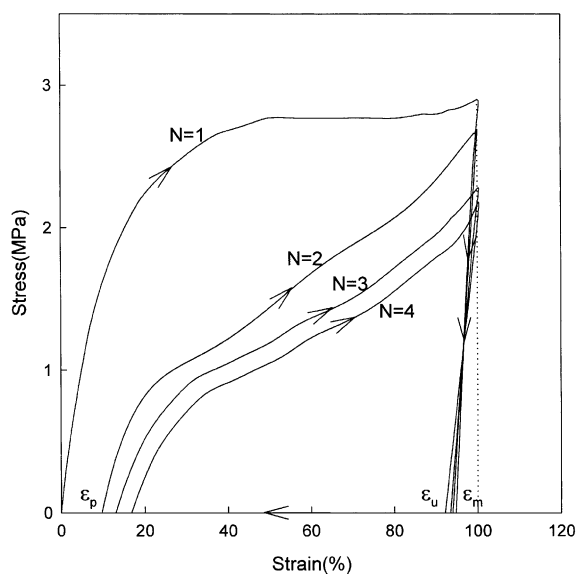


Fig. 6. Cyclic tensile behavior of 2TPU6/phenoxy resin (4/6 by weight) blend.

kind and the composition of TPU in blends. That is, ϵ_p values of the blends are: 2TPU6 < 2TPU7 and 4TPU6 < 4TPU7 according to the kind of TPU when the blend weight ratio is fixed, and 6/4 < 4/6 according to the blend weight ratio of TPU/phenoxy resin when the kind of TPU is fixed. These results show that higher amount of hard segment which acts as a fixed structure memorizing the original shape is affirmative for shape recovery. The results, that the ϵ_p values of 2TPU6 blends are smaller than those of 4TPU6 blends, and the ϵ_p values of 2TPU7 blends are smaller than those of 4TPU7

blends, suggest that shorter block length of TPU is affirmative for shape recovery as in our previous studies [14,15]. Because the hysteresis of TPU can be caused by the plastic deformation of hard segment domains and orientation [16,17], above results show that these changes are minimized at shorter block length. Because finer distribution of hard segment can be promoted by the enhanced partial miscibility between hard and soft segments at shorter block length [18], this finer distribution of hard segment which acts as a fixed structure memorizing the original shape seems to be the cause of reduced hysteresis.

4. Conclusions

When TPUs with PCL based soft segment and HDI/BD/DHBP based hard segment were blended with phenoxy resin:

1. The PCL segment in TPU and phenoxy resin made a miscible domain whose T_g varies smoothly with relative composition of PCL segment and phenoxy resin, and hard segment made a separate domain.
2. The TPU/phenoxy resin blends had shape memory effect when the miscible PCL segment/phenoxy resin domain was utilized as a reversible phase and hard segment domain was utilized as a fixed structure. And the T_g of blends, on heating above that the original shape can be recovered, could be designed variously by the blend ratio of TPU and phenoxy resin and the kind of TPU.
3. The hysteresis in shape recovery was reduced when the content of hard segment in blend was increased and the block length of TPU was decreased.

Table 3
Residual strain after cyclic tensile test

Sample (weight ratio)	Temperature (°C)			ϵ_p (%) after		
	Elongated	Quenched	Recovered	$N = 1$	$N = 2$	$N = 3$
<i>2TPU6/phenoxy resin</i>						
6/4	50	25	50	9.4	12.6	15.5
4/6	75	50	75	9.8	13.5	15.8
<i>2TPU7/phenoxy resin</i>						
6/4	40	15	40	13.9	19.5	21.1
4/6	65	40	65	14.2	20.3	21.4
<i>4TPU6/phenoxy resin</i>						
6/4	45	20	45	14.2	17.0	17.7
4/6	70	45	70	16.5	22.1	22.7
<i>4TPU7/phenoxy resin</i>						
6/4	35	10	35	15.4	19.9	22.4
4/6	65	40	65	20.3	21.4	26.8

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