Preparation and Properties of Segmented Polyurethane Elastomers with Two Different Soft Segments

Tae-Jung Lee, Jae-Ho Huh, Han-Do Kim
Dept. of Textile Eng., Pusan National University

1. Introduction

Segmented Polyurethanes Elastomers are a class of polymers having interesting properties which arise from their unique phase-separated structures resulting from the thermodynamic incompatibility of the ingredients[1].

Segmented polyurethane Elastomer generally consists of a soft segment derived from a polymeric diol and a hard segment from a diisocyanate and a low molecular weight diol(chain extender). At service temperature, the soft segment is in a viscous or rubbery state, whereas the hard segment is in a glassy or semicrystalline state. The soft segment provide elastic character to the polymer, whereas the hard segment provides dimensional stability by acting as thermally reversible and virtual cross-links and also as a reinforcing filler. Depending upon the soft segment or hard segment concentration, the polymer has a continuous hard phase with a dispersed soft phase, a continuous soft phase with a dispersed hard phase or bicontinuous phase[2~3].

In this study, two series of segmented polyurethane elastomers were prepared from 4,4-diphenylmethane diisocynate(MDI)/1,4-butanediol(BD)/poly(propylene glycol)(PPG) and MDI/BD/poly(oxytetramethylene) glycol (PTMG). The MDI/BD based hard segments of polyurethane prepared in this study were 39~65 wt%. These polyurethane elastomers had constant soft segment molecular weight (average Mn : 2,000), but variable hard segment block length (n ; 3~10.1, average Mn : 1,020~3,434). A wide spectrum of physical, thermal properties and morphologies were investigated, depending upon the composition and chemical structure of the hard segment and soft segment. And these properties of PPG based samples (MPP samples) and PTMG based samples (MPT samples) were compared respectively. As the hard segment content of MPP and MPT samples increased, dynamic storage modulus and glass transition temperature increased. The permanent set (%) increased with increasing hard segment content and successsive maximum elongation. And the permanent set of MPT sample was lower than that of MPP sample at the same hard segment content.

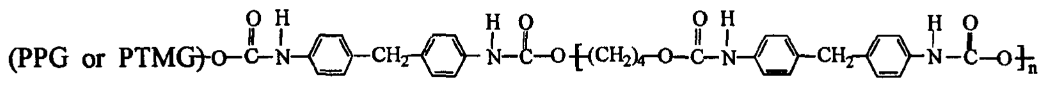
2. Experimental

Materials

4,4'-diphenylmethane diisocyanate (MDI, Aldrich reagent grade), 1,4-butanediol (BD, Aldrich reagent grade) and dibutyltin dilaurate (Aldrich reagent grade) were used as received. Poly(propylene glycol)(PPG, Aldrich, average Mn ca 2,000), and poly(oxytetramethylene) glycol (PTMG, average Mn ca. 2,000) were used after vacuum drying.

Synthesis of Polymers

The dry macroglycol was heated to 90℃ with mechanical stirring in a separable flask, then MDI was added in one portion, and the reaction between macroglycol and MDI was continued at 90℃ for 2 hours while stirring. The temperature of the reaction mixture was then raised to 140℃, and an equivalent amount of dry chain extender (glycol 1,4-butanediol) was added in one portion to the stirred mixture. The reaction mixture became thick as soon as the chain extender was added. This hot thickening mixture was stirred for 5 min, then poured into a kneader and reacted for 5 min at 140℃ while kneading. The product was compression-molded into sheets. The structure of polyurethane prepared in this study is shown in Fig 1.



soft segment　　　　Hard segment

Fig 1. Segmented polyurethane elastomer prepared in this study

Identification of Reaction

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.

Differential Scanning Calorimetry

DSC was carried out over a temperature range from -80 to 270℃ using a Seico DSC 220C. Runs were conducted at a heating rate of 20℃/min under N_2 atmosphere.

Dynamic Mechanical Measurement

The dynamic mechanical properties were obtained at 2Hz using DMTA Mk Ⅲ (Rheometrics Scientific)with a heating rate of 3℃/min over a temperature range from -80 to 250℃

Tensile Retraction Test

This test was carried out with a Tinius Oslen 1000 on dumbbell specimens of cross-sectional area 2×0.45mm^2 at room temperature. The as-compression molded sheet 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

In this study, the segmented polyurethane elastomers containing soft segment molecular weight of 2,000 g/mol, variable hard segment content with 39~65 wt% and average hard segment block length with 3.0~10.1 or average Mn 1020~3434 were synthesized(Table 1).

As the hard segment content increased, glass transition temperature shifted to higher temperature in PPG and PTMG based samples(see Fig 2).

As the hard segment content was increased, the value of H/F(hydrogen bonded area/free (non-hydrogen bonded area) was increased, and the value of MPT samples was higher than that of MPP samples.

The permanent set of both MPP sample and MPT sample increased with increasing hard segment content from 39 to 47 wt% and with successive maximum elongation from 50 to 300%. As the hard segment content incresed, it showed high permanent set(%) values for MPP and MPT samples. The permanent set of MPT samples MPT1, MPT2 were lower than those of MPP samples MPP1, MPP2 at the same hard segment content.

Reference

1. T. A. Speckhard, K. K. S. Hwang, C. Z. Yang, R. Lau Punh and S. L. Cooper. *J. Macromolec. Sci. Phy.* **B23**, 175(1984)
2. J. Ferguson and D. Patsavoudis. *Eur. Polym. J.* **8**, 385(1987)
3. K. K. S. Hwang, D. J. Hemker and S. L. Cooper. *Macromolecules* **17**, 307(1984)

Table 1 Description of Segmented Polyurethane Elastomer

Designation PPG samples	Composition (molar ratio) MDI/PPG/BD	Hard segment content(wt%)	Soft segment molecular weight (g/mol)	Hard segment molecular weight (g/mol)	Average block length of hard segment (n)
MPP1	1/0.25/0.75	39	2000	1020	3
MPP2	1/0.18/0.82	47	2000	1564	4.6
MPP3	1/0.09/0.91	65	2000	3434	10.1
PTMG samples	MDI/PTMG/BD				
MPT1	1/0.25/0.75	39	2000	1020	3
MPT2	1/0.18/0.82	47	2000	1564	4.6
MPT3	1/0.09/0.91	65	2000	3434	10.1

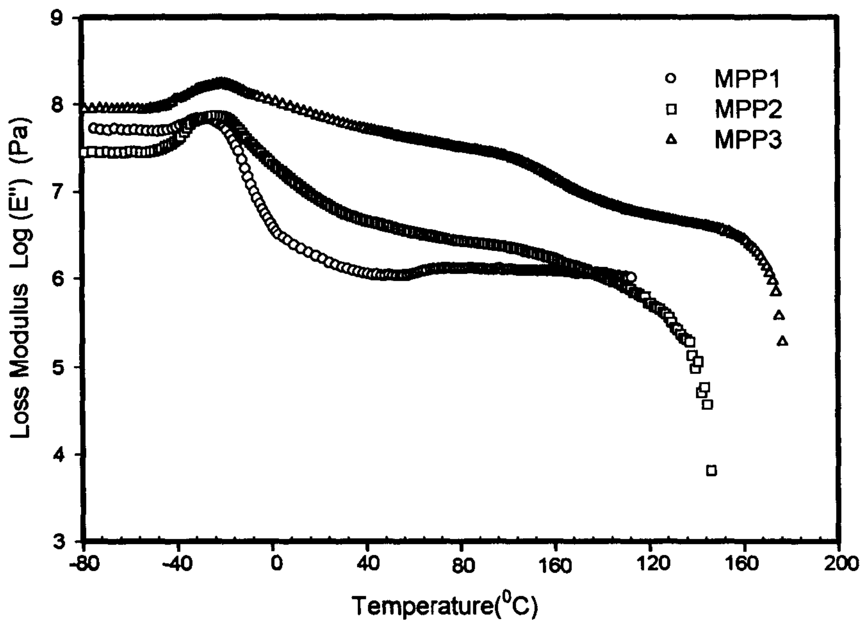


Fig 2. Effect of hard segment content on Loss Modulus of MPP samples