

형상기억 폴리우레탄의 점탄성적 거동

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Dynamic Behavior of Shape Memory Polyurethanes

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Introduction

Shape memory polymer is one of the advanced functional materials which respond to thermal stimulation[1,2]. Most important two factors in molecular design of shape memory polymers are sharp glass transition and control of this temperature. These can be acquired by the control of soft/hard segment content, length and degree of phase separation[3].

In this experiment, shape memory polyurethanes(PUs) were prepared with 1,3-BD(1,3-butane diol), HDI(1,6-hexamethylene diisocyanate) and MDI(4,4'-diphenylmethane diisocyanate). Dynamic mechanical properties and thermal properties of these polyurethanes were characterized with DMTA and DSC. Melt viscosities were measured with ARES, and stress relaxation properties were also observed at glassy and rubbery state. Shape fixability and shape recovery at various temperature were determined to observe the effects of loading temperature and recovery temperature on shape memory behavior. Increase of loading temperature decreased the shape recovery, and this phenomenon might be related to the entropy increase due to the recoiling of oriented molecular chains. However increase of recovery temperature increased shape recovery due mainly to the high mobility at high temperature.

Experimental

Synthesis of PUs

1,3-BD and HDI were reacted at room temperature for 6 hours using DBTDL(dibutyltin dilaurate) catalyst in DMF(dimethyl formamide) to give OH-terminated prepolymer(OTP), which were subsequently extended with 1,3-BD and MDI at 80°C. To introduce the allophanate crosslinks, 5 phr excess of MDI was added to the above system, followed by solution casting at 130°C. Formulations are shown in Table 1.

Characterization

Dynamic mechanical properties were characterized with DMTA(Rheometric Scientific) at 10Hz, and 0.036% strain. Melt viscosities were measured with ARES(Rheometric Scientific) at 200°C and glass transition temperatures were measured from DSC(Mac Science). Shape memory behavior of solution cast films was characterized with temperature controllable UTM(Tinius Olsen 1000). Shape fixability and shape recovery are defined as follows,

$$\% \text{ shape fixability} = \varepsilon_u / \varepsilon_m \times 100$$

$$\% \text{ shape recovery} = \varepsilon_r / \varepsilon_m \times 100$$

where ε_u is strain upon unloading, ε_m is maximum strain, and ε_r is recovered strain[3].

Table 1 Formulations

Sample Designation	Soft Segment			Hard Segment		
	1,3-BD (moles)	HDI (moles)	OTP ^a (moles)	1,3-BD (moles)	MDI (moles)	HSC ^b (wt%)
S7500 H05	29.7	28.7	1	4.0	5.0	22.21
S7500 H07	29.7	28.7	1	6.0	7.0	27.45
S7500 H09	29.7	28.7	1	8.0	9.0	32.03
S7500 H11	29.7	28.7	1	10.0	11.0	36.06
S7500 H13	29.7	28.7	1	12.0	13.0	39.64

^a OTP : OH - Terminated Prepolymer ^b HSC : Hard Segment Content

Results and Discussion

Figure 1 shows the effect of hard segment content on dynamic mechanical property. General PU elastomer shows a transition related to the glass transition of soft segment below room temperature[4], however all curves in Figure 1 have single transition peaks(T_g in dynamic mechanical view) above room temperature region. Single peak designates phase mixing of HDI-1,3BD based soft segment and MDI-1,3BD based hard segment. All transition ranges are within $\pm 20^\circ\text{C}$, where the peak temperatures depend on the soft/hard segment content. From this result, it is estimated that the phase mixed system maintains its morphology throughout the change in molecular composition. In this series, 5,7,9, moles of diisocyanate were reacted with one mole of OTP to give a high T_g and rubbery modulus due to the increased rigid MDI block.

Figure 2 shows the dynamic melt viscosity of S7500H07 and S7500H11 samples. It shows a typical linear shear thinning behavior on account of the existence of crosslinked structure.

In Figure 3, increase of hard segment content gives a rise of T_g from 37.6°C to 61.0°C , and this results are consistent with dynamic mechanical thermal analysis(Figure 1). No crystallization peak was observed, because bulky pendant methyl group of 1,3-BD disturbs the stacking of molecular chains. Moreover, excess diisocyanates introduce crosslink points, so this gives defects for the crystallization of molecular chains[5].

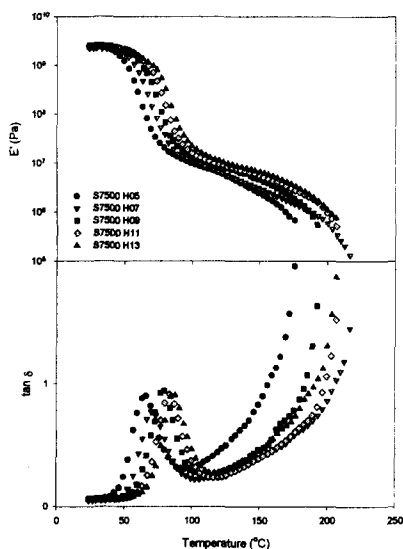


Figure 1 Dynamic mechanical properties of S7500 Series.

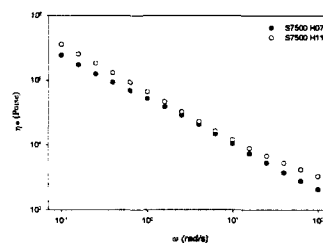


Figure 2 Complex viscosity vs. shear rate of S7500H07 and S7500H11.

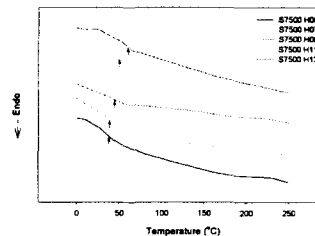


Figure 3 DSC profiles of S7500 series.

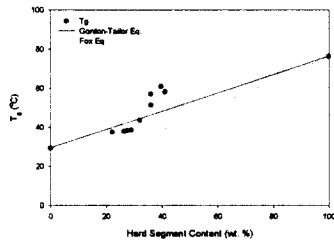


Figure 4 Relationship between Tg and hard segment content.

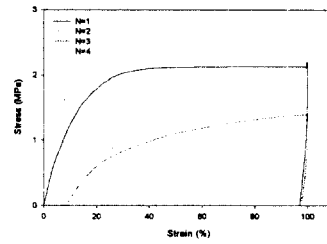


Figure 5 Thermomechanical cyclic tes of S7500 H09.

DSC data were plotted in Figure 4, together with two additive rules including Fox equation(Eq.(1)) and Gordon-Taylor equation(Eq.(2)).

$$1/T_g = W_s/T_{gS} + W_H/T_{gH} \tag{1}$$

$$T_g = [W_s T_{gS} + k(1 - W_s)T_{gH}] / [W_s + k(1 - W_s)] \tag{2}$$

$$k = (\alpha_{RH} - \alpha_{GH}) / (\alpha_{RS} - \alpha_{GS})$$

$$T_g = W_s T_{gS} + W_H T_{gH} \quad (\text{if } k = 1.0)$$

In these equations, T_g is the glass transition temperature of mixed phase, T_{gS} and T_{gH} are those of soft and hard phases, and W_s and W_H are the weight fraction of soft and hard segment. Parameter k , the ratio of thermal expansion coefficient differences at rubbery and glassy state of each phase should be unity in copolymer and polymer blends[6]. It was observed that T_g increased rapidly around 35wt% of hard segment content. This phenomenon might indicate that the excess MDI could react more easily with MDI-urethane block at higher MDI-urethane block content.

Cyclic loading and unloading test for shape memory property of cast film is shown in Figure 5. Shape fixability increased and shape recovery decreased with the number of cycles(N). The irreversible parts of the extended molecular chains might cause the hysteresis in thermomechanical cycle. Thermal hardening was observed during the first cycle upon cooling to room temperature.

Figure 6 shows that shape recovery decreases with the increase of loading temperature. It means that the slip or recoiling of extended molecular chains takes place during the loading process. This can be explained by the increase of entropy in accordance with the theory of rubber elasticity. However, in Figure 7, increase of recovery temperature enhances shape recovery because molecular chains have greater mobility at higher temperature.

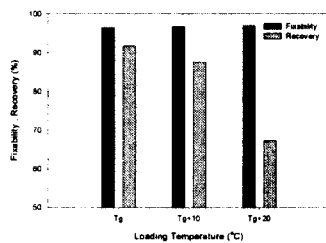


Figure 6 Shape memory behavior at different loading temperature of S7500H09.

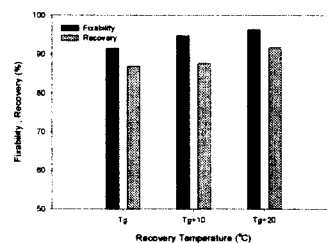


Figure 7 Shape memory behavior at different recovery temperature of S7500H09.

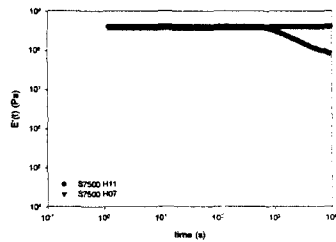


Figure 8 Stress relaxation behavior of S7500H07 and S7500H11 at room temperature.

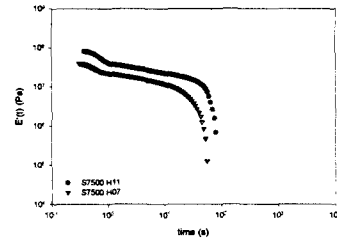


Figure 9 Stress relaxation behavior of S7500H07 and S7500H11 at T_g .

Stress relaxation behavior at glassy and rubbery state supports the above results(Figure 8 and 9). Rapid stress relaxation which comes from the slip or recoiling of molecular chains at higher temperature properly explains that part of the orientation obtained during loading is relaxed. This is so since the time scale of relaxation is the same order of magnitude with the cyclic loading test.

Conclusions

Introduction of 1,3-BD induced the phase mixed morphology of PU. Various techniques(DMTA, ARES, DSC) were employed for the analysis of this phase mixed system, and shape memory properties were observed at different loading and unloading temperatures. We found that shape memory behaviors are strongly dependent on loading and recovery temperature.

References

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