

상온함계 형상기억 폴리우레탄의 점탄성적 거동

김종희, 김진우, 김병규  
부산대학교 고분자공학과

**Dynamic Behavior of Phase Mixed Polyurethane with Shape Memory Effect**

Jong Hee Kim, Jin Woo Kim, Byung Kyu Kim  
Department of Polymer Science & Engineering, Pusan National University,  
Pusan 609-735, Korea

**Introduction**

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

In this experiment, shape memory polyurethanes(PUs) were synthesized from poly(propylene glycol)(PPG,  $M_n=400$ ), MDI(4,4'-diphenylmethane diisocyanate), NPG(neopentyl glycol), TDI(2,4-toluene diisocyanate). Dynamic mechanical properties were characterized with DMTA. Melt viscosities were measured with RDA and stress relaxation properties were also observed at glassy and rubbery states. 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. However increase of recovery temperature increased shape recovery due mainly to the high mobility at high temperature.

**Experimental**

**Polymer Synthesis**

PPG and MDI were reacted at 70°C for 4 hours to give OH-terminated prepolymer (OTP), which were subsequently extended with NPG and TDI at 80°C. To introduce the allophanate crosslinks, 5phr excess of TDI was added, followed by solution casting at 130°C.

**Characterization**

Dynamic mechanical properties were characterized with DMTA(Rheometric Scientific) at 10Hz and 0.036% strain. Melt viscosities were measured with RDA(Rheometric Scientific) at 250°C. 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,

Table 1. Formulations

Sample Designation	Soft segmnet		Hard segment		
	PPG (mol)	MDI (mol)	NPG (mol)	TDI (mol)	HSC <sup>a</sup> (wt%)
S3000H09	26.22	20.97	8	9	47.55
S5000H09	30.97	27.14	8	9	36.06
S7500H09	34.23	31.36	8	9	28.20
S10000H09	36.18	38.89	8	9	23.49

<sup>a</sup>HSC: Hard segment content

$$\text{shape fixability}(\%) = \frac{\epsilon_u}{\epsilon_m}$$

$$\text{shape recovery}(\%) = \frac{\epsilon_r}{\epsilon_m}$$

Where  $\epsilon_u$  is strain upon unloading,  $\epsilon_m$  is maximum strain and  $\epsilon_r$  is recovered strain[3].

### Results and Discussion

Figure 1 shows the effect of hard segment content on dynamic mechanical property. Phase separated PU elastomers generally show two glass transition temperatures(soft and hard segment)[4]. However all curves in Figure 1 have single transition peak(Tg in dynamic mechanical view). Single peak designates phase mixing of PPG-MDI based soft segment and NPG-TDI based hard segment and the peak temperatures depend on the soft and hard segment contents. This results indicate that the phase mixed system maintains its morphology throughout the change in molecular composition.

Figure 2 shows the dynamic melt viscosity of S5000 series. It shows a newtonian plateau, followed by a linear shear thinning behavior.

Cyclic loading and unloading test for shape memory property of cast film is shown

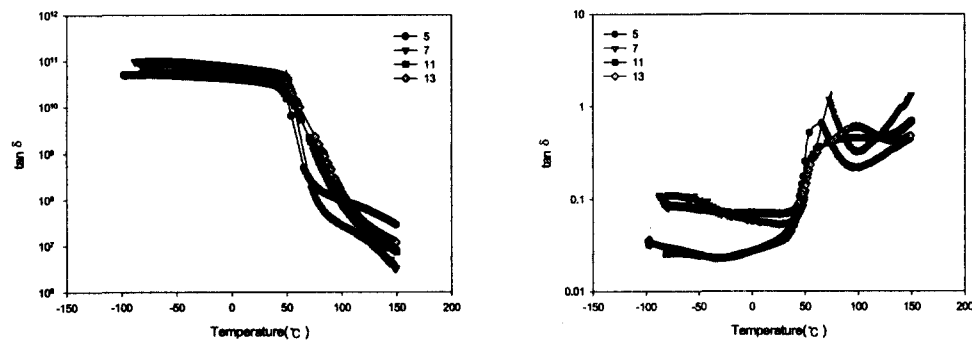


Figure 1. Dynamic mechanical properties of S5000 series.

in Figure 3. Shape fixability increased and shape recovery decreased with increasing the number of cycles(N). The irreversible parts of the extended molecular chains

might cause the hysteresis in thermomechanical cycle.

Figure 4 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, the increase of recovery temperature enhances shape recovery because molecular chains have greater mobility at higher temperature.

Stress relaxation behavior at glassy and rubbery state supports the above results(Figure 5). Rapid stress relaxation which comes from the slip or recoiling of molecular chains at higher temperature property 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.

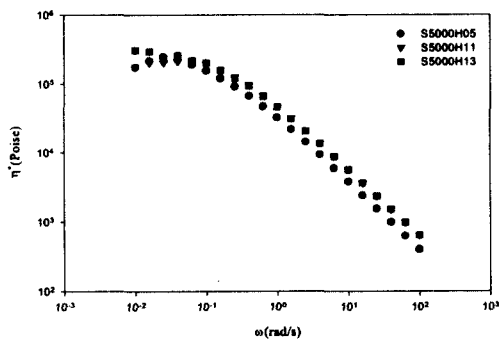


Figure 2. Complex viscosity vs. shear rate of S5000 series

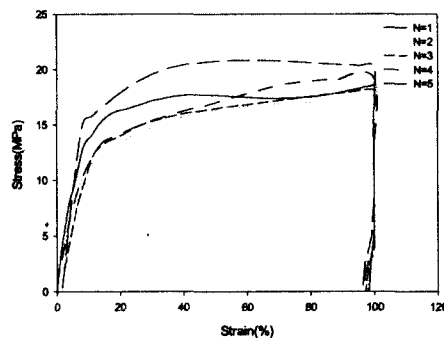
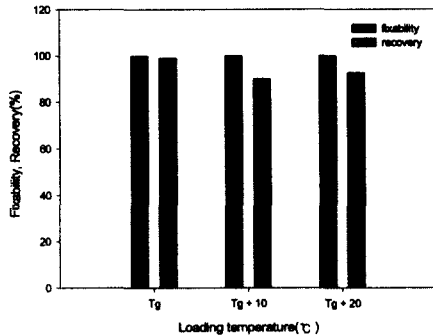
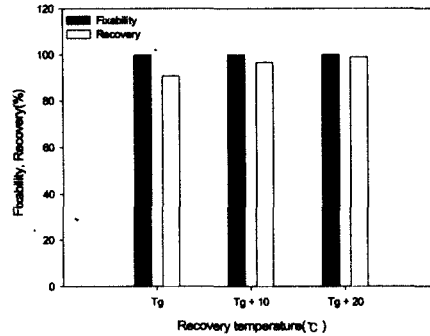


Figure 3. Thermomechanical cyclic test of S7500H09



(a)



(b)

Figure 4. Shape memory behavior of S7500 H09 at (a) different loading temperature and (b) different recovery temperature.

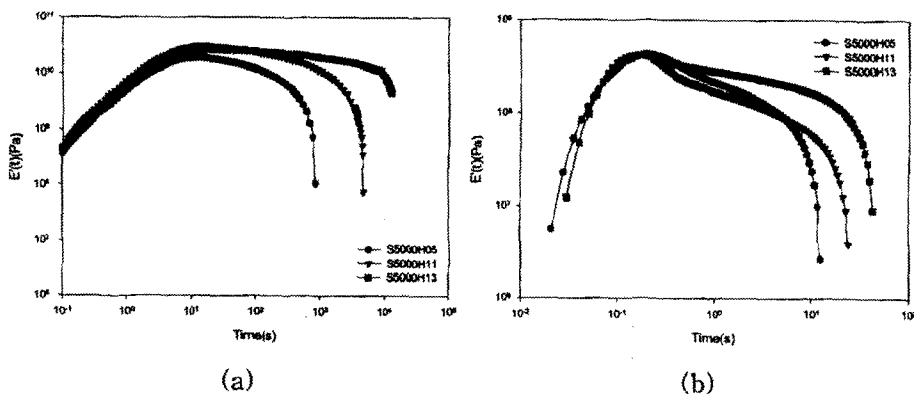


Figure 5. Stress relaxation behavior of S5000 series at (a) room temperature and (b)  $T_g$ .

### Conclusions

Various techniques 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 behavior strongly depends on the loading and recovery temperatures.

### References

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