일반강연 I-1

경질 분절 함량이 분절된 폴리우레탄/DMF/물 계에서 액-액상분리에 미치는 효과

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Effects of Hard Segment Content on Liquid-Liquid Phase Separation in a Segmented Polyurethane/DMF/Water System

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1. Introduction

Segmented polyurethanes(SPUs) are multiblock copolymers consisting of hard segments and polyether or polyester soft segments. These polymers possess many applications as biomaterials due to their excellent physical properties and relatively good biocompatibility[1]. The preparation of biomedical devices such as vascular prostheses often involves formation of porous polyurethane membranes via an immersion precipitation process.

In this presentation, we are concerned with the thermodynamic analysis of a SPU/dimethylformamide(DMF)/water system. In order to investigate the effects of the hard segment content of SPU on liquid-liquid phase separation, we prepared a series of SPUs based on poly(tetramethylene oxide)(PTMO), 4,4'-methylenebis(phenyl isocyanate) (MDI), and ethylene glycol (EG) with different molar ratios of MDI and PTMO. Because a greater crystallizability of the polymer is expected with increasing hard segment length[2,3], liquid demixing during immersion precipitation would be coupled with crystallization[4] when

the SPU has a high amount of the hard phase volume fraction. We obtained the phase diagram in the ternary system of SPU/DMF/water by a titration method and calculated the binodal curves to investigate the phase separation phenomena involved in polyurethane membrane formation.

2. Experimental

Segmented polyurethanes were prepared with a one-step solution polymerization method. Predetermined amounts of PTMO(Shinwha Petrochemical, *Mn* of 1990) and EG(Junsei Chemical) were added in dehydrated DMF(Aldrich). Stoichiometric amounts of MDI(Kumho Chemical) were added to the reaction mixtures while maintaining the reaction temperature at 65-70℃. The reaction was continued until it was impossible to stir the reaction mixture having 50 wt% of DMF, and then the methanol was introduced to the mixture to terminate the reaction.

Table I. Characterization of Segmented Polyurethanes

Sample code	MDI:PTMO:EG molar ratios	Hard segment weight %	M_n[a]	Density[b] (*g/cc*)
SPU-1	2.5 : 1.5 : 1.0	18.6	19533	1.0122
SPU-2	1.46 : 0.46 : 1.0	31.7	20222	1.0422
SPU-3	1.2 : 0.2 : 1.0	47.5	27330	1.0809
SPU-4	1.1 : 0.1 : 1.0	62.7	25457	1.1210

[a]measured by size exclusion method
[b]estimated from additive group contributions

Cloud-point curves were determined by a titration method at 20℃. A flask with a rubber septum stopper was charged with 50 *g* of polymer solution. Distilled water was introduced into the flask by a syringe through the septum, while thorough mixing was applied using a mechanical stirrer. Composition at the cloud point was determined by measuring the amount of water added when visual turbidity was achieved.

3. Results and Discussion

The results of the titration experiments to obtain cloud point curves are shown in Figure 1, in which the precipitation value of water (grams of water per 100 g of polymer solution in DMF to achieve phase separation) is plotted against the polymer concentration. As the hard segment content in the SPU increased, the amount of water to induce phase separation increased systematically below 20 wt% polymer concentration. The precipitation values for the SPU-4 solution decreased suddenly in a high concentration region and dropped to zero above 21.9 wt%: the 21.9 wt% SPU-4 solution in DMF was hazy at the titration temperature. The titration experiments revealed that the formed precipitate disappeared easily on stirring for the solutions of SPU-1, SPU-2, and SPU-3 when the amount of water introduced was below the precipitation value. However, the precipitate of SPU-4 solutions near the onset of phase separation was hardly solubilized when the polymer concentration was above 10 wt% and it seemed to result in formation of fine particles on stirring above 20 wt%. We were also able to observe a spherulitic morphology in the cross section of the SPU-4 membrane prepared by immersion precipitation, similar to the structures observed in membranes of crystallizable polymers[5]. Thus liquid-liquid phase separation was coupled with crystallization during membrane formation when the hard segment content in the SPU was high.

4. References

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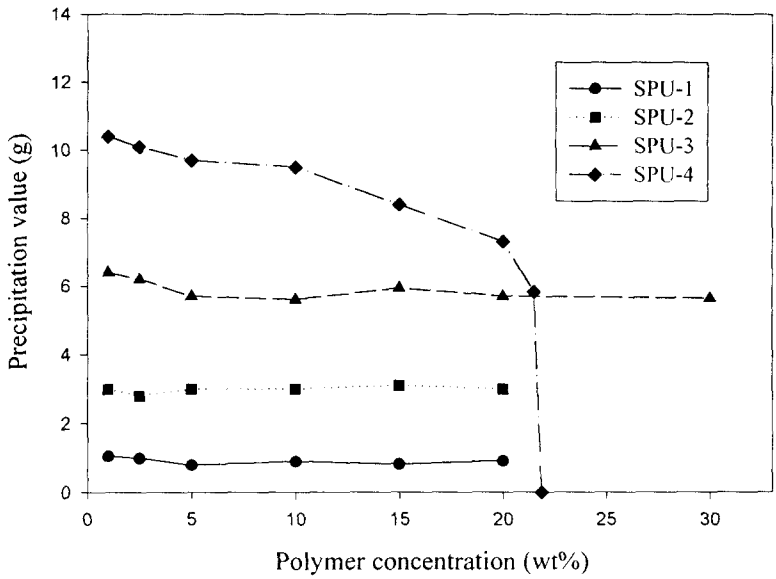

Figure 1. Precipitation values of water at 20℃ as a function of polymer concentration (grams of water per 100 g of polymer solution in DMF).