

Preparation and Properties of Thermoplastic Polyurethane Elastomers (I)

- Relationship Between Chemical Structure and Thermal Properties -

Je Ho Huh, Eun Young Kim, *Young Soo Whang, and Han Do Kim

Dept. of Textile Eng., Pusan National University, Pusan, Korea

*Technical Research and Development Center, Hanil Synthetic Fiber Co. Ltd., Masan, Korea

1. Introduction

Thermoplastic polyurethane elastomers¹ are linear segmented copolymers with an (S-H)_n type structure, where the soft segment(S) is usually formed from polyester or polyether macroglycol, and the hard segment(H) is formed by extending a diisocyanate with a low molecular weight diol such as 1,4-butanediol. At room temperature, the soft segments are incompatible with the polar hard segments, which leads to a microphase. Upon heating above the glass transition temperature of the hard segments, the polymer forms a homogeneous viscous melt which can be processed by thermoplastic techniques such as injection molding, extrusion, blow molding, etc., subsegment cooling leads again to segregation of hard and soft segments.

The long flexible soft segment largely controls the low temperature properties, the solvent resistance and the weather resistant properties of thermoplastic polyurethane elastomers. The polar nature (hydrogen bonding) of the hard urethane segments causes a strong mutual attraction leading to micro domain formation. The so-called hard domains provide both physical crosslink sites, and filler like reinforcement to the soft segment matrix.

Many studies deal with the effect of structure on the properties of thermoplastic polyurethane elastomers.^{2,3} The morphology and properties of thermoplastic polyurethane elastomers are greatly influenced by the ratio of hard and soft block components,^{4,5,6} and the average block lengths.^{4,5,7,8} Hard segment content significantly affects physical properties such as hardness, the modulus, and mechanical strength. When the diisocyanate content is in excess, chemical cross-linking through allophanate is also introduced in the polymer.⁹ Both the existence of hard domains through hydrogen bonding, namely the physical cross-linking, and the chemical cross-linking, are responsible for the elastic behavior of polyurethanes. When the diisocyanate is equal to the stoichiometric one, the number of chemical cross-link is almost negligible, and the rubbery behavior is entirely due to the physical cross-links. In this study, the effect of the polymerization method(one- or two-stage) on the properties was studied and the relationship between chemical structure and thermal properties was also investigated.

2. Experimental

IPDI (Isophorone diisocyanate : 1-isocyanate-3-isocyanate ethyl-3,5,5-trimethyl cyclohexane), 1,4-butanediol, PPG (polypropylene glycol : Mw 2000), and PTMG (polyoxytetramethylene glycol : Mw 2000) were manufactured by Aldrich Chemical Company. PPG, and PMG were dehydrated under vacuum at 50°C for 48h. Dibutyltin dilaurate was obtained from Fluka Chemical Company. Dibutyltin dilaurate as a catalyst was used without further purification.

Preparation of the thermoplastic polyurethanes involved One- and Two-stage polymerization conditions were used to prepare the thermoplastic polyurethane in this study. One-Stage polymerization conditions : The dry macroglycol was heated to 120°C with mechanical stirring in a 1L reaction flask. Then the dry chain extender glycol , 1, 4-butanediol, was added and the mixture was heated to 140°C with stirring. At this point, (140°C) IPDI and dibutyltin dilaurate (catalysis : 0.01 wt%) were added in one portion and stirring was continued for 5 min, after which the thickening reaction mixture was poured into a kneader and reacted for 3 min at 140 °C. Two-Stage polymerization conditions : The dry macroglycol was heated to 90°C with mechanical stirring in a 1L reaction flask, then (90°C) IPDI and dibutyltin dilaurate (catalysis : 0.01 wt%) were added in one portion, and stirring was continued at 90°C for 2 h. The temperature of the reaction product was then raised to 140°C, and an equivalent amount of dry chain extender glycol and 1, 4-butanediol at 140°C was added in one portion to the stirred mixture. This hot thickening mixture was stirred for 5min then poured into a kneader and reacted for 3 min at 140°C. The composition and hard segment content are shown in Table I.

Table I. Description of Thermoplastic polyurethane series.

Designation (stage of polymerization)	Composition (molar ratio) PP series : IPO/BD/PPG PT series : IPO/BD/PTMG	Hard segment content (wt%)	Soft segment (mol wt%)	Hard segment (mol wt)	n	Number of urethane moieties per hard segment	T _m	heat of fusion, ΔH (J/mg)	α-transition temp.(°C)	β-transition temp.(°C)
pp1 (2)	1/0.83/0.17	41.3	2000	1562.1	5	10	304.1	219.2	52.02	-25.42
pp2 (2)	1/0.89/0.11	52.9	2000	2499.3	8	16	328.2	333.7	72.78	-32.54
pp3 (2)	1/0.92/0.08	60.7	2000	3436.5	11	22	329.6	380.0	81.80	-35.34
pp4 (2)	1/0.93/0.07	66.3	2000	4373.7	14	28	330.9	408.6	97.84	-36.58
pp5 (2)	1/0.94/0.06	70.5	2000	5312.0	17	34	332.2	438.9	102.00	-40.70
pt1 (2)	1/0.83/0.17	41.3	2000	1562.1	5	10	321.8	240.9	54.86	-52.8
pt2 (2)	1/0.89/0.11	52.9	2000	2499.3	8	16	328.5	252.3	76.04	-70.18
pt3 (2)	1/0.92/0.08	60.7	2000	3436.5	11	22	333.3	274.5	84.5	-69.7
pt4 (2)	1/0.93/0.07	66.3	2000	4373.7	14	28	333.5	335.1	89.48	-68.14
pt5 (2)	1/0.94/0.06	70.5	2000	5312.0	17	34	333.7	353.7	94.56	-74.72
pp1 (1)	1/0.83/0.17	41.3	2000	1562.1	5	10	318.9	256.2	33.06	-27.86
pp3 (1)	1/0.92/0.08	60.7	2000	3436.5	11	22	328.3	367.6	99.32	-32.00
pt1 (1)	1/0.83/0.17	41.3	2000	1562.1	5	10	329.6	215.8	61.6	-50.68
pt3 (1)	1/0.92/0.08	60.7	2000	3436.5	11	22	335	326.6	91.06	-66.76

Thermal and dynamic mechanical thermal behaviors of samples were examined by using a DSC 220C (SEIKO) differential scanning calorimetry and DMTA (Rheometrics MKIII) respectively. Initial DSC scans were run at 20°C/min to upper temperature limit when the sample was held isothermally for 30 sec see before cooling at 40°C/min. A second was then made at 20°C/min. Dynamic mechanical testing was carried out on DMTA (Rheometrics MKIII) with a heating rate of 3°C/min and frequency setting of 2Hz.

3. Result and Discussion

The polyurethane elastomers synthesized in this study had a constant soft segment

composition and block length, a constant hard segment composition, but a variable hard segment block length and content (41.3 ~ 70.5 wt%). Fig. 1 shows the molecular structure of the thermoplastic polyurethane prepared in this study.

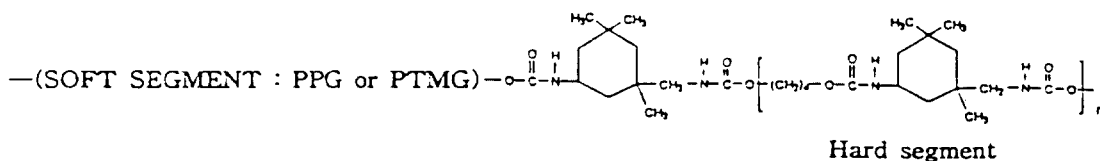


Fig. 1 Molecular structure of polyurethane ($n = 5 \sim 17$).

The thermoplastic polyurethane elastomers are identified in Table I. The average molecular weights and hard segment lengths are calculated from the relative amounts of reactants charged. The number of urethane moieties per average hard segment block length were calculated in order to better understand the variation in potential hydrogen bonding sites with hard segment content.

The reaction between diol and diisocyanate was determined by FTIR. The characteristic peak of N=C=O group around 2270 cm^{-1} was used to determine the extent of reaction between diol and diisocyanate. The peak disappeared completely after 3 min reaction in a kneader at 140°C .

Differential Scanning Calorimetry (DSC) is a common tool to determine changes in the state of organization of the molecules in a sample, e. g., phase segregation, glass transitions and melting. The effect of hard segment content on thermal response for pp and pt series samples are shown in Figure 2. The specimens of this series were prepared from the same components, but with differing molar ratios of PPG (or PTMG), BD, and IPDI (see Table I). The T_m of PPG based and PTMG based samples increased from 304.1°C to 332.2°C and from 321.6°C to 333.7°C respectively.

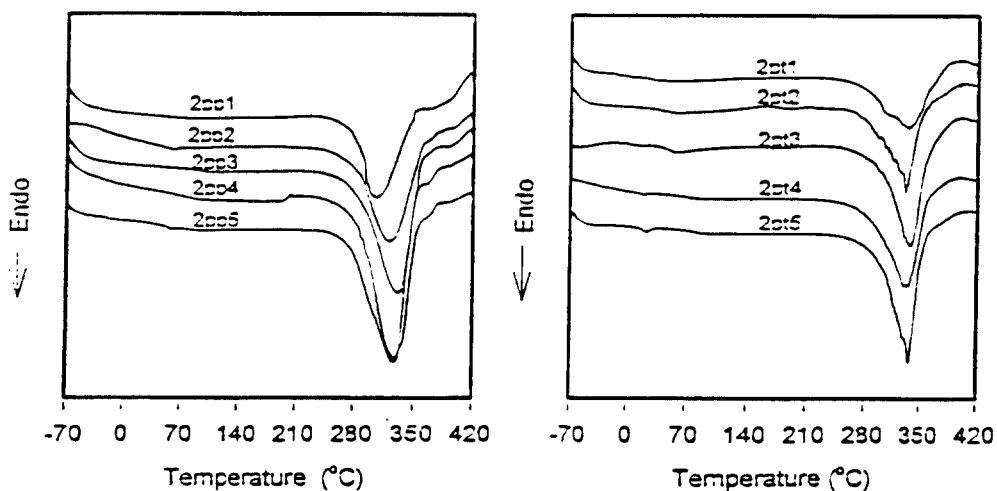


Fig. 2. Effect of hard segment contents on thermal response for PP and PT series samples.

Fig. 3. illustrate the dynamic mechanical behavior of each samples.

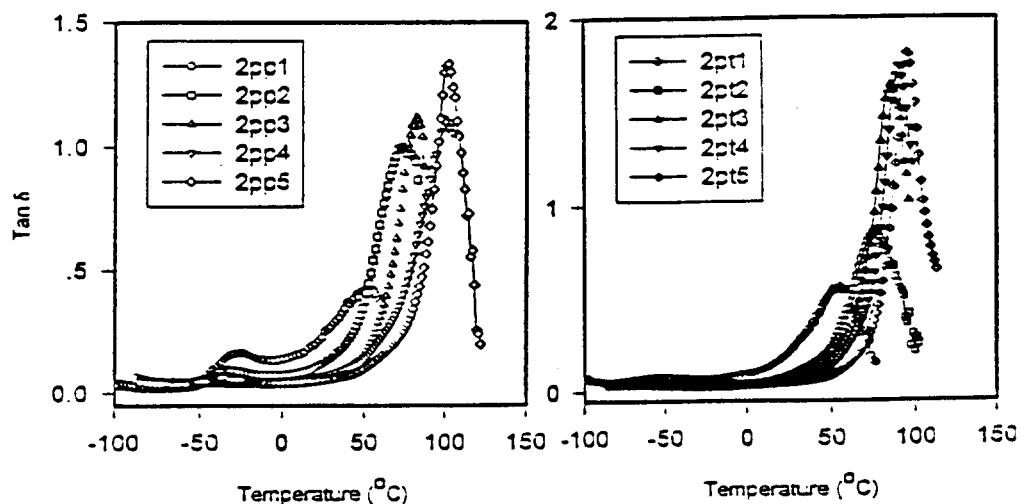


Fig. 3. Effect of hard segment contents on the dynamic mechanical behavior of PP and PT series samples.

Ng et al.⁷ employed DMTA method to characterize several linear segmented polyurethanes of well-defined hard and soft segments molecular weights and molecular weight distributions. Chen et al.¹¹ showed that for a fixed hard/soft segment composition ratio increasing the hard and soft segment length, provides more complete phase separation, an increase in modulus, and a decrease in soft domain T_g (due to pure soft phase)^{15,6} The glass transition temperature (T_g) of hard segment increased with increasing hard segment content. However, the β -type glass transition temperatures (β -transition temperature) decreased with increasing hard segment content. The glass transition (α -type transition) temperature of PPG based and PTMG based samples increased from 52.02°C to 102.00°C and from 54.7°C to 94.6°C respectively, however, their β -type transition decreased from -25.4°C to -40.70°C and -52.8°C to -74.72°C as hard segment content is increased. This phenomenon indicates that high molecular weight PPG (or PTMG) is not miscible with hard segment. The $\tan \delta$ curves for the polyurethane elastomers indicate the glass transition region discussed in loss modulus curves.

At ambient temperature, dynamic tensile modulus values show a systematic increase in the stiffness of the polyurethane elastomers with increasing hard segment content. The modulus of the almost plateau region increases and extends to higher temperatures as the hard segment content is increased. The system investigated the polymerization technique was somewhat more

influential on thermal properties when the soft segment was a PPG (Mw 2000) than when it was a PTMG (Mw 2000)

4. Conclusions

Thermoplastic polyurethane elastomers were prepared via melt polymerization process using isophorone diisocyanate(IPDI), 1,4-butanediol as hard segment, and polypropylene glycol(PPG, Mw 2000), polytetramethylene ether glycol(PTMG, Mw 2000) to give a soft segment. These polyurethane elastomers had a constant soft segment composition and block length, a constant hard segment composition, but a variable hard segment block length and content (41.3 ~ 70.5 wt%). Studies have been made on the relationship between chemical structure and thermal properties of polyurethane elastomers.

The dynamic storage modulus of PT sample was higher than that of PP sample at the same content of hard segment. The dynamic storage modulus of PT samples polymerized by 1-stage was higher than that polymerized by 2-stage. The glass transition (α -type transition) temperature of samples based on PPG and PTMG increased from 52.02°C to 102.00°C and from 54.7°C to 94.6°C respectively, however, their β -type transition decreased from -25.4°C to -40.70°C and -52.8°C to -74.72°C as hard segment content is increased. It is concluded that polymerization technique was somewhat more influential on thermal properties when the soft segment was a PPG (Mw 2000) than when it was a PTMG (Mw 2000)

References

1. R. K. Adams, G. K. Hoeschele in "Thermoplastic Elastomers" (N. R. Legge, G. Holden, and H. E. Schroeder Ed.), Hanser Publishers, New York, pp. 13 ~ 46, 1989.
2. D. J. Martin, G. F. Meijs, G. M. Renwick, P. A. Gunatillake, and S. J. Mccarthy, *J. Appl. Polym. Sci.*, **60**, 557(1996).
3. R. F. Harris, M. D. Joseph, C. Davidson, *J. Appl. Polym. Sci.*, **41**, 509 (1990).
4. J. W. C. Van Bogart, P. E. Gibson, and S. L. Cooper, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 65 (1983).
5. D. S. Huh and S. L. Cooper, *Polym. Eng. Sci.*, **11**, 369 (1971).
6. S. Abouzahr and G. L. Wilkes, *Polymer*, **23**, 1077 (1982).
7. H. N. Ng, A. E. Allegrezza, R. W. Seymour, and S. L. Cooper, *Polymer*, **14**, 255 (1973).
8. Z. S. Petrovic and I. Javni, *J. Polym. Sci. Polym. Phys. Ed.*, **27**, 545 (1989).
9. Meyer DA (1964) Chapter 10, "Vulcanization of Polyurethane Elastomers", in: *Vulcanization of Elastomers*, Alliger G, Sjothun J, Eds New York, Reinhold.
10. Brunette CM, Hsu SL, Macknight WJ (1982) *Macromolecules* **15**:71-77.
11. W. Chen, K. C. Frisch, D. J. Kenney, and S. Wong, *J. M. S. Pure Appl. Chem.*, **29**, 567 (1992)