

Morphology–Property Relationship of Segmented Polyurethaneurea: Influences of Soft-Segment Structure and Molecular Weight*

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SYNOPSIS

The relationships of the morphology and properties of a series of segmented polyurethaneurea (PUU) were studied in film form by using SEM and tensile stress–strain data. The polyether-based and polyester-based PUU block copolymers were synthesized using poly(propylene oxide)–ethylene oxide polyether or poly(butylene adipate) polyester with different molecular weights, 4,4-methylene bis(phenyl isocyanate), and diethyltoluene diamine. The extent of phase separation increased with increasing molecular weight of the soft segment. The polyether-based PUU showed better phase separation than did polyester-based PUU with the same molecular weight soft segment. The polyether–ester-based PUU showed the morphology of both polyether-based and polyester-based PUU but with larger domain size and interface. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethaneurea (PUU) block copolymers are made up of soft segments based on polyether or polyester and hard segments formed by reaction of diisocyanate and diamine extender. From the structural point of view, segmented PUU elastomers could be further divided into polyether-based and polyester-based PUU.

Sung et al.^{1–3} described the properties of segmented poly(tetramethylene oxide) (PTMO)-based PUUs and poly(butylene adipate) (PBA)-based PUUs. The morphological investigation of these materials, by means of small angle X-ray scattering (SAXS), has been carried out by Wilkes and Abouzahr.⁴

In this study, several kinds of segmented PUUs were investigated in film form using scanning electron microscopy (SEM) and tensile stress–strain measurements. The polyether-based and polyester-based PUU block copolymers were synthesized using

poly(propylene oxide) (PPO) polyether and PBA polyester with different molecular weights, 4,4-methylene bis(phenyl isocyanate) (MDI), and diethyltoluene diamine (DETDA). Moreover, polyether–ester polyol ($M_n = 2000$), prepared by reacting PPO polyether ($M_n = 1000$) with maleic anhydride (MA), following which the free carboxylic acid groups are oxyalkylated,⁵ is also used in this investigation.

EXPERIMENTAL

A. Syntheses

Segmented PUUs of MDI, DETDA, and a linear PPO polyether, PBA polyester, or PPO–MA polyether–ester were made by a two-step solution polymerization method,⁶ using *N,N*-dimethyl formamide (DMF) as solvent (dried over 4A molecular sieves, then vacuum distilled). MDI was also vacuum-distilled before use.

PUU films of 0.5–1.0 mm thickness were cast slowly from DMF solution at room temperature under a dry nitrogen environment followed by vacuum drying at 70°C for 1 week. A series of PUUs with

* Financially supported by the National Natural Science Foundation of China.

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Table I Chemical Composition for PUUs

Sample	Soft Segment Molecular Weight	Molar Ratio	Hard-segment Content (Wt %)
PPO : DETDA : MDI			
ET-42-1000	1000	1 : 1 : 2	42
ET-43-2000	2000	1 : 3 : 4	43
ET-41-3000	3000	1 : 4 : 5	41
PBA : DETDA : MDI			
ES-42-1000	1000	1 : 1 : 2	42
ES-43-2000	2000	1 : 3 : 4	43
PPO-MA : DETDA : MDI			
TS-43-2000	2000	1 : 3 : 4	43

different soft-segment structures and molecular weights was obtained and is listed in Table I.

B. Experimental Methods

SEM images were observed on a JEM-200CX. The PUU films were suspended in a bottle in which there

was a small amount of DMF solvent and the suspended films were selectively etched by DMF vapor at ambient for 2 weeks. The surfaces of these samples were coated by gold vapor before examination. Tensile tests were carried out at a strain rate of 20 mm/min with an Instron-1185.

RESULTS AND DISCUSSION

Figure 1(a)–(c) shows the SEM micrographs of the polyether-based PUU with different soft-segment molecular weights. Since the polyether (or polyester) soft segments are etched more easily than are the polyurea hard segments, corresponding relief on the sample surfaces could be observed. Hence, the dispersed phase on the surface of the systems investigated is a hard-segment-rich phase, whereas the continuous isotropic phase is formed by soft segments. It is clear that the granular aggregates of such a dispersed phase were enlarged with increasing soft-segment molecular weights from 1000 to 3000. By increasing the polyol molecular weight and enlarging the length of the segments, the compatibility between the two phases should be expected to decrease.

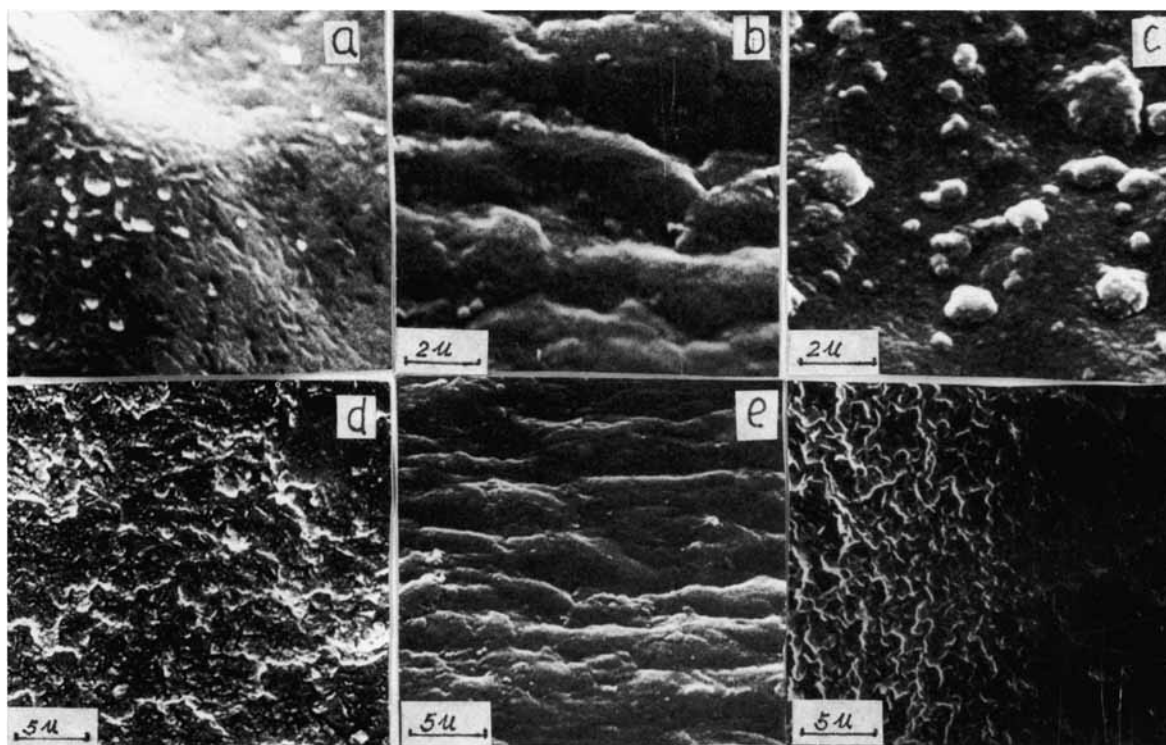


Figure 1 SEM micrographs of PUU samples. a. ET-42-1000; b. ET-43-2000; c. ET-41-3000; d. ES-43-2000; e. ET-43-2000; f. TS-43-2000.

Table II Tensile Properties of PUUs

Sample	Elongation at Break (%)	Ultimate Tensile Strength (MPa)	Young's Modulus (MPa)
ET-42-1000	150	9.33	53.30
ET-43-2000	186	10.35	76.67
ET-41-3000	200	10.90	112.00
ES-42-1000	267	14.75	—
ES-43-2000	284	54.90	—
TS-43-2000	64	23.70	286.00

Figure 1(d)–(f) exhibits the SEM micrographs of the polyester-based, polyether-based, and polyether-ester-based PUU with the same molecular weights of soft segment and hard segment. Obviously, the size of the phase region in the polyester-based PUU [Fig. 1(d)] is smaller than that in polyether-based PUU [Fig. 1(e)], indicating better phase separation in polyether-based PUUs. The polyether-ester-based PUU [Fig. 1(f)], however, exhibits a peculiar morphology, in which two morphologies for polyester-based PUU and polyether-based PUU can be found, respectively. Furthermore, a clear boundary exists between these two different morphologies. It seems likely that the morphologies of these PUUs depend mainly on the structure of the soft segment.

In general, the soft segment of polyester was found to contribute to greater phase miscibility than did that of the polyether, due to the stronger hydrogen bonding between the hard and soft segment.^{1,7} Thus, the distinct amorphous regions in Figure 1(f) may be attributed to the different polarity and capacity of forming hydrogen bonds between the polyether segments or polyester segments and hard segments. On the polyester-rich-phase side in the polyether-ester block copolymer, more hy-

drogen bonding could be formed than on the polyether side and it displays similar morphology to the polyester-based PUU.

The morphology of samples has a decisive influence on the physical properties. Table II indicates the mechanical properties of samples in terms of tensile strength, Young's modulus, and elongation at break. The experimental data showed that an increase in soft-segment molecular weight and, thereby, an increased sequence length of hard segment in the PUUs, confers increased mechanical properties. PUUs based on polyesters showed much better physical properties than those of polyether-based PUU, due to their ability to crystallize and to stronger forces between the macromolecular chains. Polyether-ester-based PUU displayed higher Young's modulus and tensile strength but less elongation, due primarily to the larger interface within it.

The authors wish to acknowledge financial support from the National Natural Science Foundation of China and Ethyl Co. for supplying us DETDA gratuitously

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Received April 2, 1992

Accepted May 27, 1992