Formation of Polyurethane Membranes by Immersion Precipitation. I. Liquid–Liquid Phase Separation in a Polyurethane/DMF/Water System

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ABSTRACT: Liquid-liquid phase separation phenomena of polyurethane/DMF/water were studied. Two polyurethanes having different hydrophobicity were synthesized by varying the polyol components. The cloud-point curves for the ternary system of polyurethane/DMF/water were determined by the titration method. A small amount of water is needed to induce liquid-liquid demixing, and the region of the homogeneous phase is enlarged with increased hydrophilicity of the polyurethane. We measured the interaction parameters, and calculated the binodal and spinodal curves based on the thermodynamics of polymer solutions. The light transmission experiment showed that precipitation time increased with the higher content of DMF in a coagulation bath. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2377-2384, 1999

Key words: polyurethane membrane; phase separation; interaction parameter; binodal; spinodal

INTRODUCTION

Polyurethanes possess a wide range of properties to suit requirements in many applications such as foams, fibers, adhesives, synthetic leathers, and biomedical products. The preparation of synthetic leathers or biomedical products often involves formation of polyurethane membrane via an immersion precipitation process. Porous polyurethane membranes can be used for the soles of sports shoes with improved breathing, and also for biomedical applications with higher biodegradability. In this process, the homogeneous polymer solution is contacted with nonsolvent, and subsequent exchange of solvent and nonsolvent across the interface results in phase separation into a polymer-rich phase and a polymer-lean phase. The former results in a rigid, structural part of the membrane, while the latter gives a porous substructure. Phase separation is continued until the polymer-rich phase is solidified by gelation and/or crystallization of the polymer.¹⁻⁴

To investigate the final morphology obtained by immersion precipitation, we need to know both the thermodynamics and kinetics of phase separation. Knowledge of the thermodynamics such as the phase diagrams (binodal and spinodal lines, and critical compositions) enables one to change the compositions of the casting solution or the coagulation bath to obtain optimal membrane structure. Thus, the equilibrium phase diagram

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Polyurethane	Diisocyanate	Polyol	Chain Extender	${M_n}$ of Polyol	$\stackrel{M_n}{\operatorname{of}\operatorname{PU}}$	MWD of PU
PEA/MDI-PU PHA/MDI-PU	MDI MDI	PEA PHA	Ethylene glycol Ethylene glycol	2008 2016	$34960 \\ 33720$	2.42 2.34

 Table I
 Molecular Weight of Polyols and Polyurethanes

provides a tool to control and interpret the final morphology of the membrane. In this work, we were concerned with the thermodynamic analysis of a polyurethane/DMF/water mixture. We synthesized polyurethanes having different chemical structures. The interaction parameters were measured, and the binodal and spinodal curves were calculated.^{5,6} Our objective was to provide useful thermodynamic information to investigate the phase separation phenomena involved in polyurethane membrane formation.

EXPERIMENTAL

Materials

The polyols used in the synthesis of these polyurethanes were poly(ethylene adipate)diol and poly(hexamethylene adipate)diol. The polyester polyols were synthesized by the esterification reaction of adipic acid (Du Pont) with ethylene glycol (Junsei Chem. Co., reagent grade) and 1,6hexanediol (Junsei Chem. Co., reagent grade). The molecular weights of the polyols were about 2000. Polyols were dried overnight at 100°C under vacuum before use, and glassware was also dried overnight at 80°C in a convection oven to remove remaining moisture. The reaction of polyurethane synthesis was carried out by a one-shot process. Polyol, 4,4'-Diphenylmethane diisocyanate (MDI, Kumho Mitsui Chem. Co.), and ethylene glycol were mixed simultaneously in dimethylformamide (DMF, Tedia Company) to obtain the solution having 50 wt % of reactants. The ratio of equivalent weights of the components is 2.5 : 1 : 1.5 for MDI : polyol : ethylene glycol. Reaction temperature was 65°C, and the reaction was continued until it was almost impossible to stir the reaction mixture, then DMF was slowly added to resume stirring. The total reaction time was 5 h, and the final solid content of the reaction mixture was 30 wt %. Table I shows the components of the polyurethane and molecular weights of the synthesized polyurethane. Notation of PEA/MDI-PU means that poly(ethylene adipate)diol and MDI were used as polyol and diisocyanate, respectively. A similar notation was used for PHA/MDI-PU. The chain extender was ethylene glycol for both polyurethanes. Distilled water was used as a coagulant.

Cloud-Point Measurement

The cloud-point curves were determined by a titration method at 20°C. A flask with a rubber septum stopper was charged with 50 g of polymer solution. Distilled water was added 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.

Evaluation of the Water–Polymer Interaction Parameter χ_{13}

From the Flory-Rehner theory, χ_{13} is expressed as a simple equation:⁷

$$\chi_{13} = -[\ln(1 - \phi_3) + \phi_3]/\phi_3^2 \tag{1}$$

where ϕ_3 is the volume fraction of polymer and can be obtained by swelling experiments. Dried strips of homogeneous polyurethane films (about 0.3–0.4 g with a thickness of 50–70 μ m) were immersed in distilled water at 20°C. After 24 h the strips were removed, pressed between tissue papers and weighed. This procedure was continued until no further weight increase was observed and then ϕ_3 was calculated from the ratio of dried and water-swollen film.⁸

Evaluation of Solvent–Polymer Interaction Parameters χ_{23}

Solution viscosities of polyurethane in DMF at 20°C were measured with a Ubbelohde viscometer. The intrinsic viscosity was determined by the usual extrapolation to zero concentration, and the solvent-polymer interaction parameter was obtained by Kok's method.⁹

Light Transmission Experiment

At the onset of phase separation, the originally clear membrane solution turns cloudy. Because a cloudy solution scatters light, measuring the transmitted light intensity provides information on the precipitation process. A He/Ne laser was used as a light source, and the intensity profiles during immersion precipitation were recorded. For detailed experimental setup and procedures, one can refer to the work of Reuvers.¹⁰

Gibbs Free Energy of Mixing ΔG_M in Ternary Solutions

In this study, the Flory-Huggins lattice treatment^{5,11} was used to describe the thermodynamics of the ternary system. The Flory-Huggins expression was extended with a concentration dependent interaction parameter, the Gibbs free energy of mixing ΔG_M in ternary solutions is given by

$$\Delta G_M / RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12} (u_2) n_1 \phi_2 + \chi_{13} n_1 \phi_3 + \chi_{23} n_2 \phi_3 \quad (2)$$

where n_i is the number of mol, ϕ_i is the volume fraction of component *i*, *R* is the gas constant, and *T* is the absolute temperature. The g_{12} is the nonsolvent-solvent interaction parameter, χ_{13} is the nonsolvent-polymer interaction parameter, and χ_{23} is the solvent-polymer interaction parameter. The subscripts refer to nonsolvent (1), solvent (2) and polymer (3). For more details about the calculation of binodal and spinodal curves, one can refer to the previous publication of our group.¹² g_{12} is assumed to be a function of u_2 with $u_2 = \phi_2/(\phi_1 + \phi_2)$.¹³ Because there are no data available for concentration dependent interaction parameters of g_{13} and g_{23} , constant interaction parameters χ_{13} and χ_{23} are adopted instead.

RESULTS AND DISCUSSION

Phase Diagram of the Polyurethane/DMF/water Mixture

To calculate the phase diagram numerically, the three interaction parameters, namely g_{12} , χ_{13} , and χ_{23} , should be determined at a given temper-

Table IIInteraction Parameters forLiquid-Polyurethane

Solvent	PEA/MDI-PU	PHA/MDI-PU
DMF	-0.2	0.1
Water	3.2	4.1

ature. The concentration-dependent interaction parameter g_{12} for the water/DMF system is available from the literature, and varied from 0.5 to 0.96 with increasing the DMF content.¹⁴ The small value of g_{12} suggests that strong polar interaction exists in the water-DMF mixture. The DMF-polyurethane interaction parameter χ_{23} , determined by the measurement of the intrinsic viscosity, was 0.1 for the DMF/(PHA/MDI-PU) and -0.2 for the DMF/(PEA/MDI-PU) at 20°C. These χ_{23} values are quite low compared with the reported value of 0.45 for DMF–polyethersulfone and 0.48 for DMF–Polysulfone,^{15,16} which is indicative of a stronger hydrogen bonding between polyurethane and DMF. Because PEA/MDI-PU has a higher ester concentration in the backbone than PHA/MDI-PU, there should be more chance to form hydrogen bonding with DMF in the PEA/ MDI-PU system, resulting in a lower χ_{23} value. The values of the water-polyurethane interaction parameters χ_{13} were 4.1 for water/(PHA/MDI-PU) and 3.2 for water/(PEA/MDI-PU), which were determined from the equilibrium swelling experiment. The values of interaction parameters are summarized in Table II.

Experimental cloud points for the polyurethane/DMF/water system are plotted, with the calculated phase diagram, in Figure 1. An obvious feature is that a small amount of water is needed to induce liquid-liquid demixing, and that the region of the homogeneous phase is enlarged when changing the polymer component from PHA/MDI-PU into PEA/MDI-PU, which reflects the enhanced hydrophilicity of the polyurethane. The effects of the type of polyurethane on the precipitation value of water (grams of water per 100 g of polymer solution in DMF to obtain phase separation) as a function of polymer concentration are shown in Figure 2. Thus, 5.2 g of water is required to induce phase separation for 100 g of 10 wt % PHA/MDI-PU solution in DMF, while 11.8 g of water is required for the same concentration of the PEA/MDI-PU system.

Based on the Flory-Huggins thermodynamics,^{5,11} one can calculate the phase diagram in

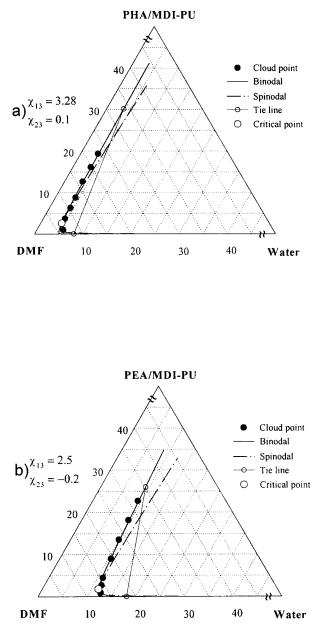


Figure 1 Cloud point at 20°C and calculated phase diagrams for the polyurethane/DMF/water systems (a) (PHA/MDI-PU)/DMF/water, and (b) (PEA/MDI-PU)/DMF/water.

terms of volume fraction of each component given a set of binary interaction parameters and molar volume ratios of v_1/v_2 and v_1/v_3 . Figure 1 gives calculated phase diagrams including binodal lines, spinodal lines, critical compositions, and tie lines for both systems of (PHA/MDI-PU)/DMF/ water and (PEA/MDI-PU)/DMF/water, in which the composition was converted into weight percentage. The calculated binodal lines were not in

good agreement with the experimental cloud point using the interaction parameters obtained experimentally. There may be uncertainty in the value of χ_{13} and χ_{23} , because the concentrationindependent interaction parameters were used. We were able to fit the calculated binodals with the experimental cloud points using the χ_{13} value of 3.28 for (PHA/MDI-PU)/DMF/water and 2.5 for (PEA/MDI-PU)/DMF/water, as shown in Figure 1, in which χ_{13} values were lower than those obtained by the swelling experiment. Similar trends were reported for the PES/NMP/water system¹⁷ and the polysulfone/solvent/water system.¹² Since the equilibrium swelling experiment should be carried out in extremely high concentrations of the polymer, due to the hydrophobic character of polyurethanes, the χ_{13} value in the practical concentration range would be lower than that obtained by a water sorption technique. In fact, for the PES/NMP/water system, the χ_{13} was 2.66 by the water sorption technique but 1.6 for 5-25 wt polymer concentration by the light-scattering method.17

Considering the change of the polymer from PHA/MDI-PU to PEA/MDI-PU, we could observe several interesting features. First, we observed that the slope of the tie line of the (PEA/MDI-PU)/ DMF/water system was steeper than that of the (PHA/MDI-PU)/DMF/water system. As the slope of the tie line increases to infinity for a given location in the phase diagram, the polymer concentration in the polymer-rich phase may decrease, resulting in the delay of solidification. Another important feature is a change of the metastable region. The metastable region, which is located between the binodal and spinodal lines,

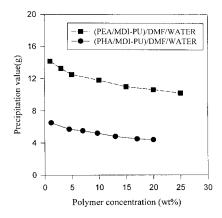


Figure 2 Precipitation values of water as a function of polymer concentration (grams of water per 100 g of polymer solution).

increased slightly for the (PEA/MDI-PU)/DMF/ water system. The stability of the system dictates the mechanisms of phase separation. If the composition stays at the metastable region for enough time to form the critical nucleus, phase separation occurs by the nucleation and growth mechanism. This indicates that phase separation by nucleation and growth may be more dominant for the (PEA/MDI-PU)/DMF/water system than for the (PHA/MDI-PU)/DMF/water system, assuming that other conditions are the same.

The critical compositions are shown as unfilled circles in the calculated binodal lines in Figure 1, and the polymer concentration at critical composition were very low for both the (PEA/MDI-PU)/ DMF/water system and the (PHA/MDI-PU)/DMF/ water system. The critical composition determines which phase is nucleated for the nucleation and growth process in membrane formation. There are two possibilities, depending on the composition of the initial polymer solution, with respect to the critical point. For $\phi_3 > \phi_{cr,3}$, where $\phi_{cr,3}$ is the critical polymer concentration, the nuclei consist of the dilute phase. For $\phi_3 < \phi_{cr,3}$, the nuclei consist of the polymer-rich phase. When phase separation starts at the critical composition $(\phi_3 = \phi_{cr,3})$, the structure formation is dominated by the spinodal decomposition.¹⁸ A typical membrane forming solution contains higher than 10 wt % of polymer concentration. In such a case, phase separation occurs by nucleation of the dilute phase, assuming that phase separation occurs by the nucleation and growth mechanism.

In the calculated phase diagrams, we have shown that the region of the homogeneous phase becomes larger when changing PHA/MDI-PU to PEA/MDI-PU as the polymer component. Because molecular weights of the two polymers are similar, we can assume that calculated phase diagrams depend solely on χ_{13} and χ_{23} at a given temperature. Therefore, we can recognize that the effect of changing the polymer from PHA/ MDI-PU to PEA/MDI-PU in a ternary phase diagram results from the decrease of χ_{13} and χ_{23} . We attempted to determine which interaction parameter significantly influenced the phase diagram upon changing the polymer from PHA/MDI-PU to PEA/MDI-PU. Figure 3 shows the change of binodal lines for the polyurethane/DMF/ water system with varying χ_{13} and χ_{23} values. To elucidate the effect of the interaction parameter, we used a combination of the χ_{13} and χ_{23} values of the (PHA/MDI-PU)/DMF/water and (PEA/MDI-PU)/ DMF/water systems. Curve (a) in Figure 3 repre-

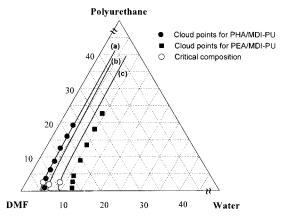


Figure 3 The change of binodal lines for the polyurethane/DMF/water system with varying χ_{13} and χ_{23} values (a) $\chi_{13} = 3.28$, $\chi_{23} = 0.1$; (b) $\chi_{13} = 3.28$, $\chi_{23} = -0.2$; (c) $\chi_{13} = 2.5$, $\chi_{23} = 0.1$.

sents the phase diagram corresponding to the original (PHA/MDI-PU)/DMF/water system with a χ_{13} of 3.28 and χ_{23} of 0.1. Curves (b) and (c) in Figure 3 represent the case for substituting χ_{23} and χ_{13} values with -0.2 and 2.5, respectively. The homogeneous region in case (c) becomes wider than in case (b). This result clearly indicates that the change of the polymer from PHA/MDI-PU to PEA/MDI-PU influenced the phase behavior more significantly by the nonsolvent–polymer interaction parameter χ_{13} rather than by the solvent–polymer interaction parameter χ_{23} .

Light Transmission during Immersion Precipitation

As the polyurethane solution is immersed in a nonsolvent bath, phase transition by liquid-liquid phase separation may occur. Precipitation time is defined as the time to induce liquid-liquid demixing upon immersion, and can be determined by measuring the elapsed time until the transmitted light intensity starts to decrease. We will discuss the light transmission profiles in terms of the composition of the initial coagulation bath and the dope polymer content, which are important parameters for membrane formation.

To investigate the effect of the coagulation bath composition, light transmission curves were obtained by immersing initial dope solutions into the bath having various concentrations of DMF in water. It is shown in Figure 4 that precipitation time increases with a higher content of DMF in the coagulation bath. Thus, the type of demixing changes from instantaneous demixing to delayed demixing. This is reasonable, because concentra-

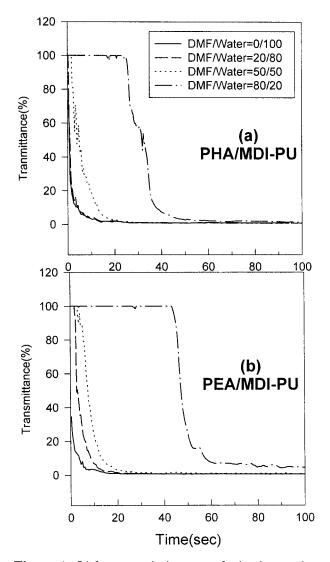


Figure 4 Light transmission curve during immersion of 20 wt% polyurethane solution in DMF into a coagulation bath having various compositions of DMF and water (a) (PHA/MDI-PU)/DMF/water and (b) (PEA/MDI-PU)/DMF/water.

tion gradients for the solvent/nonsolvent exchange rates decrease with the high concentration of DMF in the coagulation bath. Precipitation time is plotted, with the content of DMF in the coagulation bath, in Figure 5. It is observed that precipitation time slightly increases until about 50 wt % of DMF in the coagulation bath, and significantly increases regardless of the polymer type. This may indicate the presence of a critical composition of coagulation bath causing delayed demixing conditions. The precipitation time of the (PHA/MDI-PU)/DMF/water system is smaller in the whole composition range of the coagulation bath than that of the (PEA/MDI-PU)/DMF/water system. This is attributed to the increase of the homogeneous region in the phase diagram with PEA/MDI-PU.

The effect of the dope concentration on the precipitation time is summarized in Tables III and Table IV. It appears that the precipitation time is always longer for the initial dope having a higher polymer content until the solvent content in the coagulation bath does not exceed 50 wt %. This result agrees with the work of Cheng et al.¹⁹ for the cellulose acetate/acetone/water system. One has to consider two effects for this result. First, the flux of the solvent outflow would decrease in the concentrated solution, which increases the precipitation time. Second, in a solution with a higher polymer content, water inflow may also be reduced due to the inherent hydrophobicity of the polymer component. On the other hand, an interesting feature is observed when the coagulation bath contains 80 wt % of solvent, in which condition precipitation time shows the highest value with the polymer content of 20 wt % in the dope. This may be attributed to the decrease of the miscibility gap with a higher polymer concentration, as can be seen in Figure 1.

CONCLUSIONS

The cloud-point curves for the ternary systems of polyurethane/DMF/water were determined by the titration method. A small amount of water (3.1–6.1 wt % for PHA and 9.3–12.4 wt % for PEA) is needed to induce liquid–liquid demixing, and the

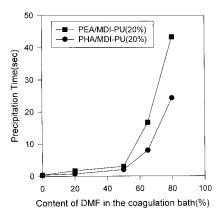


Figure 5 Experimental precipitation time for 20 wt % polyurethane solution in DMF into a coagulation bath having various compositions of DMF and water.

		Composition of Coagulation Bath				
Dope Polymer Concentration	DMF/Water = 0/100	DMF/Water = 20/80	DMF/Water = 50/50	DMF/Water = 80/20		
30%	0.3	0.3	3.3	11.6		
20%	0.3	0.7	3.0	24.3		
15%	0.3	0.3	1.0	15.0		

 Table III
 Precipitation Time for the Onset of Liquid-Liquid Demixing in (PHA/MDI-PU)/DMF/Water

 System (Time in Seconds)

region of the homogeneous phase is enlarged with PEA/MDI-PU, which is attributed to the enhanced hydrophilicity of polyurethane. Based on the Flory-Huggins theory, we can calculate the phase diagram in terms of volume fraction of each component given a set of binary interaction parameters and molar volume ratios of v_1/v_2 and v_1/v_3 .

The χ_{23} values at 20°C were 0.1, for DMF/ (PHA/MDI-PU) and -0.2 for DMF/(PEA/MDI-PU). By fitting the experimental cloud point with the calculated binodal lines, the χ_{13} values of 3.28 for the water/(PHA/MDI-PU) pair and that of 2.5 for the water/(PEA/MDI-PU) pair were obtained. We observed that the slope of the tie line of the (PEA/MDI-PU)/DMF/water system was steeper than that of the (PHA/MDI-PU)/DMF/water system. As the slope of the tie line increases to infinity for a given location in the phase diagram, the polymer concentration in the polymer-rich phase may decrease, resulting in a delay of solidification. Calculation showed that the metastable region in the phase diagram slightly increased for the (PEA/MDI-PU)/DMF/water system, which indicates that phase separation by the nucleation and growth may be more dominant for the the (PEA/MDI-PU)/DMF/water system.

The light transmission experiment showed that precipitation time increased with the higher content of DMF in the coagulation bath, and precipitation time of the (PHA/MDI-PU)/DMF/water system was smaller than that of the (PEA/MDI-PU)/DMF/ water system due to the increased hydrophilicity of PEA/MDI-PU. It appears that the precipitation time is always longer for the initial dope having a higher polymer content until the solvent content in the coagulation bath does not exceed 50 wt %.

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ABBREVIATIONS AND NOMENCLATURE

MDI:	4,4'-diphenylmethane diisocyanate
PEA:	poly(ethylene adipate)diol
PHA:	poly(hexamethylene adipate)diol
DMF:	dimethylformamide
g_{ij} :	concentration-dependent interaction pa-
	rameter between components i and j
χ_{ij} :	constant interaction parameter between
	components i and j
ϕ_i :	volume fraction of component I
n_i :	number of mol

Table IV Precipitation Time for the Onset of Liquid-Liquid Demixing in (PEA/MDI-PU)/DMF/Water System (Time in Seconds)

Composition of Coagulation Bath				
DMF/Water = 0/100	DMF/Water = 20/80	DMF/Water = 50/50	DMF/Water = 80/20	
0.3	2.0	3.3	39.0	
0.3 0.3	1.7	3.0 2.3	$\begin{array}{c} 43.3\\ 20.3\end{array}$	
	= 0/100	$\begin{array}{c c} \hline & & & & \\ \hline DMF/Water & & DMF/Water \\ = 0/100 & & = 20/80 \\ \hline & & & & & \\ 0.3 & & & & & \\ 0.3 & & & & & 1.7 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

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