

Segmented Polyurethanes with BHPP, 2, 2-bis[4-(2-hydroxy-ethoxy)phenyl] propane, as a Chain Extender.

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1. Introduction

Polyurethane elastomers are segmented copolymer with an [HS] n -type structure. Typically, these materials are two-phase systems, prepared from relatively polar and stiff component called the hard segment(H) and relatively flexible component known as the soft segment(S).

Diisocyanate and chain extender together form the hard segment, which is dispersed within a matrix of the soft segment, composed of the macrodiols. 4,4'-Diphenylmethanediisocyanate(MDI) is a common diisocyanate for preparing elastomers, while 1,4-Butandiol(BDO) is a common chain extender. Macrodiol are usually polyester- or polyether- based. Polyether macrodiols afford elastomers with improved resilience, good performance at relatively low temperature, and resilience to hydrolytic and microbiological degradation.

Segmented polyurethanes are a class of polymers whose structure and properties can be varied relatively simply from tough plastics to soft elastomers by varying the molar ratio of the macrodiol and the chain extender. Owing to the differences in chemical structure and thermodynamical immiscibility between hard and soft segment, phase separation takes place.

Phase separation of the hard segment and soft segment is considered to contribute to the outstanding mechanical properties of these materials.

In the solid state, unique elastomeric properties are observed due to microdomain formation.

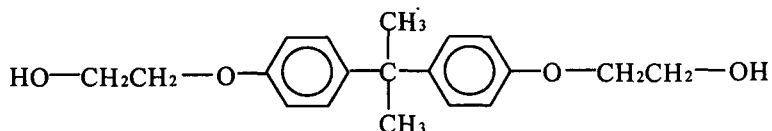
The so-called hard segment provides both physical crosslink sites and fillerlike reinforcement to the soft-segment matrix. At higher temperature, a homogeneous melt can be formed, allowing the material to be thermally processed.

An understanding of morphology is crucial to the rational design of improved polyurethanes. Morphological factors such as degree of hard/soft-phase separation, crystallinity, and domain size influence properties such as hardness, stiffness, tensile strength and clarity.

The morphology and properties of thermoplastic polyurethane elastomers are greatly influenced by the compatibility of starting compounds, the ratio of hard- and soft-block compounds, the average block lengths employed(including molecular weight distribution),

the thermal history of the material and the mechanical history endured by the material.

In this study the synthesis and properties of segmented polyurethane composed of PTMG, MDI, and BHPP, (2,2-bis[4-(2-hydroxy-ethoxy)phenyl] propane) as a chain extender by varying the molar ratio of the macrodiol and the chain extender was investigated. The influence of the hard segment content on the thermal and morphological properties of the segmented polyurethanes was studied and discussed in comparison with the analogous 1,4-butanediol chain extended MDI-products.



2. Material and Experiments

2.1 Materials

PTMG(Poly tetramethylene glycol) was obtained from BASF and dried in vacuum for 15 h at 50°C before use. MDI(4,4' diphenylmethane diisocyanate), Aldrich Co. Inc., was used as received after drying without further purification.

1,4-Butanediol was obtained from Junsei Chemical Co. LTD. Dimethylacetamide was dried over activated 4Å molecular sieves.

2.2 Synthesis

Synthesis of the polyurethanes involved a two-step bulk polymerization. PTMG was weighted into a reaction flask fitted with a condenser, stirrer, nitrogen inlet, and an additional funnel. The reaction flask was placed into an oil bath at 60°C and dried MDI was then added slowly and reacted for a total time of 2hrs while stirring. As the prepolymer was cooled DMAc was added to the prepolymer from addition funnel and stirred at high speed for enough time to dissolve the prepolymer perfectly. Then stoichiometric amounts of BHPP or 1,4-Butanediol in DMAc was added and the reaction continued for 20 hrs at room temperature. The concentration of reactant in DMAc was 30 wt%.

The polymer obtained was precipitated in a large amount of water and dried at 50°C in vacuum for at least 3 days. Films were made by casting the polymer solution on a glass and drying in air and then in vacuum at 50°C for 3 days.

3. RESULTS

3.1 Intrinsic viscosity measurement

Intrinsic viscosity of the polyurethanes, measured at 25°C in a DMF(dimethylformamide) at the concentration of 0.1g/100ml using an Ubbelohde Viscometer, were presented in Table 1.

BHPP chain extended polyurethanes have higher intrinsic viscosity than BDO chain extended one, and the highest intrinsic viscosity was obtained when using BHPP of 1.1 molar ratio, suggesting BHPP gives greater molecular weights.

Table 1. Composition and characteristic of the investigated polyurethane.

chain extender	molar ratio PTMG : MDI : C.E	hard segment content(%)	intrinsic viscosity(dl/g)	M.W of hard segment
BDO	1 : 2 : 1	22.7	0.348	589
BHPP	1 : 2 : 1	28.9	0.396	803
	0.9 : 2 : 1.1	32.0	0.449	941
	0.8 : 2 : 1.2	35.4	0.389	1095

3.2 Theraml Analysis

Figure 1. shows the weight loss of segmented polyurethane as a function of temperature at a heating rate of 20°C/min. The weights of the sample dropped off at around 300°C. There are no distinct difference between using BHPP and BDO as a chain extender.

Figure 2. shows DSC thermogram of segmented polyurethane.

Exotherms were observed in the samples, whose composition(PTMG:MDI:C.E) is 1:2:1 and 0.9:2:1.1, at about 20°C corresponding to the crystallization of soft block composed of PTMG and followed by endotherms relative to melting of soft block crystal.

While in the case of the polyurethane in which PTMG molar ratio is 0.8 the endotherm peak disappeared. It seems that phase mixing occurs with decreasing the concentration of the soft segment.

All investigated polyurethanes show the endotherm peaks corresponding to melting of hard segment at 320°C which is the simmlar to the temperature of onset of thermal degradation.

Reference

1. Pathiraja A. Gunatillake, Gordon F. Meijs, Ezio Rizzardo, Ronald C. Chatelier, Simon J. McCarthy, Arthur Brandwood, and Klaus Schindhelm, *J. appl. polym. sci.*, 46, 319, 1992
2. Darren J. Martin, Gordon F. Mejis, Gordon M. Renwick, Pathiraja A. Gunatillake, and Simon J. McCathy, *J. appl. polym. sci.*, 60, 557, 1996

3. 유 소라, 이 한섭, 서 승원, *polymer(Korea)*, 21, 3, 467, 1997
4. Zoran S. Petrovic, *J. polym. sci., polym. phys. Ed.*, 27, 545, 1989
5. Robert F. Harris, Michael D. Joseph, Carla Davidson, Craig D. Deporter, and Virginia A. Dais, *J. appl. polym. sci.*, 41, 487, 1990
6. Xiangdong He, Wudong Jia, and Xuehai Yu, *J. appl. polym. sci.*, 54, 207, 1994

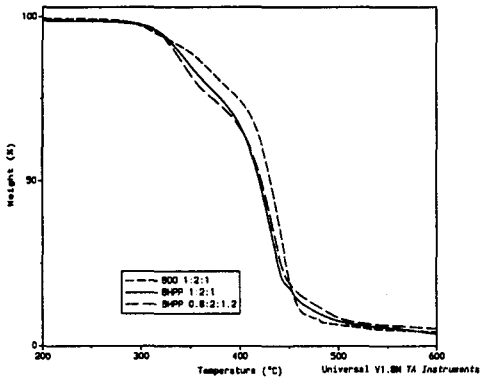


Fig. 1 TGA thermograms of Polyurethane.

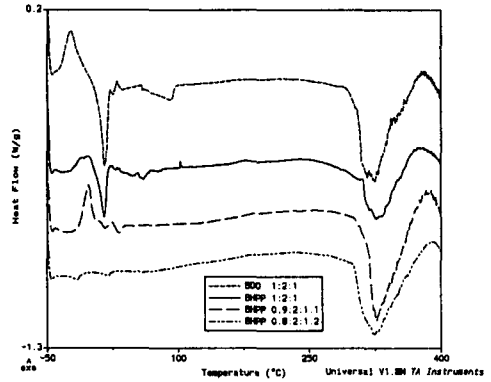


Fig. 2 DSC thermograms of Polyurethane.