

## Facile Preparation of Shape Memory Polyurethanes by Polyurethanes Blending

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**ABSTRACT:** This article presents a facile preparation method of shape memory polyurethane (SMPU) by polyurethane blending from commercial thermoplastic polyurethane (PUA) with designed polyurethane (PUB). Structure, morphology, and shape memory behaviors of SMPU blends are investigated systematically. The results show that the PUB and PUA are miscible in the SMPU blends. When the PUB content is higher than 40 wt %, the  $T_g$  of SMPU blends is adjusted to above room temperature. As the PUA content increases, the PUA phase changes gradually from a droplet-like dispersion phase to continuous soft phase, whereas the PUB phase changes from a continuous hard phase to a droplet-like dispersion hard phase. SMPU blends show good shape memory effect when the PUA is blended with more than 40 wt % PUB. Thus, the commercialization of SMPU can be promoted greatly through the polyurethane blending from the commercial thermoplastic polyurethanes with polyurethane containing higher hard segment content.

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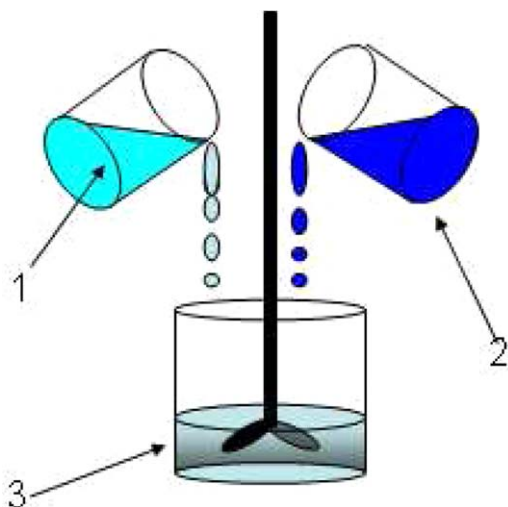
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### INTRODUCTION

Shape memory polymers (SMPs) have attracted significant attentions in recent years as they have the capability of fixing a temporary shape and recovering their permanent shape by applying an external stimulus, such as light, heat, humidity etc.<sup>1–3</sup>. Generally, SMPs are composed of two components: netpoint and switch phase. The netpoint can be achieved by either physical interactions or chemical bonds, and the switch phase can be either semicrystalline or amorphous phase.<sup>1</sup> For practical applications at room temperature, the SMPs should have high shape fixity and shape recovery as well as a suitable shape recovery temperature. Thus, the transition temperature which is usually corresponded to glass transition temperature ( $T_g$ ) or melting temperature ( $T_m$ ) of switch phase is designed to a little higher than the room temperature. Shape memory polyurethane (SMPU) is an important class of SMPs.<sup>4–6</sup> In the segmented SMPUs, the hard segment serves as the netpoints determining the permanent shape and the soft segment controls the fixing and recovering of temporary shape. By varying the hard segment content (HSC) and soft segment length (SSL), the shape memory effect can be adjusted easily. For example, in the SMPUs based on semicrystalline soft phase, the shape fixity increases with SSL, whereas it decreases with HSC. The shape recovery decreases with SSL and HSC when the HSC reaches a threshold value.<sup>7</sup> In the SMPU with amor-

phous soft phase, the shape recovery temperature increases as the HSC increases.<sup>8,9</sup> Thus, a designed shape recovery temperature can be achieved by adjusting the HSC.<sup>10–13</sup> However, in the previous literatures, the SMPUs are generally synthesized by chemistry polyaddition reaction. The molecular structure and morphology are well defined during the synthesized process. It is difficult to adjust the shape memory effect after the composition of SMPU is defined.

In addition to chemical synthesis, physical method like polymer blending is another alternative method to prepare SMPs.<sup>14–18</sup> As compared with the chemical synthesis, polymer blending offers a much simple way to fabricate various multifunctional SMPs. For example, Chang et al. prepared novel SMPs: XPCL/ENR blends by blending end-carboxylated telechelic poly( $\epsilon$ -caprolactone) (PCL) with epoxidized natural rubber.<sup>17</sup> Zhang et al. prepared polyamide (PAE)/polylactide (PLA) blends exhibited good shape memory effect by melt blending of PLA and PAE.<sup>19</sup> Liu et al. prepared linear low-density polyethylene (LLDPE)/polypropylene (PP) SMPs blends by blending with moderate cross-linked LLDPE-PP blend as compatibilizer.<sup>18</sup> Mather et al. also prepared linear/network PCL blends exhibiting shape memory assisted self-healing by blending cross-linked PCL network with linear PCL.<sup>20</sup> In addition, thermoplastic polyurethane (TPU), which has an ability to recover from a deformed temporary



**Scheme 1.** Preparation process of SMPU by solution blending. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

shape to a permanent shape by entropic elasticity, is also widely used to prepare SMPs in recent years. For example, excellent shape memory properties had been obtained by blending TPU and crystalline poly(oxyethylene) (POE).<sup>21</sup> Polyurethane/polycaprolactone (PU/PCL) blend were proposed as shape memory stents for cardiovascular implants,<sup>22</sup> because they were reported to show good shape memory properties by secondary blends.<sup>23</sup> Additionally, there were also reports about the miscibility and shape memory effect of TPU blends with phenoxy resin<sup>24</sup> or poly(vinyl chloride).<sup>16</sup> In these systems, POE and PCL played a role to fix the temporary shape by crystallization and solidification of the system. Phenoxy resin<sup>24</sup> and poly(vinyl chloride) influenced the shape fixity by adjusting the  $T_g$  of polymer blends. Therefore, polymer blending is an efficient method to prepare new kinds of SMPs. The shape memory effect can also be adjusted by polymer blending method. Most importantly, it is desirable to promote the commercialization of SMPUs if the TPU of market can be modified to show good shape memory effect.

In this article, we present a facile preparation method of SMPUs by blending method from commercial TPUs. In this experiment, the selected TPU (named PUA) is in rubber state as its  $T_g$  is usually lower than the room temperature. Polyurethane with higher HSC (named PUB) is synthesized to adjust the  $T_g$  of polymer blends. Thus, SMPU blends with various  $T_g$  can be prepared by blending PUA and PUB in different weight ratio. By using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and SEM, the morphology and structure of SMPU blends are investigated systematically. Moreover, the shape memory behavior of SMPU blends is studied carefully from the shape recovery, shape fixity and shape recovery process.

## EXPERIMENTAL

### Materials

Elastic TPU (PUA; fiber-grade, China) was commercial polyurethane HT-751 bought from Hong Kong's new high-enterprise,

China. PUB was synthesized from poly(1,4-butylene adipate) diols (PBAG;  $M_n = 600 \text{ g mol}^{-1}$ , Shanfeng Polyurethane, China), 4,4-methylenediphenyl diisocyanate (MDI; Aldrich, USA) and 1,4-butanediol (BDO; Aldrich, USA) according to our previous literature.<sup>25</sup> Dimethylformamide (DMF; Tianjing Chem., China) was dehydrated with 4-Å molecular sieves for several days before its use as a solvent.

### Synthesis of PUB

PUB containing about 80 wt % HSC was synthesized as following. The reaction to prepare polyurethane prepolymer was carried out in a 500-mL conical flask equipped with a mechanical stirrer. 20.0 g PBAG was mixed with 61.0 g MDI for 60 min at 80°C, followed by chain extension with 19.0 g BDO (added catalyst if necessary) for another 60 mins. Finally, the product was diluted to 10 wt % DMF solution, and thus PUB/DMF solution was obtained for the following preparation of PUA/PUB blends.<sup>25</sup>

### Preparation of PUA/PUB Blends

SMPU blends were prepared by solution blending PUA and PUB as shown in Scheme 1. Firstly, PUA/DMF (10 wt %) and PUB/DMF (10 wt %) solutions were prepared by dissolving the resin in DMF. Thereafter, the PUA/DMF and PUB/DMF solutions were mixed into homogenous solutions under strong mechanical stirring according to their different weight ratio as shown in Table I. Thus, samples of SMPU blends could be obtained after casting the solution onto a Teflon pan, held at 80°C for 24 h. Before testing, all samples were further dried at 80°C under a vacuum of 0.1–0.2 kPa for 24 h.<sup>25</sup>

### Characterization

**Differential Scanning Calorimetry.** DSC curves of samples were determined by using a TA Q200 instrument having nitrogen as the purged gas. Indium and zinc standards were used for calibration. Samples were firstly heated up from  $-60^\circ\text{C}$  to  $200^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  and kept at  $200^\circ\text{C}$  for 1 min, subsequently, cooled to  $-60^\circ\text{C}$  at a cooling rate of  $10^\circ\text{C}/\text{min}$ , and finally the second heating scan from  $-60^\circ\text{C}$  to  $250^\circ\text{C}$  was performed again.

**Table I.** Composition, Hardness, and Glass Transition Temperature of SMPU Blends

Samples	PUB (g)	PUA (g)	HSC (wt %)	Hardness (Shore D)	$T_g$ ( $^\circ\text{C}$ )
B1	0	10	20	24.2	-1.33
B2	2	8	32	29.2	18.29
B3	4	6	44	42.9	33.45
B4	5	5	50	58.0	38.76
B5	6	4	56	61.4	55.19
B6	8	2	68	62.0	62.26
B7	10	0	80	64.1	84.25

Notes: PUB is the polyurethane containing 80 wt % hard segment content; PUA is the commercial thermoplastic polyurethane; HSC is the hard segment content calculated from the weight fraction of PUA and PUB.  $T_g$  is the glass transition temperature of SMPU blends.

**Thermogravimetric Analysis.** The TG and DTG curves were recorded on a computer-controlled TA Instrument TG Q50 system, under the following operational conditions: heating rate was 10°C/min, temperature range 50–600°C, sample weight about 5.0 mg, using the film sample in platinum crucibles, 60 mL/min N<sub>2</sub> flow. Three or four repeated readings (temperature and weight loss) were performed on the same TG curve and DTG curve, each of them having at least 15 points.

**Wide Angle X-ray Diffraction.** XRD measurements were performed on a D8 Advance (Bruker, Germany) with an X-ray wavelength of 0.154 nm at a scanning rate of 12°/min. Specimens with 0.5 mm thickness were prepared for these measurements.

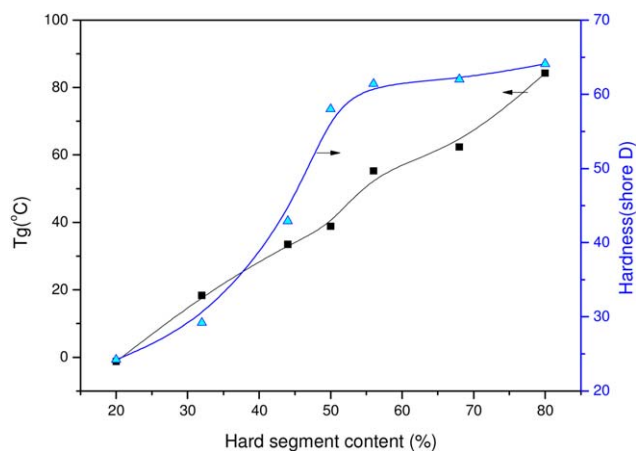
**Cyclic Tensile Test.** Cyclic tensile test was done by using a mechanical tensile testing apparatus (SANS, China) with a temperature-controlled chamber, and a personal computer was used to control and record all data. Firstly, the sample film with 5 mm width, 20 mm length, and 0.5 mm thickness was heated to  $T_{\text{high}}$ , 60°C within 600 s. Then the sample was stretched to  $\epsilon_m$ , 100% elongation at  $T_{\text{high}}$  with 10 mm/min stretching rate. Secondly, cool air would be introduced to the chamber for cooling sample film with constant strain,  $\epsilon_m$ , 100% elongation, to  $T_{\text{low}}$ , 20°C, within 900 s. Thereafter, the strain was released from  $\epsilon_m$  to 0 and the recurrent heating to 80°C for 600 s began. That was one cycle among all cyclic tensile tests and the cycle for each sample would be repeated four or five times for assessing the shape memory effect, such as shape fixity and shape recovery.

**Shape Recovery Test.** A stereo-optical microscopy (VHX-600, Japan) with a hot stage (Mettler Toledo FP90 Central Processor and FP82 Hot Stage) were used to observe and record the shape recovery process of sample film stretched in the cyclic thermal-mechanical investigation after one cycle. The heating rate of the recovery measurement was 2 K/min and the temperature range in heating process is from 25°C to 80°C.

## RESULTS AND DISCUSSIONS

### Thermal Properties of SMPU Blends

In this experiment, the selected commercial TPUs PUA (Sample B1) contains about 20 wt % HSC, whereas the synthesized PUB (Sample B7) contains about 80 wt % HSC. Thus, the PUA/PUB SMPU blending with ratio of 2/8 (e.g. sample B2) contains about 32 wt % HSC in theory. Similarly, the PUA/PUB SMPU blending with ratio of 4/6 (e.g. samples B3), 5/5 (e.g. sample B4), 6/4 (e.g. samples B5), and 8/2 (e.g. samples B6) contain about 44, 50, 56, and 68 wt %HSC, respectively. The elasticity or rigidity of SMPU blends with various HSC is characterized with shore D hardness. As shown in Table I. The pure PUA has a shore D hardness of 24.2, whereas the pure PUB has the shore D hardness above 64.1. That is, PUA is very soft, whereas PUB is very rigid at room temperature. After PUA is blended with PUB in different weight ratio, it is found that the shore D hardness of SMPU blends increases with the increase of PUB content, varying from 24.2 to 64.1 (see Table I). It indicates that the addition of PUB greatly improves the shore D hardness of SMPU blends in particular below 50 wt % PUB content. The reason is that the PUB contains much higher HSC. After PUB



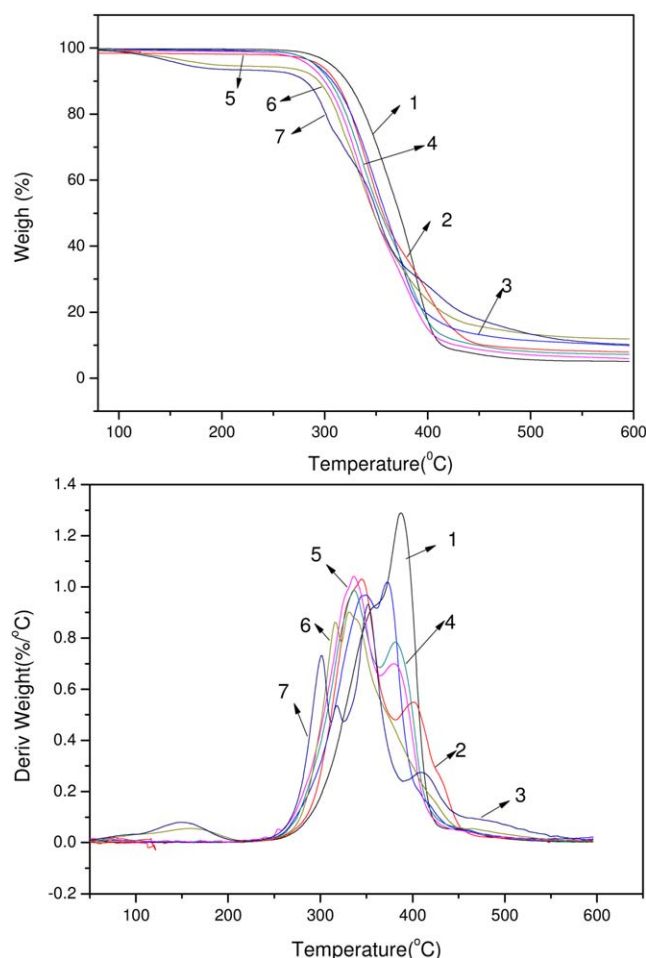
**Figure 1.** Dependency of shore D hardness and  $T_g$  on the HSC of SMPU blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

is blended with PUA, the hard segments are congregated into new hard domains in the SMPU blends, and the hard segment improves the shore D hardness of SMPU blends acting as reinforcing filler.<sup>26</sup> Therefore, the shore D hardness of SMPU blend also increases with the increase of HSC.

At the same time, the  $T_g$  recorded from the second DSC curves is also used for analysis. The  $T_g$  values are summarized in Table I. On the DSC curves, the PUA and PUB only show a typical glass transition at about  $-1.3^\circ\text{C}$  and  $84.3^\circ\text{C}$ , respectively. After blending, all SMPU blends still show a single  $T_g$  that varies between the  $T_g$  of pure PUA and PUB as the PUB content increases from 0 to 100 wt %. It is reported that full miscibility is characterized by a single  $T_g$ , which lies between the  $T_g$  of pure component. However, there are two  $T_g$  values that depend on composition in incompatible systems, and the  $T_g$  values do not change with composition in immiscible polymer system.<sup>27</sup> Thus, the DSC result shows that PUA and PUB are full miscible in the SMPU blends. The reason is that the PUA and PUB are both polyurethanes having very similar molecular structure and morphology. Considering the influence of HSC in the SMPU blends, it is also found that the  $T_g$  increases linearly with the increase of HSC as shown in Figure 1. It is confirmed that the hard segment improves the stiffness of SMPU blends. The  $T_g$  of SMPU blends can be adjusted by varying the PUB content or HSC. Therefore, the  $T_g$  of a commercial elastic TPU like PUA can be improved to the above room temperature for utilization as shape memory materials by polymer blending with polyurethane containing higher HSC like PUB.

### Thermal Stability of SMPU Blends

Aiming at investigating the thermal stability of SMPU blends, TGA has been employed in this experiment. Figure 2 presents the TG and DTG curves of SMPU blends with different weight ratio. It is observed that the pure PUB shows a complex thermal degradation behavior with more than three-step decomposition, whereas the pure PUA shows two-step decomposition. Some little molecules or oligomers are firstly decomposed below 150°C in PUB, whereas the onset decomposition temperature ( $T_i$ ) of PUA is higher than 320°C. After blending with more than 40



**Figure 2.** (a) TG and (b) DTG curves of SMPU blends (1-B1; 2-B2; 3-B3; 4-B4; 5-B5; 6-B6; and 7-B7). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

wt % PUA, the decomposition of oligomers cannot be determined anymore because they form miscible and stable homogeneous morphology. In addition, it is observed that the SMPU blends tend to have different decomposition behaviors from the pure PUA and PUB. The decomposition temperature of SMPU blend is changed in different composition. In Figure 2, it also can be found that  $T_i$  of SMPU blend which lies between the  $T_i$  of pure PUA and PUB increases with the increase of PUA content. It implies that the decomposition process of PUA macromolecules and PUB macromolecules is interrelationship in the SMPU blends. It is thus confirmed again that the PUA and PUB is miscible in the SMPU blends. The miscible SMPU blends get more stable as the PUA content increases. This improved thermal stability of SMPU blends is benefit to the processability of polymers products, such as melting spinning of fibers.

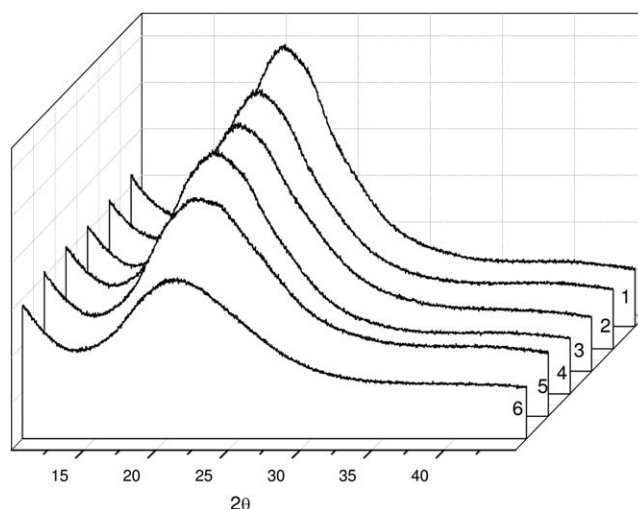
#### WAXD Analysis of SMPU Blends

The WAXD patterns of SMPU blends with different weight ratio are presented in Figure 3. It is observed that these patterns all feature as only one broad peak from  $15^\circ$  to  $35^\circ$ , ascribing to the diffraction peak of amorphous soft phase.<sup>7</sup> It suggests that the obtained SMPU blends are almost in amorphous state, which is

consistent with the DSC results. At the same time, it is found that the peak area or peak density is varied in the SMPU blends with different compositions. The pure PUA (sample B1) shows the highest peak density, whereas the pure PUB (sample B7) has the smallest one. As the PUA content increases, the peak area of SMPU blends also increases in sequence from sample B2 to B5. These results suggest that the pure PUA contains the largest fraction of amorphous soft phase as they are elastic at room temperature, whereas the pure PUB forms small fraction of amorphous soft phase as they contain large fraction of hard segments. Therefore, after blending, as the PUA content increases in the SMPU blends, the fraction of amorphous soft phase increases, whereas the amorphous hard domains decreases. It is confirmed that the addition of PUB influences the fraction of amorphous soft phase or the glass transition of soft phase. It thus will influence the shape recovery or shape fixity of SMPU blends.

#### Morphology of SMPU Blends

SEM observation is further performed on the broken surfaces of SMPU blends to investigate the morphology of SMPU blends. The SEM images of SMPU blends are presented in Figure 4. The fracture morphology indicates that the pure PUA (sample B1) is fractured in ductile mode [see Figure 4(a)], whereas the pure PUB (sample B7) is fractured in brittle mode [see Figure 4(f)].<sup>28</sup> This result is very consistent with the DSC and hardness results that the PUA is ductile, whereas the PUB is brittle at room temperature. When 20 wt % PUA is blended with 80 wt % PUB (e.g. sample B6), it is observed that some nano-sized spherical domains are dispersed homogeneously in the polymer matrix as shown in Figure 4(e). On the contrary, when 20 wt % PUB is blended with 80 wt % PUA, it is also found that some spherical domains are also dispersed in the polymer matrix as shown in Figure 4(b). As the PUA content increases to 40 wt %, the sphere domains are deformed and gradually combined into continuous phase [as shown in Figure 4(d)]. The cross section also gets rough, suggesting that the PUA and PUB get more compatible. When the PUA and PUB contents are increased to both 50 wt %, the ductile



**Figure 3.** WAXD profile of SMPU blends (1-B1; 2-B2; 3-B3; 4-B4; 5-B5; and 6-B7).

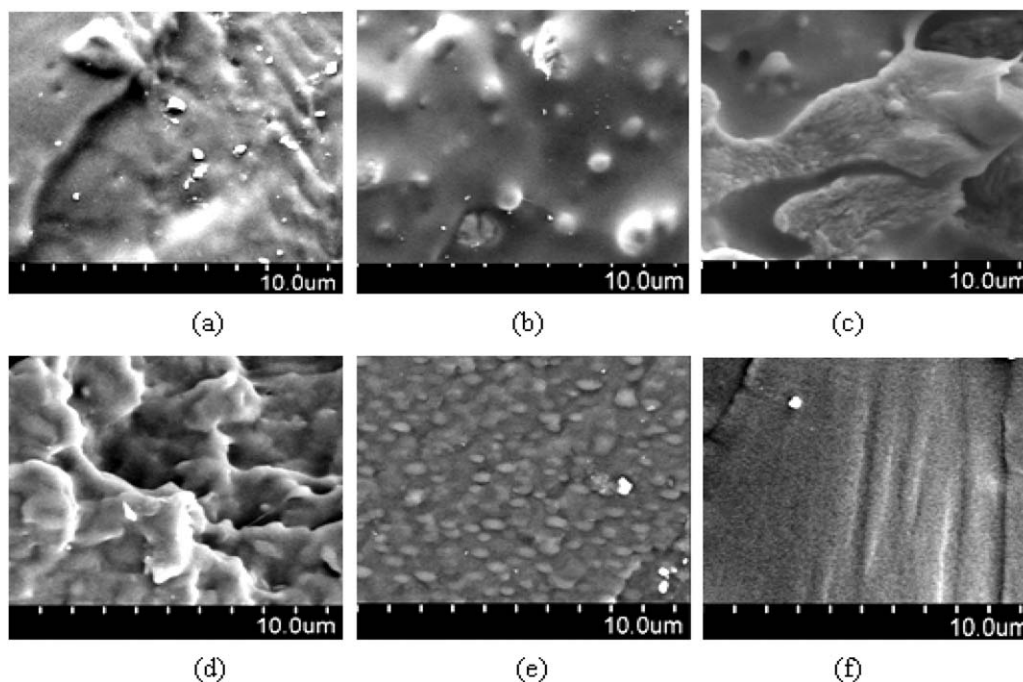
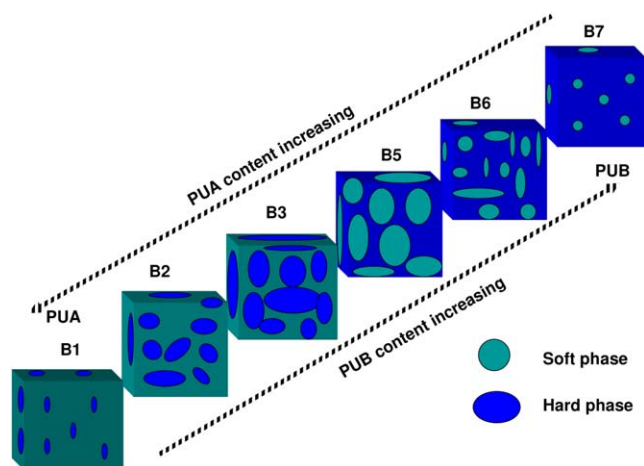


Figure 4. SEM image of SMPU blends (broken surfaces; a-B1; b-B2; c-B4; d-B5; e-B6; and f-B7).

fracture cross section and brittle fraction cross section can both be found in sample B4 [as shown in Figure 4(c)]. It indicates that both hard phase and soft phase grow into big domains. Thus, the SEM images demonstrate that PUA and PUB are miscible in all SMPU blends. As the PUA content increases, the soft phase tends to change gradually from a droplet-like dispersion phase to continuous soft phase, whereas the hard phase changes from a continuous phase to a droplet-like dispersion phase. The morphology change of SMPU blends is illustrated in Scheme 2. Accordingly, it is desirable to adjust the morphology with suitable hard domain content or soft phase content to satisfy the SMPU blend showing good shape memory effect.



Scheme 2. Illustration of morphology change of SMPU blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Shape Memory Behaviors of SMPU Blends

Now, there is less commercial SMPU resin though the TPU resin is very common in the market. The basic difference between TPU resin and SMPU resin is that the SMPU has good shape fixity within the practical application temperature range though the deformed strain of TPU recovers immediately after unloading. To achieve good shape memory effect, SMPUs generally have stable reversible phase and fixing phase by controlling well-defined molecular structure and molecular weight. Figure 5 shows the cyclic tensile curves of pure PUA and pure PUB. The shape fixity and shape recovery of pure PUA and PUB as well as the SMPU blends are illustrated in Figure 6. In this experiment, similar to the common TPU resin, the pure PUA has very low shape fixity because of their very low  $T_g$  though the strain recovery is thought to be good [as shown in Figure 5(a)]. Thus, the pure PUA cannot be used as shape memory materials. However, the synthesized PUB is composed of high fraction of hard segment forming fixing phase. The  $T_g$  of PUB is also much higher than the application temperature. Thus, the synthesized PUB shows very good shape fixity, closing to ca. 100% [as shown in Figure 5(b)]. After blending, it is known that the hard segment and soft segment are re-congregated into new reversible phase and fixing phase as discussed in morphology of SMPU blends. Thus, it is found in Figure 6 that the shape fixity is improved significantly to above 80% in the sample B2 containing only about 20 wt % PUB; and it is increased to above 95% when the PUB content is higher than 40 wt %. In addition to sample B4, the shape recovery of SMPU blends is beyond 83%. In addition, the dependency of shape recovery on temperature clearly shows the shape recovery process by applying stimulus of temperature. As shown in Figure 7, the SMPU blends show a typical S-shape shape recovery process.<sup>29</sup> That is, within

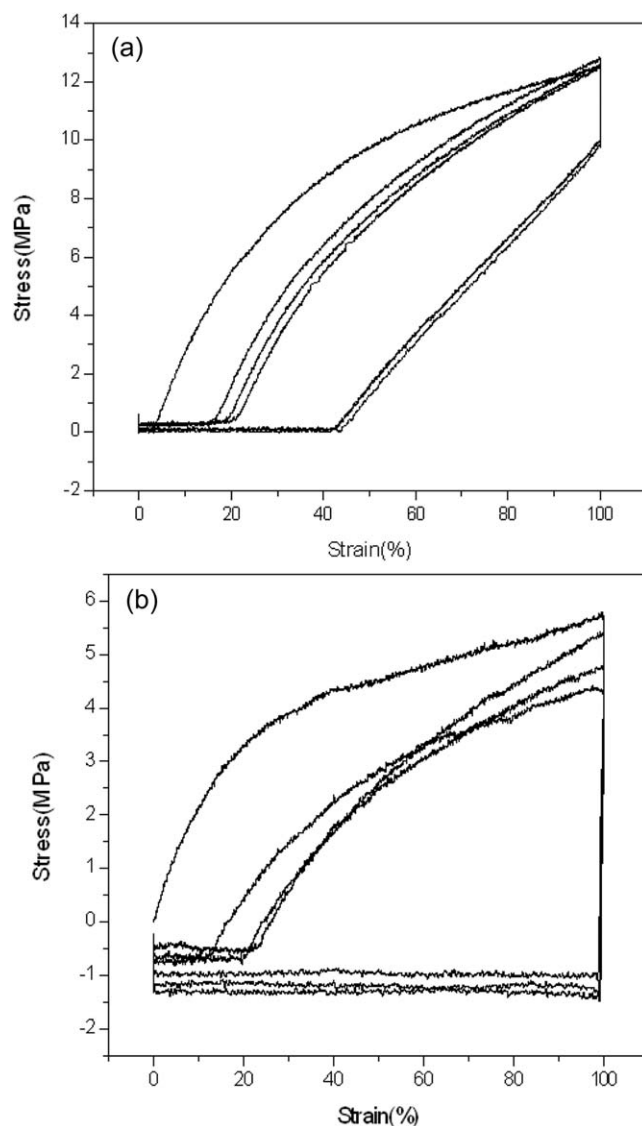


Figure 5. Cyclic tensile curves of pure (a) PUA and (b) pure PUB.

the lower temperature range, e.g. below 40°C, the samples including B3, B4, B5, B6, and pure PUB (B7) all tend to fix their deformed strain. When the temperature is heated to a critical value, e.g. 56°C for B5, 63°C for B4, 59°C for B3, the deformed strain is released rapidly. When the temperature is higher than 80°C, most of the deformed strain is recovered, and the shape recovers to its original state. However, the pure PUA (sample B1) and sample B2 do not show shape recovery under this testing condition as little deformed stain is fixed at room temperature (not shown here). It is therefore confirmed that SMPU blends show good shape memory effect when the PUA is blended with more than 40 wt % PUB.

## CONCLUSIONS

In this article, SMPU blends are prepared facilely by blending commercial TPU (PUA) with designed polyurethane (PUB).

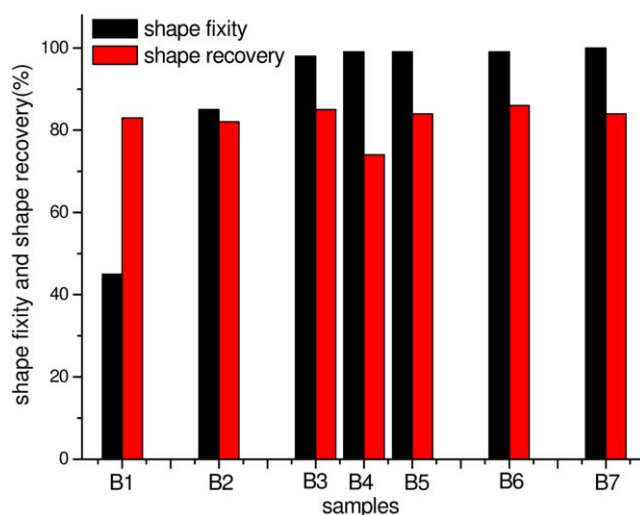


Figure 6. Shape fixity and shape recovery of SMPU blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

DSC, TGA, XRD, SEM, and shape memory behaviors are investigated systematically. Results show that the PUB and PUA are miscible in the SMPU blends. As the PUB content increases, the  $T_g$  shifts to high temperature range. As the PUA content increases, the PUA phase tends to change gradually from a droplet-like dispersion phase to continuous soft phase, whereas the PUB phase changes from a continuous hard phase to a droplet-like dispersion hard phase. Shape memory testing shows that the SMPU blends show good shape memory effect when the PUA is blended with more than 40 wt % PUB. Thus, commercial TPU can be endowed with good shape memory effect by blending with polyurethane containing higher HSC.

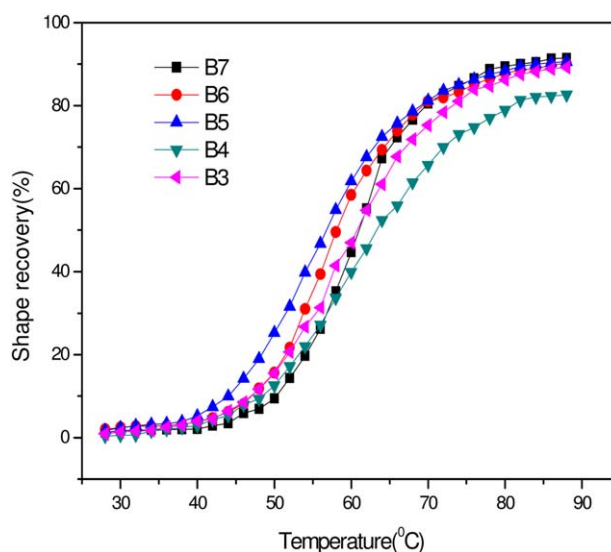


Figure 7. Dependency of shape recovery on temperature of SMPU blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

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## REFERENCES

- Hu, J. L.; Chen, S. J. *J. Mater. Chem.* **2010**, *20*, 3346.
- Ratna, D.; Karger-Kocsis, J. *J. Mater. Sci.* **2008**, *43*, 254.
- Liu, C.; Qin, H.; Mather, P. T. *J. Mater. Chem.* **2007**, *17*, 1543.
- Ronda, J. C.; del Rio, E.; Lligadas, G.; Galia, M.; Cadiz, V.; Meier, M. A. R. *Macromol. Chem. Phys.* **2011**, *212*, 1392.
- Romo-Urbe, A.; Alvarado-Tenorio, B.; Mather, P. T. *Macromolecules* **2011**, *44*, 5682.
- Su, Z. H.; Wang, W.; Jin, Y.; Ping, P.; Chen, X. S.; Jing, X. B. *Macromolecules* **2010**, *43*, 2942.
- Chen, S. J.; Hu, J. L.; Liu, Y. Q.; Liem, H. M.; Zhu, Y.; Liu, Y. J. *J. Polym. Sci. B Polym. Phys.* **2007**, *45*, 444.
- Maiti, P.; Mishra, A. *J. Appl. Polym. Sci.* **2011**, *120*, 3546.
- Kim, B. K.; Shin, Y. J.; Cho, S. M.; Jeong, H. M. *J. Polym. Sci. B Polym. Phys.* **2000**, *38*, 2652.
- Chen, S. J. PhD thesis of The Hong Kong Polytechnic University, **2010**.
- Chen, S. J.; Cao, Q.; Jing, B.; Cai, Y. L.; Liu, P. S.; Hu, J. L. *J. Appl. Polym. Sci.* **2006**, *102*, 5224.
- Kim, B. K.; Jang, M. K.; Hartwig, A. *J. Mater. Chem.* **2009**, *19*, 1166.
- D'hollander, S.; Van Assche, G.; Van Mele, B.; Du Prez, F. *Polymer* **2009**, *50*, 4447.
- Zhang, W.; Chen, L.; Zhang, Y. *Mater. Res.* **2009**, Pts 1 and 2 610–613, 1312.
- Zhang, S.; Yu, Z. J.; Govender, T.; Luo, H. Y.; Li, B. *J. Polymer* **2008**, *49*, 3205.
- Jeong, H. M.; Song, J. H.; Lee, S. Y.; Kim, B. K. *J. Mater. Sci.* **2001**, *36*, 5457.
- Chang, Y. E.; Joon, P.; Kim, J. G.; Kim, H. T.; Kim, D. K. *J. Ind. Eng. Chem.* **2010**, *162*, 256.
- Liu, H.; Shu-Cai, L.; Liu, Y.; Mahmood, I. *J. Appl. Polym. Sci.* **2011**, *122*, 2512.
- Zhang, W.; Chen, L.; Zhang, Y. *Polymer* **2009**, *50*, 1311.
- Rodriguez, E. D.; Luo, X.; Mather, P. T. *ACS Appl. Mater. Interfaces* **2011**, *3*, 152.
- Kurahashi, E.; Sugimoto, H.; Nakanishi, E.; Nagata, K.; Inomata, K. *Soft Matter* **2012**, *8*, 496.
- Ajili, S. H.; Ebrahimi, N. G.; Soleimani, M., *Acta Biomater.* **2009**, *5*, 1519.
- Jankauskaite, V.; Laukaitiene, A.; Mickus, K. V. *Mater. Sci. Medziagotyra* **2009**, *15*, 142.
- Jeong, H. M.; Ahn, B. K.; Kim, B. K. *Eur. Polym. J.* **2001**, *37*, 2245.
- Chen, S. J.; Hu, J. L.; Liu, Y. Q.; Liem, H. M.; Zhu, Y.; Meng, Q. H., *Polym. Int.* **2007**, *56*, 1128.
- Rueda-Larraz, L.; d'Arlas, B. F.; Tercjak, A.; Ribes, A.; Mondragon, I.; Eceizaa, A., *Eur. Polym. J.* **2009**, *45*, 2096.
- Brostow, W.; Chiu, R.; Kalogeras, I. M.; Vassilikou-Dova, A., *Mater. Lett.* **2008**, *62*, 3152.
- Demma, G.; Martuscelli, E.; Zanetti, A.; Zorzetto, M. *J. Mater. Sci.* **1983**, *18* 89.
- Chen, S.; Hu, J.; Zhuo, H.; Yuen, C. M.; Chan, L. *Polymer* **2010**, *51*, 240.