

Physical and Chemical Cross-linking Effects in Thermoplastic Polyurethane Elastomers with Different Macrolycol

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ABSTRACT

A series of Thermoplastic polyurethane elastomers was prepared via a two-step polymerization process. The NCO/OH feed ratio of polyurethane synthesized in this study was varied from 1 to 1.3. Studies have been made on the effects of chemical and physical cross-linking, and the properties of thermoplastic polyurethane elastomers based on isophorone diisocyanate (IPDI)/1,4-butanediol (BD)/poly(propylene glycol) (PPG, MW: 2000), isophorone diisocyanate (IPDI)/BD /poly(oxytetramethylene) glycol (PTMG, MW: 2000) was compared.

These materials were characterized using FTIR spectrometer, dynamic mechanical thermal analyzer, and tensile retraction tester. PTMG based polyurethane elastomers showed higher elasomeric behavior than PPG based polyurethane elastomers at the same NCO/OH ratio. This feature has been connected with the specific nature of the polyols. The permanent set(%) was decreased with increasing maximum elongation from 50% to 300%.

1. INTRODUCTION

Thermoplastic polyurethane elastomers are linear segmented copolymers with a (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 lead 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.. Subsequent cooling again leads to segregation of hard and soft segments.

When the diisocyanate content is in excess, chemical cross-linking through allophanate linkage is also introduced into the copolymer. 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 polyurethane.

This study, by keeping the molar ratio of the OH of macroglycol to the NCO of aliphatic diisocyanate constant, obtained a prepolymer of the same chain length. By using different macroglycol and values of the NCO/OH ratio above the stoichiometric

one, linear thermoplastic and cross-linked polyurethane block copolymers were prepared. Studies have been made on the effects of chemical and physical cross-linking, and macroglycol type on the properties of polyurethane elastomers.

2. EXPERIMENTAL

2.1 Materials

Isophorone diisocyanate (IPDI, Aldrich reagent grade), 1,4-butanediol (BD, Aldrich reagent grade) and dibutyltin dilaurate (Aldrich reagent grade) were used as received. PPG (polypropylene glycol, Mw: 2000), and poly(oxytetramethylene) glycol (PTMG, Mw: 2000) were dehydrated at 80°C under vacuum (1-2mmHg) until no bubbling was observed.

2.2 Synthesis of Polymers

The dry macroglycol was heated to 120°C with mechanical stirring in a separable flask, then IPDI/dibutyltin dilaurate (catalysis : 0.01 wt%) was added in one portion, and the reaction between macroglycol and IPDI was continued at 120°C for 30 minute while stirring. The temperature of the reaction mixture was then raised to 140°C, and dry chain extender (1, 4-butanediol) was added one portion to the stirred mixture. The reaction mixture became thick as soon as the chain extender was added. This hot thickening mixture was compression-molded into sheets and post-cured in an oven for 24h at 110°C

Four types of polyurethane block copolymers, of various molecular weight, were prepared, based on the same prepolymer composition, with a IPDI/PPG (or /PTMG) ratio equal to 6/1 (mols) NCO/OH ratio, during the second step of polymerization, was 1, 1.1, 1.2, and 1.3 for each type of sample.

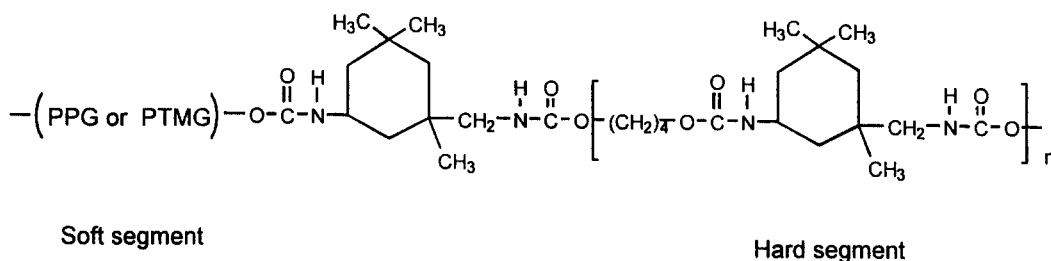


Fig. 1 Molecular structure of thermoplastic segmented polyurethane elastomers prepared in this study

2.3 FTIR Spectra

For the purpose of identifying the remained NCO groups in reaction mixture, FTIR

spectrometer (Impact 400D, Nicolet) was used. For each sample, 32 scans at 2 cm^{-1} resolution were collected in the absorption mode.

2.4 Dynamic Mechanical Measurement

The dynamic mechanical Properties were measured by using DMTA MkIII (Rheometrics Scientific) in a fixed frequency mode of 2 Hz using a heating rate of $3^\circ\text{C}/\text{min}$ over a temperature range of -80 to 150°C .

2.5 Tensile Retraction Test

This test was carried out with a Tinius Olsen 1000 on dumbbell specimens of cross-sectional area of $(2 \times 0.45)\text{ mm}^2$ at room temperature. The sample was clamped in the tester and subjected to successive maximum elongation of 50, 100, 150, 200, and 300%. The cross-head speed was 20 mm/min, while the chart drive speed was 50 mm/min. The permanent set (percentage set) was taken as the percentage of elongation at which the retraction curve returns to zero stress.

3. RESULTS AND DISCUSSION

Thermoplastic polyurethane elastomer in this study were varied by altering the NCO/OH ratio, while the hard segment content was fixed at 47%, and the prepolymer composition was kept constant with the ratio IPDI/PPG (or /PTMG) equal to 6/1 (mols).

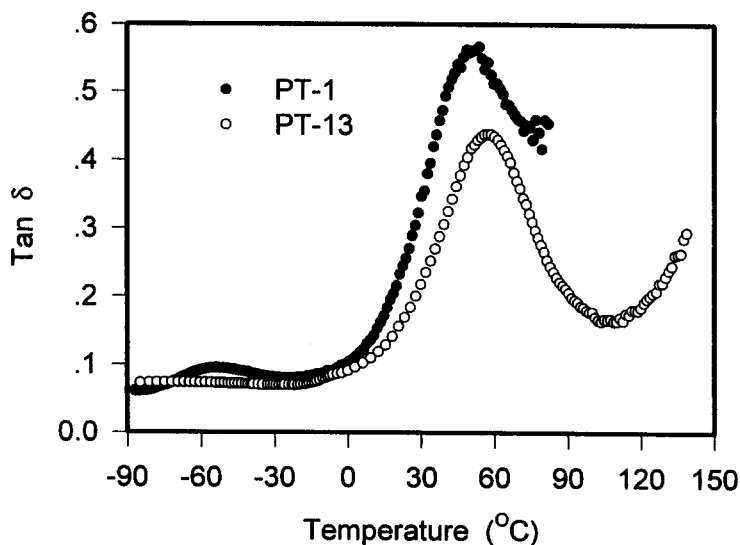


Fig 2. Tan δ of two representative samples with NCO/OH ratio values 1 and 1.3 respectively.

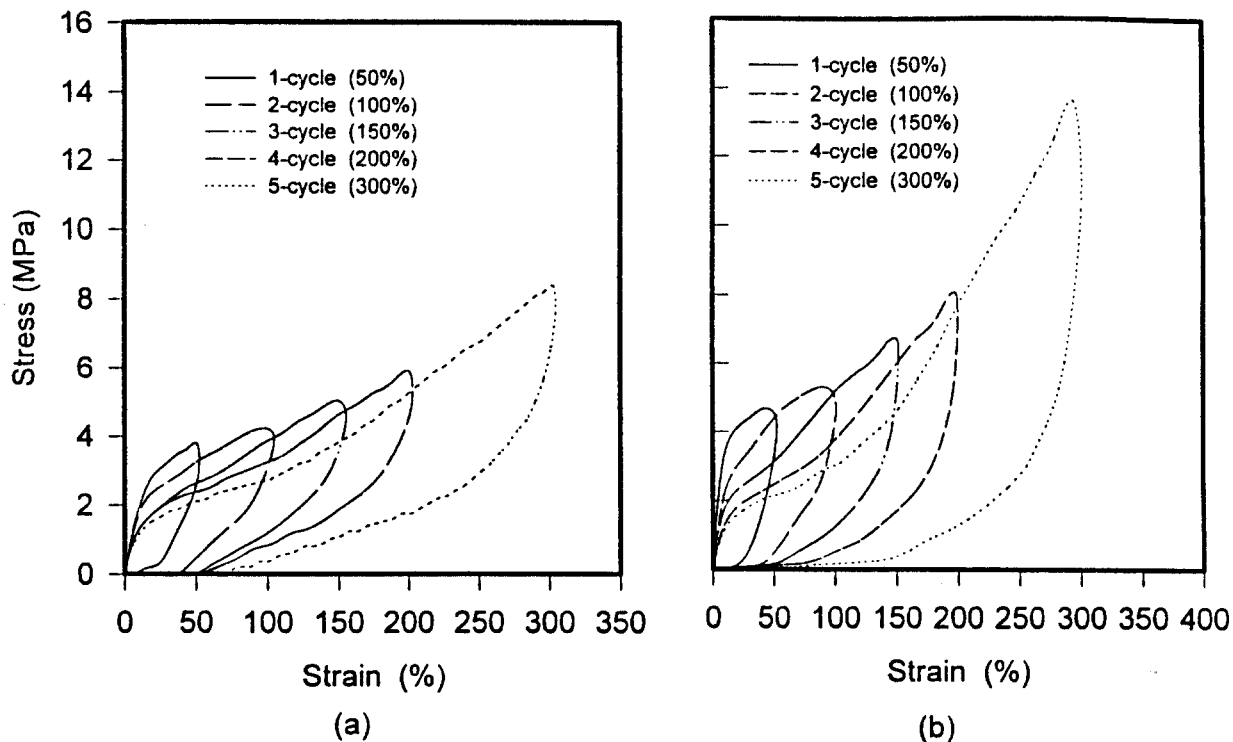


Fig 3. Stress-Strain hysteresis curve for sample (a) PT1 and (b) PT13 at 25°C.

These polyurethane elastomers had constant soft segment block length and constant hard segment composition, but variable NCO/OH ratio (1~ 1.3). As the NCO/OH ratio increased, the α type glass transition temperature (T_g) and β type T_g increased for PPG and PTMG systems. In case of PT-13, the β type T_g peak was disappeared.

The permanent set was taken as the percentage of elongation at which the retraction curve returns to zero stress, for both PPG and PTMG, increased with increasing maximum elongation from 50% to 300%. When the NCO/OH ratio and the maximum elongation were same, the permanent set of PTMG system was lower than that of PPG system. It was found that PTMG based polymer have higher elastomeric behavior than PPG based polymer at the same

For NCO/OH ratio of 1, it showed the low values of permanent set at the lower elongation from 50% to 150%. However, for NCO/OH ratio of 1.1, 1.2 and 1.3, these samples showed lower value of permanent set at the range of 200%, and 300%

Table I Description of thermoplastic polyurethane elastomers.

Designation (stage of polymerization)	Composition (molar ratio)		Hard segment content (wt)	Soft segment (Mw)
	NCO/OH	PPG series : IPDI / PPG / BD		
PP-1	1	6/1/5	47	2000
PP-11	1.1	6/1/4.45	46.5	2000
PP-12	1.2	6/1/4	45.9	2000
PP-13	1.3	6/1/3.61	45.3	2000
PTMG series (IPDI / PTMG / BD)				
PT-1	1	6/1/5	47	2000
PT-11	1.1	6/1/4.45	46.5	2000
PT-12	1.2	6/1/4	45.9	2000
PT-13	1.3	6/1/3.61	45.3	2000