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A Novel Method for Modification of SMPU by Micro-phase Separation Promoters

Shao Jun CHEN, Jing Cang SU, Peng Sheng LIU*

Research Institute of Polymeric Materials, Xiangtan University, Xiangtan 411105

Abstract: A novel method of controlling the shape memory properties of shape memory polyurethane (SMPU) by addition of micro-phase separation promoters including 1-octadecanol (ODO) and liquid paraffin (LP) is reported. The results indicate that the strain recovery temperature and the strain modulus rate (E_g/E_r) were increased significantly with addition of small amount of micro-phase separation promoters. Thus it can increase the shape memory fixity rate and other shape memory behaviors of SMPU.

Keywords: Shape memory, polyurethane, modification, micro-phase separation.

Shape memory polyurethane (SMPU) is a typical temperature-sensitive functional polymer having an excellent shape memory behavior[1], which has been extensively studied since 1988[2, 10]. B. K. Kim *et al.*[3] reported the effect of hard segment contents (HSC) and soft segment length (SSL) of SMPU on its modulus, hardness and recovery strain. They attributed these effects to its micro-phase separation of its soft segment and hard segment as well as its soft segment crystallization. F. K. Li *et al.*[4] found that high crystallinity in soft segment regions at room temperature and the formation of stable hard segment domains are necessary for a block copolymer with shape memory behavior. B. S. Lee *et al.*[2] described that strong interaction among hard segments probably leads to phase separation or domain formation, which is quite desirable for shape memory behavior. In order to improve the shape memory behavior, B. K. Kim *et al.*[1] synthesized polycaprolactone diol (PCL) based on polyurethane ionomers by adding dimethylol propionic acid (DMPA) to the reaction mixture and neutralized its carboxyl group with triethyl amine (TEA). These ionomers show more excellent shape memory behavior than that of non-ionomers at room temperature. More recently, the same research group reported the synthesis of a new type SMPU with amorphous soft segments and crystalline hard segments[5], and further modified this PU by hydrophilic poly(ethylene oxide)(PEO) and DMPA[6]. They observed that hysteresis in the shape memory behavior decreased as the block lengths decreased due to the phase mix increasing, and PEO increased the hysteresis by reducing the crystallinity of the hard segment. Based on the research mentioned above, all of these effects are related to the

* E-mail: lpsh@xtu.edu.cn

micro-phase separation. Their work focused on the effect of the type of soft segments, SSL and HSC of SMPU on its shape memory behavior, as well as modification of SMPU by enhancing hard segment congregation. However, in some cases, especially for thermoplastic polyurethane (TPU), only adjusting the composition can not achieve desired shape memory behavior. Thus it is necessary to explore a new method to control shape memory behavior.

Z. Q. Fang[7, 8] reported that, for TPU, 1-octadecanol (ODO) and liquid paraffin (LP) are both excellent micro-phase separation promoters. On one hand, ODO can be capped at the end of TPU chain (Shown in **Scheme 1**), thus it is impossible to be macro-phase separated from system. On the other hand, ODO has a long alkane chain (-CH_2-) and can disperse at the interface between soft segment domains and hard segment domains due to the thermodynamic immiscibility with PU chain. Moreover, it can lubricate PU chain during the extension solidification process due to its flexibility. As comparison, LP is macro-phase separated from the system, acting as an outer lubricant; hence it can also promote micro-phase separation. Therefore both ODO and LP can enhance micro-phase separation of soft segment-hard segment of TPU. It can be expected that this effect should affect the shape memory behavior of TPU. In this study, we describe the effect of some micro-phase separation promoters on the shape memory behavior of poly(butylenes adipate)glycol (PBAG)based TPU. In the sample designation code, BA designates PBAG, the number preceding BA designates the Mn of the glycol, the one following BA designates the ODO wt% or LP wt%, and the last number designates the HSC, for example, 28BA-0.6-25 designates that the SMPU based on PBAG with Mn=2800 contains 0.6 wt% ODO, and 25 wt% HSC.

In this experiment, for a pure TPU synthesized from soft segment PBAG with molecular weight 2800 and hard segment of liquefied 4,4-diphenylmethane diisocyanate (L-MDI)-1,4-butanediol (BDO) with HSC of 25%, only slight shape memory behavior was observed. However, addition of small amount of ODO can significantly influence

Scheme 1 Synthesis of the ODO-capped polyurethane

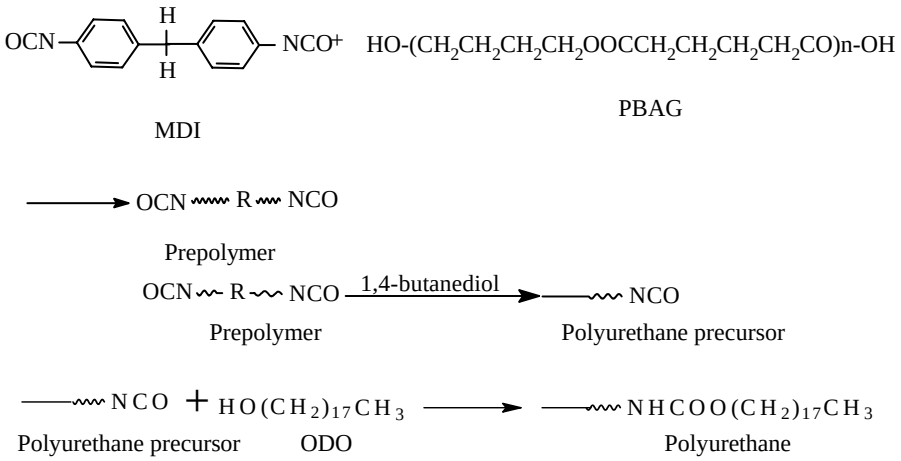


Figure 1 Strain recovery curves of ODO (A) or LP (B) modified SMPU

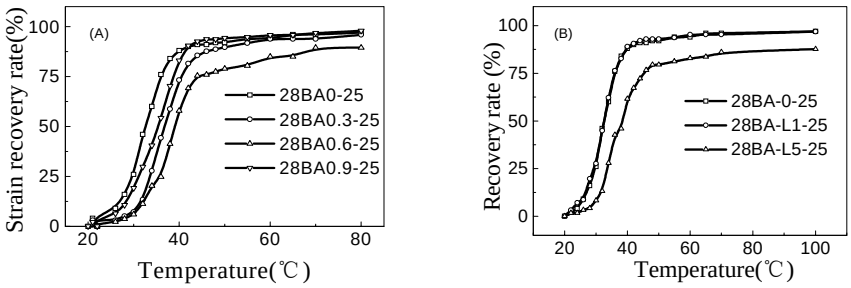
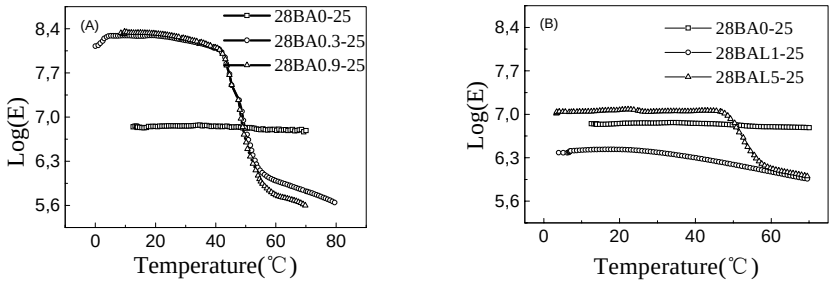


Figure 2 Tensile storage modulus *vs* temperature for ODO (A) or LP (B) modified SMPU



the shape memory properties. As shown in **Figure 1**, the recovery temperature (Tr) increases with the addition of the micro-phase separation promoters. Tr is related to the reversible phase transition temperature, which is determined by the soft-segment crystal melting. The increase of Tr implies the more stable reversible phase, and the more perfect soft segment crystallites. Thus the addition of the phase separation promoters can well control Tr of TPU. Without changing SSL and HSC, only small amount of micro-phase separation promoter can significantly increase Tr (> 6℃ for SMPU with 0.6 wt % ODO). In this experiment, it was observed that the pure TPU could only be drew about less than 400% at above 50℃, and its fixity rate was less than 60% at room temperature, while the modified TPU with addition of ODO or LP, the deformation ratio was beyond 600% and its fixity rate was closed to 100% at the same temperature. But it should be pointed out that the strain of pure TPU was recovered immediately when the temperature increased to above 50℃, while the modified TPU, especially with the addition of LP, there was still a little permanent strain without being recovered. The reason perhaps is that the crystal-structure is destroyed at an excess draw ratio (>600%) and some parts of molecular chains slip which cannot be recovered again with some micro-phase separation promoters.

Figure 2 shows the effect of micro-phase separation promoters on storage modulus (E). It was observed that the glassy state modulus (E_g) significantly increased, while the rubber state modulus (E_r) decreased; hence the modulus rate (E_g/E_r) increased greatly with the addition of the micro-phase separation promoters. E curve of pure TPU was a straight line in the range of 0-80℃, suggesting that the pure TPU soft segment phases

were predominantly amorphous in this temperature range, which was confirmed by the DSC studies (not shown), at the same time, it explained that the strain recovery process (shown in **Figure 1**) was just a thermal-sensitive shrinkage process like as the common shrinkage polymer materials. However, as only 0.3 wt% of ODO was introduced, a sharp transforming was observed at about 50 ℃. The modulus ratio between 30℃ and 70℃ was 429, which was much larger than that reported in the literatures[1-5]. Accordingly, the fixity of SMPU increased with the addition of micro-phase separation promoters as point out above. Therefore, a lot of block segment polymers might be modified to show shape memory effects by this method.

In summary, the shape memory properties were significantly controlled by addition of small amount of micro-phase separation promoter without changing the SSL and the HSC of TPU. This method can be also applied to enhance thermal properties, mechanical properties, and dynamical mechanical properties of PU.

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