

Preparation and Properties of Thermoplastic Polyurethane Elastomers (II)

- Hydrogen Bonding and Elastic Behavior -

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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 separation. 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 hard segment contents, the various macroglycol and the polymerization method (one- or two-stage) on the properties were studied by stress-strain, stress hysteresis, and infrared experiments.

2. Experimental

IPDI (Isophorone diisocyanate : 1-isocyanate-3-isocyanate ethyl-3,5,5-trimethyl cyclohexane), 1,4-butanediol, and PPG (polypropylene glycol : Mw 2000), and PTMG (polyoxytetramethylene glycol : Mw 2000) were manufactured by Aldrich Chemical Company. PPG and PTMG were dehydrated under vacuum at 50°C for 48h. Dibutyltin dilaurate as a catalyst was obtained from Fluka Chemical Company and 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. For the purpose of identifying the thermoplastic polyurethane elastomer, IR spectrometer (Impact 400D, Nicolet) was used. For each sample, 32 scans at 2 cm⁻¹ resolution were collected in the absorption mode. Equilibrium stress-strain measurements were made in simple extensions on dumbbell specimens of an average cross-sectional area of (2×0.45) mm². The measurements were carried out with a Tinius Oslen 1000 at 25°C, at a cross-head speed 20mm/min. (Each values reported here were averages of at least 10 specimens.) Stress hysteresis measurements were carried out with the same tester as above, at 25 °C. The sample was clamped in the tester and subjected to successive maximum 300%. The percentage set was taken as the percentage of elongation at which the retraction curve returns to zero stress.

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.

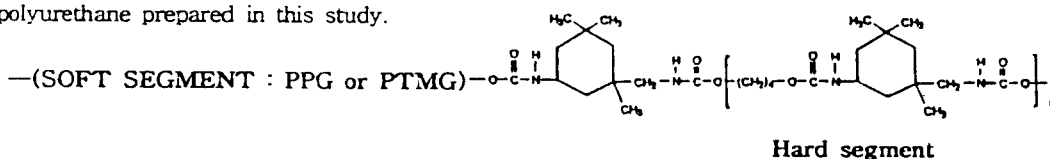


Fig. 1 Molecular structure of polyurethane (n = 5~19).

The composition , mechanical, and elastic properties of the thermoplastic polyurethane elastomers synthesised in this study are shown in Table 1.

Table 1. Effect of hard segment content on dynamic tensile modulus, and permanent sets.

Designation (stage of polymerization)	Composition (molar ratio) PP series : DL/BD/PPG PT series : IPDI/BD/PTMG	Hard segment content (wt%)	Ambient temperature dynamic tensile modulus (Pa)	Permanent set (%)			
				Cycle 1(50%)	Cycle 2(100%)	Cycle 3(150%)	cycle 4(300%)
pp1 (2)	1/0.83/0.17	41.3	7.0	25.10	29.99	32.98	35.77
pp2 (2)	1/0.89/0.11	52.9	8.3	38.07	39.85	37.92	-
pp3 (2)	1/0.92/0.08	60.7	8.8	62.91	61.0	58.1	-
pp4 (2)	1/0.93/0.07	66.3	8.8	-	-	-	-
pp5 (2)	1/0.94/0.06	70.5	9.1	-	-	-	-
pt1 (2)	1/0.83/0.17	41.3	7.0	33.03	34.27	27.47	21.11
pt2 (2)	1/0.89/0.11	52.9	8.4	62.68	54.33	-	-
pt3 (2)	1/0.92/0.08	60.7	8.8	-	-	-	-
pt4 (2)	1/0.93/0.07	66.3	8.7	-	-	-	-
pt5 (2)	1/0.94/0.06	70.5	9.0	-	-	-	-
pp1 (1)	1/0.83/0.17	41.3	6.7	6.91	12.68	9.15	14.07
pp3 (1)	1/0.92/0.08	60.7	8.6	47.58	50.34	44.54	-
pt1 (1)	1/0.83/0.17	41.3	7.2	6.80	12.65	9.10	23.51
pt3 (1)	1/0.92/0.08	60.7	8.9	67.18	71.14	65.68	-

() : indicates maximum elongation %

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 time in a kneader at 140°C . By FTIR spectroscopy, the identification of hydrogen bonding between the N-H and C=O groups gives sufficient information about the network (physical cross-linking) formed.¹⁰ Fig. 2 shows the FTIR spectra of samples (pp1(2) and pp5(2)).

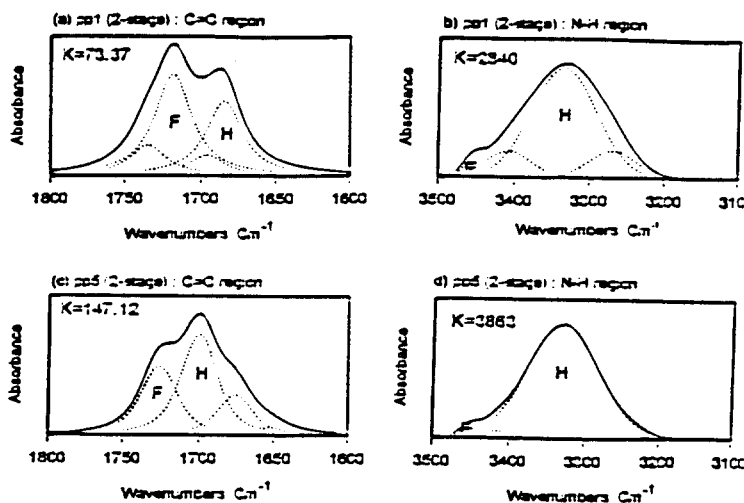


Fig. 2. The FTIR spectra of the N-H and C=O regions for pp1 and pp5 (2-stage).

$$K = (\text{Area of the hydrogen bond (H)} / \text{Area of the free (F)}) \times 100$$

The N-H stretching region contains mainly two infrared bands attributed to "free" and hydrogen bonded N-H groups. The spectra were then analysed employing a curve-resolving technique based on a linear least-squares analysis to fit a combination of the Lorentzian and Gaussian curve shapes. The "free" N-H stretching band occurs at $3450 \sim 3454\text{ cm}^{-1}$ in all samples appearing as a weak shoulder on the high frequency side of the hydrogen-bonded band. The area of hydrogen bonded N-H absorbance of pp5(2) is higher than that of pp1(2). The band of 1736 cm^{-1} is assigned to the free C=O stretch, while that at 1700 cm^{-1} is assigned to the hydrogen-bonded C=O stretch, appearing as a shoulder. The value of H/F (hydrogen bonding area / free area) increased with increasing hard segment content. The hydrogen bonding are responsible for hardness and elastic behavior of polyurethanes.

Fig. 3. shows the tensile retraction curves of four cycles for samples ppl(2) and ptl(2) respectively.

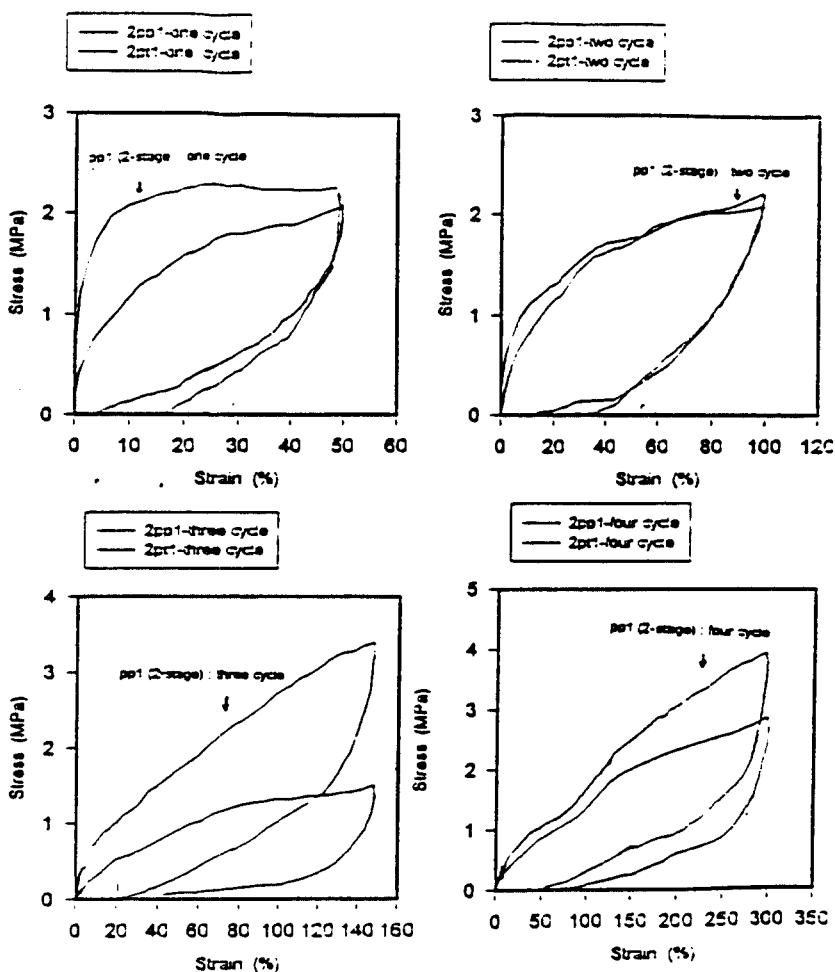


Fig. 3. The stress-strain hysteresis curves for PPI (2-stage) and PTI (2-stage).

The permanent set data for various max elongation are shown in Table I. As the hard segment content was increased, the permanent set was increased. The permanent set of PT sample was higher than that of PP sample at the same composition. The permanent set of PP sample increased with increasing maximum elongation (cycle number), however, that of PT sample decreased. It is concluded that PP based thermoplastic polyurethane shows better elastic behavior than that of PT based one.

4. Conclusions

Thermoplastic polyurethane elastomers were prepared via melt polymerization process (one-and two-stage) using isophorone diisocyanate(IPDI), 1,4-butanediol as hard segment, and polypropylene glycol(PPG, Mw 2000) (or polyoxytetramethylene 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 effects of the hard segment content (length) and polymerization method on the properties of polyurethane elastomers. As the hard segment content was increased, the value of H/F (hydrogen bonded area / free (non-hydrogen bonded) area), the dynamic tensile modulus, and the permanent set were increased. The permanent set of PT sample was higher than that of PP sample at the same composition. The permanent set of PP sample increased with increasing maximum elongation (cycle number), however, that of PT sample decreased. It is concluded that PP based thermoplastic polyurethane shows better elastic behavior than that of PT based one.

5. References

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