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Miscibility and shape memory property of poly(vinyl chloride)/thermoplastic polyurethane blends

HAN MO JEONG, JI HUN SONG
Research Center for Machine Parts and Materials Processing, Department of Chemistry, University of Ulsan, Ulsan 680-749, Republic of Korea
E-mail: hmjeong@uou.ulsan.ac.kr

SANG YOON LEE, BYUNG KYU KIM
Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Republic of Korea

The miscibility and the shape memory effect of PVC blends with segmented thermoplastic polyurethanes (TPUs), synthesized from diol-terminated polycaprolactone (PCL), hexamethylene diisocyanate, 4,4′-dihydroxy biphenyl, were studied. PVC was miscible with PCL segment in TPU and the glass transition temperature of this miscible amorphous domain varied smoothly with composition. When PVC was blended with TPU by the weight ratio of 8/2, the hysterisis in repeated cyclic tensile test was reduced compared with PVC. However, in 6/4 blends, unrecoverable permanent deformation was increased compared with PVC. Dynamic mechanical properties were examined to explain these results.

1. Introduction

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 segment or the melting temperature of crystalline segment can be used as a T_s [1–3].

Because physical entanglement can do its role as a fixed structure, some amorphous polymers such as poly(vinyl chloride)(PVC), poly(methylmethacrylate), or polycarbonate show shape memory effect [4, 5]. That is, when they were deformed at the rubbery plateau just above the glass transition temperature (T_g) and subsequently cooled below T_g under constant strain, the deformed shape is fixed because the micro-Brownian movement is frozen. When they were reheated above T_g, the original shape is recovered by the elastic force generated during the deformation. However, hysterisis increases by the repeated deformation-recovery cycles, when the fixed structure is not rigid enough. In order to minimize the hysterisis, high molecular weight material is used for polynorbornene to enhance the physical entanglement [6], and crosslinked materials are utilized for polyethylene or PVC [7, 8].

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 shape memory effect of polymer blends are limited [9].

When PVC was blended with segmented thermoplastic polyurethanes (TPUs), we observed that the T_g of the miscible PVC/aliphatic polyester segment domain changed smoothly with composition and the phase separated hard segment domain did its role as a physical crosslinker [10–12].

So, in this study we blended PVC with some amounts of TPUs to get the shape memory polymer blends with various T_s (i.e. T_g) and with fixed structure strengthened by the hard segment of TPU. The miscibility, the thermal and mechanical properties, and the shape memory effect of these blends were examined.

2. Experimental procedures

2.1. Materials

The polycaprolactone (PCL) diol (from Daicel) with number average molecular weight (X_n) of 2000 and 4000 were dried under vacuum at 80°C for 12 h. Dimethylacetamide (DMAc) was used after dehydration with 4 Å molecular sieve for 2 days. PVC (average molecular weight: 95000), hexamethylene diisocyanate (HDI), 4,4′-dihydroxy biphenyl(DHBP), and dibutyltin dilaurate(DBTDL) (all from Aldrich) were used as received.

TABLE I Characteristics of TPUs prepared

	Feed (mol)				Hard segment content (wt%)		
	Hard segment		Soft segment				
Sample designation	HDI	DHBP	PCL2000	PCL4000	In feed	In polymer[a]	[η] (m^3/kg)
2TPU4	8.38	6.38	2.00	–	40	38	5.3
2TPU6	17.56	15.56	2.00	–	60	62	5.9
4TPU4	7.86	6.86	–	1.00	40	41	5.1
4TPU6	17.06	16.06	–	1.00	60	63	5.7

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

2.2. Synthesis of TPUs

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, 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 + DHBP) was kept at 1.0/1.0 to yield linear polymer. The feed ratio, hard segment content, and intrinsic viscosity are shown in Table I. In the sample designation code, the number preceding TPU means the X_n of soft PCL segment and the number following TPU means the content of hard segment. For example, 2TPU4 means that this TPU has the soft PCL segment whose X_n is 2000 and has the hard segment content of 40 wt%.

2.3. Characterization

The viscosity of TPU solution in DMAc was measured with Ostwald viscometer at 25°C.

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

Blends of PVC 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 calorimetry (d.s.c.) was carried out with a TA Instruments DSC-2100 at a heating rate of 10°C/min. All runs were carried out with a sample of ca. 5 mg.

FT i.r. spectra were taken from Nicolet model Impact 400D spectrophotometer. To get the thin films of PVC blends with TPUs adequate for the FT i.r. measurement, the blended solution in DMAc was cast on an NaCl i.r. cell.

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

Tensile test were done using a tensile tester (Tinius Olsen Series 1000), attached with a constant

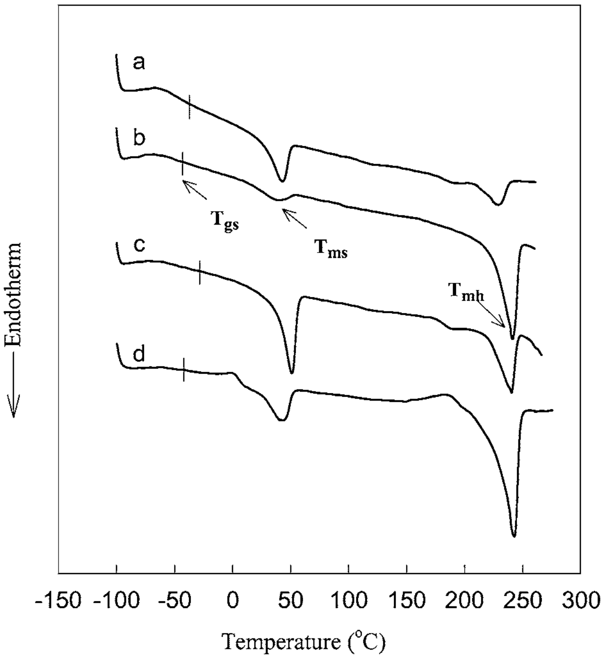


Figure 1 D.s.c. thermograms of TPUs: (a) 2TPU4, (b) 2TPU6, (c) 4TPU4, (d) 4TPU6.

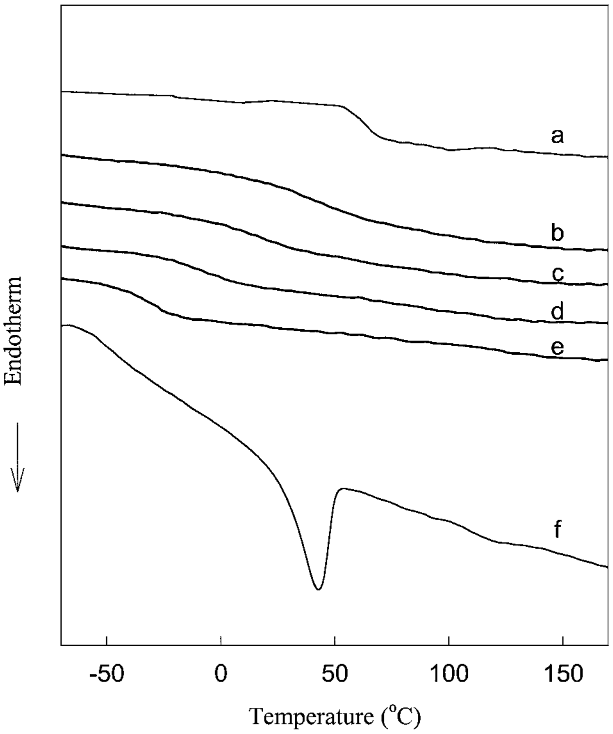
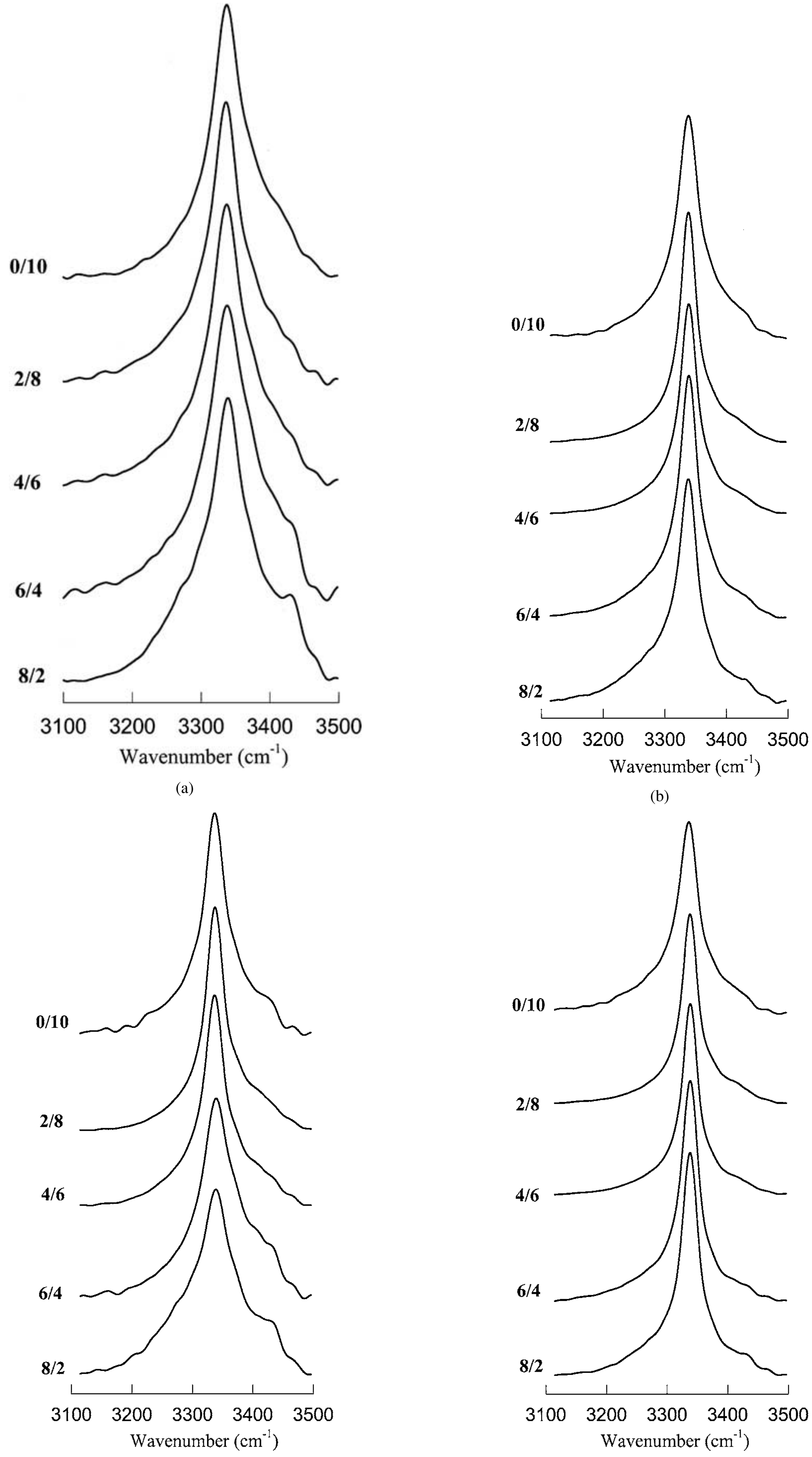


Figure 2 D.s.c. thermograms of PVC/2TPU4 blends: (a) 10/0, (b) 8/2, (c) 6/4, (d) 4/6, (e) 2/8 (f) 0/10 by weight.



(a) (b) (c) (d)

Figure 3 FT i.r. spectra of PVC blends with (a) 2TPU4, (b) 2TPU6, (c) 4TPU4, (d) 4TPU6 in the region of 3100–3500 cm^{-1}. (Number on the spectrum is the weight ratio PVC/TPU.)

temperature heating chamber. Microtensile specimen for test has the dimensions of 25 mm length, 5 mm width, and 1 mm thickness. The specimen was elongated at the rate of 10 mm/min.

The recovery at various temperature was measured by preserving the elongated film at the recovery temperature for 10 min. Before the recovery test, film was elongated to 100% strain at $T_g + 30°\mathrm{C}$ and subsequently cooled to 20°C at 100% strain. The recovery was calculated by the following equation.

$$\text{Recovery (\%)} = \frac{\text{recovered length}}{\text{elongated length}} \times 100$$

3. Results and discussion

3.1. Thermal properties

The d.s.c. thermograms obtained on heating of TPUs used in this study are shown in Fig. 1 and the thermal properties are summarized in Table II. All the thermograms show the heat capacity change at the glass transition temperature of soft PCL segment (T_{gs}), the melting endothermic peak of soft segment (T_{ms}), and the melting endothermic peak of hard segment (T_{mh}). These thermograms show that these TPUs are phase separated and both soft and hard segment domains are crystalline. When we compare the thermal properties of 2TPU4 with those of 4TPU4, or compare 2TPU6 with 4TPU6 in Table II, we can see that T_{ms}, T_{mh}, the heat of fusion at T_{ms} (ΔH_{ms}), the heat of fusion at T_{mh}(ΔH_{mh}) all decrease as the block length of PCL segment is decreased at the fixed content of hard segment. These results show that partial phase mixing between soft and hard segments is enhanced at shorter block length of PCL segment [13].

In Fig. 2, we can see that PVC/2TPU4 blends have single T_g that moves smoothly with composition at the temperature range between the T_g's of PVC and 2TPU4. No endothermic melting peak of PCL segment was observed upto 200°C, where the thermal degradation of PVC occurred. These results show that PVC and PCL soft segment are miscible and the crystallization of PCL segment is hindered severely even when the content of PVC in PVC/2TPU4 blend is 20 wt% [14]. The PVC blends with other TPUs also showed similar T_g behavior, and the results are shown in Table III, and this shows that all the TPUs make an amorphous region of miscible PVC/PCL segment domain in blends with PVC.

3.2. FT i.r. spectra

The FT i.r. spectra in the region 3100–3500 cm^{-1} for PVC/TPU blends are given in Fig. 3. The spectra do not vary so much in blends from that of TPU. That is, the large peak in the region 3300–3400 cm^{-1}, which can be assigned as peaks due to stretching vibration of hydrogen-bonded NH group [12], shows that most of NH groups are hydrogen bonded. Small shoulder at 3420 cm^{-1}, which can be assigned as a peak due to stretching vibration of free NH [12], develops slightly only when the PVC content in PVC/TPU blend is 80 wt% and hard segment content in TPU is 40 wt%. This result shows that the structure of hard segment does not vary so much in the blends with PVC. So, the results from d.s.c. and FT i.r. suggest that PVC/TPU blends have the amorphous domain of PVC/PCL mixed phase and crystalline domain of hard segment in TPU.

3.3. Dynamic mechanical properties

Dynamic mechanical properties of PVC blends with 2TPU4 are shown in Fig. 4. We can see that the tan δ peak moves smoothly with composition in the temperature range between those of PVC and 2TPU4, which shows that PVC and PCL segment are miscible as in the results of d.s.c.. The higher rubbery plateau modulus

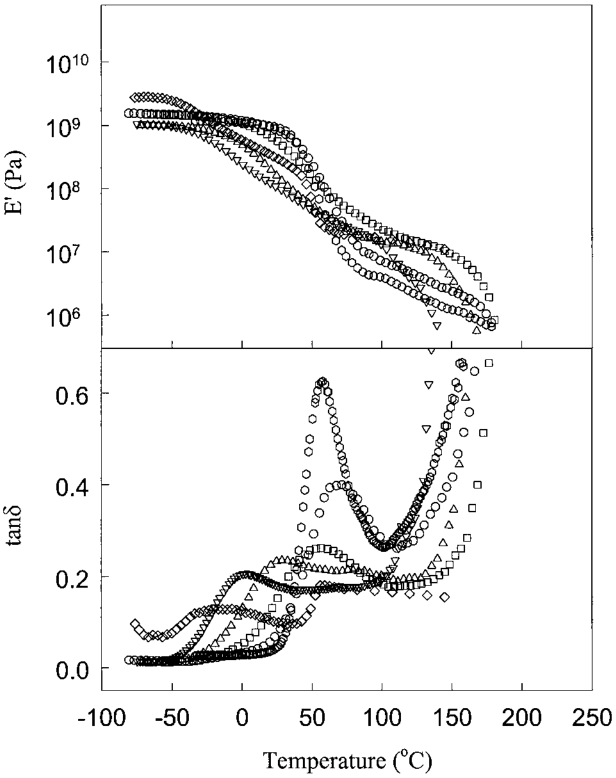


Figure 4 Storage tensile modulus and tan δ of PVC/2TPU4 blend: (⬡) 10/0, (□) 8/2, (○) 6/4, (△) 4/6, (▽) 2/8, (◇) 0/10 by weight.

TABLE II Thermal properties of TPUs

	Soft segment			Hard segment	
Sample	T_{gs} (°C)	T_{ms} (°C)	ΔH_{ms} (J/g-soft segment)	T_{mh} (°C)	ΔH_{mh} (J/g-hard segment)
2TPU4	−40.7	42.6	36.0	229.0	51.7
2TPU6	−47.5	36.5	21.6	241.2	87.8
4TPU4	−37.8	50.9	60.1	240.2	80.5
4TPU6	−47.0	40.4	49.1	242.8	109.2

TABLE III Thermal properties of TPUs

	T_g(°C) of PVC/TPU blends at the weight ratio of					
Sample	10/0	8/2	6/4	4/6	2/8	0/10
PVC blends with						
2TPU4	66.1	46.1	18.7	−7.3	−27.0	−40.7
2TPU6	66.1	47.7	44.2	7.7	−14.1	−47.5
4TPU4	66.1	42.8	17.4	−18.1	−34.8	−37.8
4TPU6	66.1	55.2	48.3	7.4	−13.9	−47.0

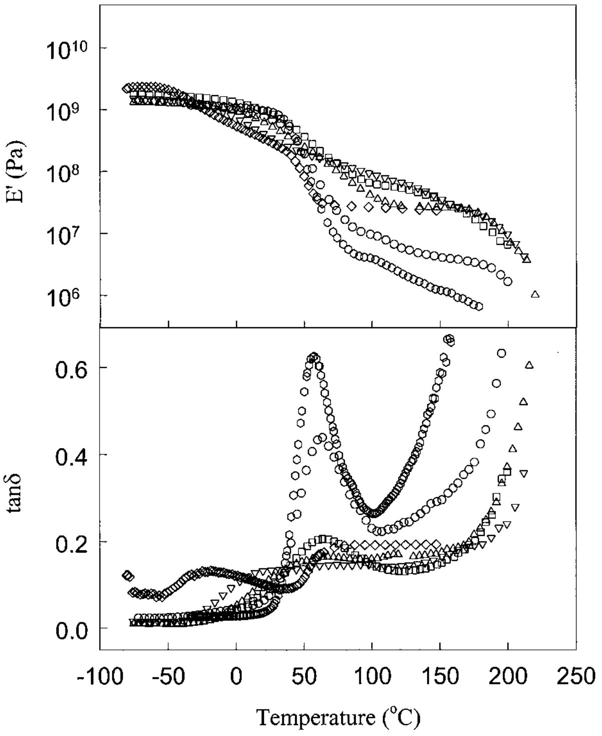


Figure 5 Storage tensile modulus and tan δ of PVC/2TPU6 blend: (◯) 10/0, (□) 8/2, (○) 6/4, (△) 4/6, (▽) 2/8, (◇) 0/10 by weight.

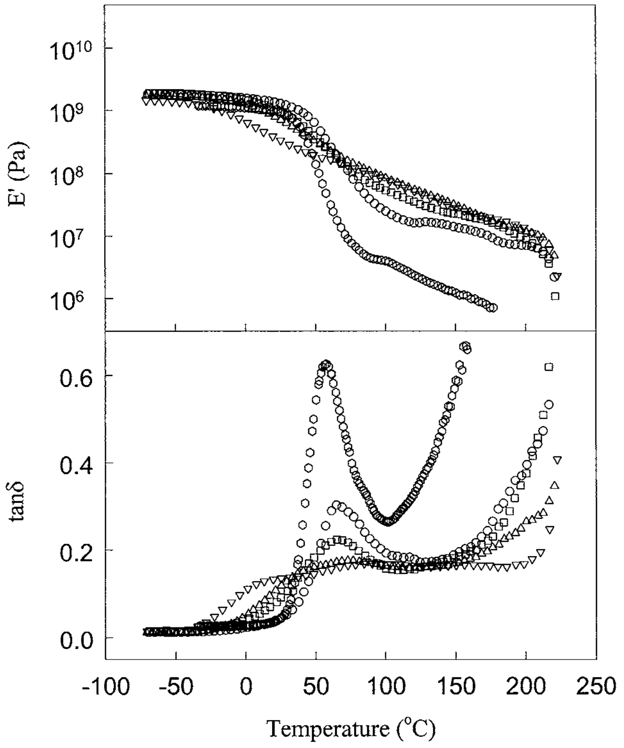


Figure 7 Storage tensile modulus and tan δ of PVC/4TPU6 blend: (◯) 10/0, (□) 8/2, (○) 6/4, (△) 4/6, (▽) 2/8 by weight.

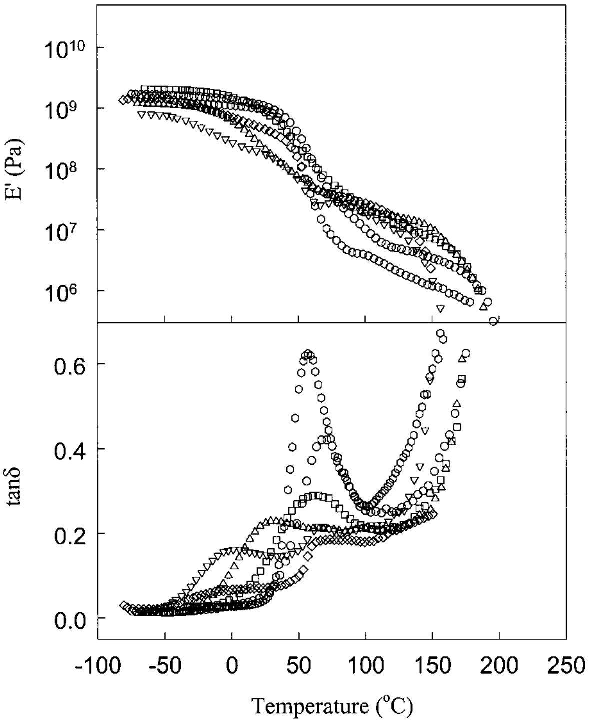


Figure 6 Storage tensile modulus and tan δ of PVC/4TPU4 blend: (◯) 10/0, (□) 8/2, (○) 6/4, (△) 4/6, (▽) 2/8, (◇) 0/10 by weight.

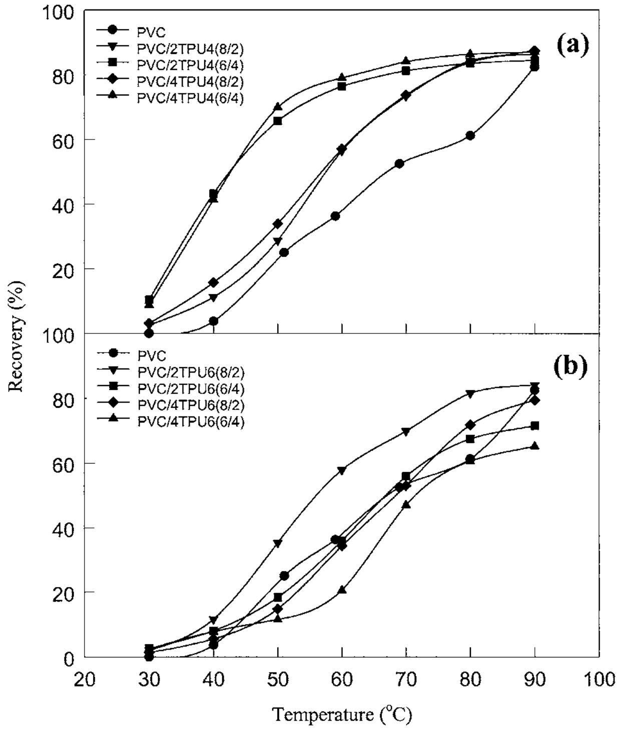


Figure 8 Recovery of PVC/TPU blends.

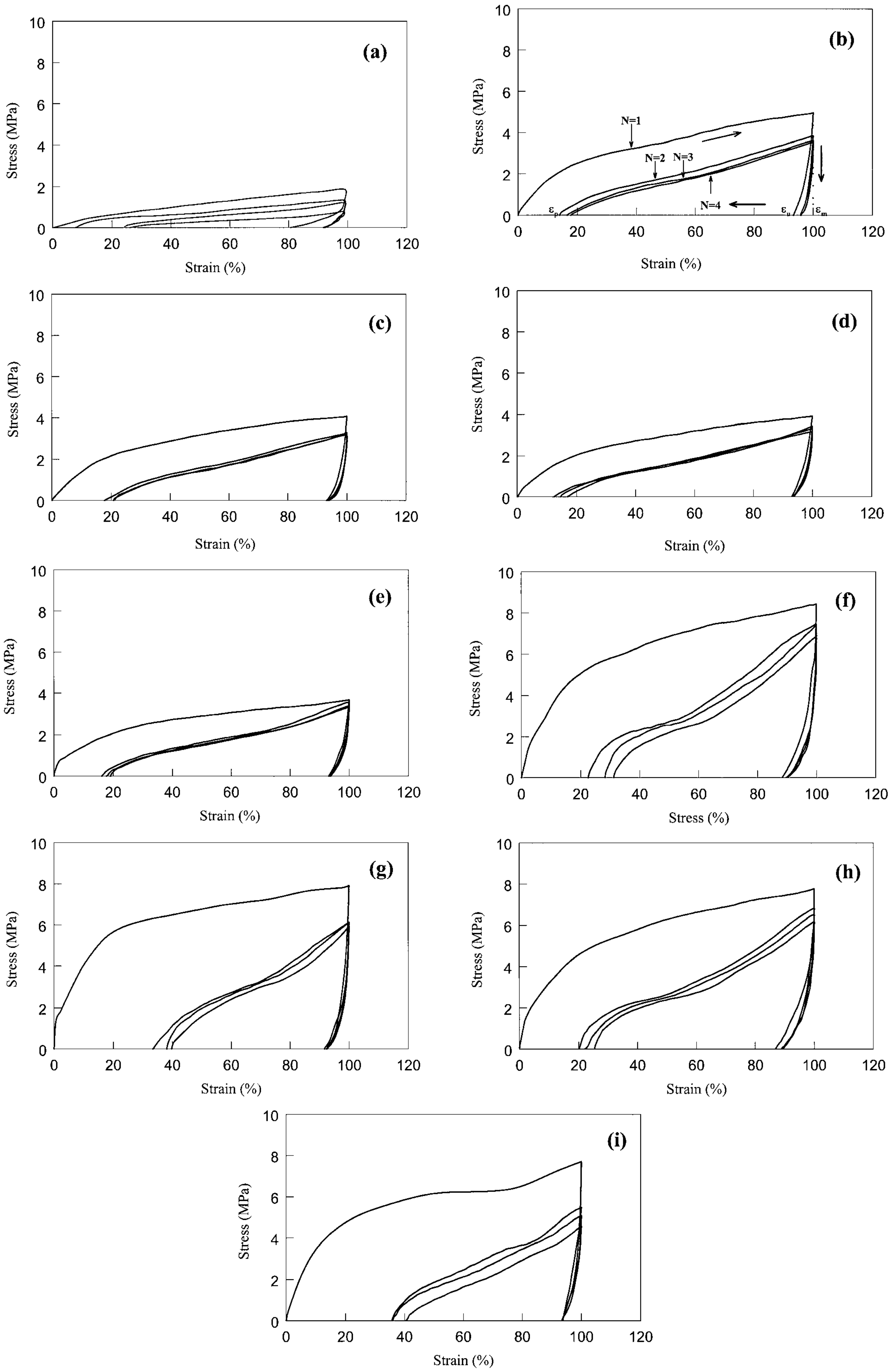


Figure 9 Cyclic tensile behavior of (a) PVC, and (b) PVC/2TPU4(8/2), (c) PVC/2TPU6(8/2), (d) PVC/4TPU4(8/2), (e) PVC/4TPU6(8/2), (f) PVC/2TPU4(6/4), (g) PVC/2TPU6(6/4), (h) PVC/4TPU4(6/4), (i) PVC/4TPU6(6/4) blends.

of PVC/2TPU4 blends compared with PVC homopolymer shows that hard segment domain do effectively its role as a physical crosslinker or filler at rubbery state. The PVC/2TPU6 blends in Fig. 5 also show similar variation of tan δ peak. However the increase of rubbery plateau modulus is more evident due to the higher content of hard segment in TPU. In Figs 6 and 7, we can also observe similar behaviors in tan δ and in rubbery plateau modulus of the PVC blends with 4TPU4 or 4TPU6. All these results on dynamic mechanical properties support that PVC/TPU blends are phase separated into hard segment domain and the miscible domain of PVC/PCL segment mixture.

3.4. Shape memory effect

The results of recovery test are shown in Fig. 8. We can see in Fig. 8a that the recovery temperature moves to lower temperature than that of PVC as some amount of 2TPU4 or 4TPU4 is blended with PVC, as anticipated from the T_g behavior of Table III. However, the recovery temperature does not reduce so much in Fig. 8b when 2TPU6 or 4TPU6 is blended with PVC. The broad glass-rubber transition region and high value of rubbery plateau modulus (Figs 4–7) seem to be the causes. These results show that TPUs with PCL segment as a major component can be used to modify the shape recovery temperature (T_s) of PVC effectively.

To examine the shape memory effect of PVC and PVC/TPU blends, utilizing the amorphous domain of miscible PVC/PCL segment phase as a reversible phase, cyclic tensile test was carried out [1, 15]. As shown in Fig. 9, sample was elongated at 30°C above the T_g of reversible phase to 100% strain (ε_m) at a constant elongation rate of 10 mm/min. While maintaining the strain at ε_m, sample was cooled to 20°C and unloaded. Upon removing the constraint at 20°C, small recovery of strain to ε_u occurs. The sample was subsequently heated to $T_g + 30°\text{C}$ 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. Fig. 9a shows that PVC deforms at small stress less than 2 MPa, and that hysterisis develops, i.e. ε_p increases and stress for deformation decreases, as the thermomechanical cycles are repeated. This shows that the physical entanglement of PVC chains are not rigid enough to sustain its original shape when the deformation-recovery is repeated at rubbery plateau. When PVC was blended with TPUs by the weight ration of 8/2, the stress for deformation increases and the cyclic tensile test curves maintain their shapes almost identically after first tempering cycle, as shown in Fig. 9b–e. This shows that the fixed structure memorizing the original shape is strengthened by the presence of hard segment domain in TPU. However, we can see in Fig. 9f–i that large value of ε_p develops at the first tempering cycle when PVC was blended with TPUs by the weight ratio of 6/4. This shows that when the ratio of glassy/rubbery plateau modulus is reduced much than one hundred (Figs 4–7), the permanent deformation in hard segment domain is liable to occur together with the recoverable deformation of reversible phase of miscible PVC/PCL segment, even at rubbery plateau.

4. Conclusions

When PVC was blended with TPU based on PCL diol, DHBP, and HDI:

1. The blends were phase separated into the domain of hard segment in TPU, and miscible domain of PVC/PCL segment whose T_g varied smoothly with the relative compositions of PVC and PCL segment.
2. The hysterisis of PVC after first tempering cycle in repeated cyclic tensile test was reduced when PVC was blended with TPU by the weight ratio of 8/2. This result shows that the fixed structure memorizing the original shape is strengthened by the presence of hard segment domain.
3. When PVC was blended with TPU by the weight ratio of 6/4, the unrecovered deformation in the first tempering cycle was increased. This result show that the permanent deformation in fixed structure, occurred together with the recoverable deformation of reversible phase of miscible PVC/PCL segment, become more evident at rubbery state when the modulus ratio of glassy/rubbery state was much reduced than one hundred.

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