Vitrification Phenomena in Polysulfone/NMP/Water System

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ABSTRACT: The vitrification line for the ternary system of polysulfone (PSf)/N-methyl-2-pyrrolidinone (NMP)/water was determined by differential scanning calorimeter (DSC) measurements with varying compositions. Pure PSf showed both α - and β -transition temperatures ($T_{g,\alpha} = 187.5^{\circ}$ C, $T_{g,\beta} = -21.4^{\circ}$ C). The $T_{g,\alpha}$ of PSf decreased with increasing solvent concentration. The $T_{g,\alpha}$ of PSf decreased linearly with the addition of NMP in the concentration range of 70–90 wt % polymer. The vitrification line was indicated in the phase diagram for the ternary system of PSf/NMP/water at 15 and 60°C. As the temperature is increased, a high polymer concentration was needed to reach the vitrification condition. The vitrification composition of the polymer in the binary system of PSf and NMP was 72.0 wt % at 15°C and 79.8 wt % at 60°C. We also found that the slope of the vitrification line changed with the temperature and that a small amount of water (10–20 wt %) can induce the vitrification of the polymer solution in the PSf/NMP/water system at 15°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 431–438, 1999

Key words: vitrification; polysulfone; phase separation; phase diagram; glass transition temperature

INTRODUCTION

Even though membranes have been successfully used in a large number of applications and in previous theoretical work, it is quite surprising that the production of membranes with optimum structures is still a matter of "art." Also, even though tremendous improvement has been made to understand the formation mechanism during the past four decades, only a few studies have investigated the solidification process.^{1–3} The preparation of polymeric membranes usually involves a phase-transition process, in which a homogeneous polymer solution undergoes phase separation into a polymer-rich phase and a polymer-lean phase by the exchange of a solvent with a nonsolvent in a coagulation bath. Phase separation would continue to form the membrane structure until the polymer-rich phase is solidified.⁴ Generally, solidification during phase sepa-

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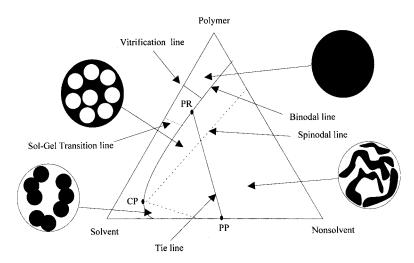


Figure 1 Schematic representation of a ternary phase diagram of polymer/solvent/ nonsolvent system.

ration may occur by gelation⁵ and/or by crystallization of the polymer.^{5,6}

Liquid–liquid phase separation was also reported to play a role in this gelation process. Wellinghoff et al.,⁷ in studying the thermoreversible gelation of atatic polystyrene solutions, postulated that the gelation in these systems occurs by liquid–liquid phase separation followed by a vitrification process of the polymer-rich phase.

Since knowledge of the vitrification phenomena can lead to a better understanding of the mechanism of membrane formation, it is desirable to include a vitrification line into the phase diagrams. While the final morphology obtained during phase inversion depends upon the kinetics as well as upon the thermodynamics of the phase separation, the equilibrium phase diagram and vitrification line for amorphous polymers is still a good tool for controlling the morphology and interpreting the membrane structure.

There are a few articles reporting on the vitrification lines of ternary mixtures of amorphous polymer/solvent/nonsolvent systems.^{1,5} In this study, we chose the system of amorphous polysulfone (PSf) which is widely used as a membrane material, since it has excellent chemical resistance, mechanical strength, thermal stability, and transport properties,⁸ and *N*-methyl-2-pyrrolidone (NMP) as a solvent and water as a nonsolvent.

In this article, we studied the vitrification process of PSf solutions. Our objective was to measure the glass transition temperature of PSf with varying contents of the solvent, which could determine the vitrification lines for the specified temperatures. On the basis of the results, the relationship between vitrification and membrane formation process is discussed.

THEORETICAL CONSIDERATIONS

Liquid-Liquid Phase Separation

When a homogeneous solution becomes thermodynamically unstable, for example, by the introduction of a nonsolvent, the original solution undergoes phase separation by splitting up into two liquid phases of different composition. In Figure 1, a schematic drawing of a ternary phase diagram is represented and one can see that all the compositions indicated by the points between the polymer-rich (PR) phase and the polymer-poor (PP) phase of the phase diagram will split up into two phases of the composition of PR and PP, which is called the liquid–liquid (L–L) phase separation. There are two kinetic ways for L-L phase separation to occur: either by nucleation and growth or by spinodal decomposition. Entering the metastable region, the area surrounded by the binodal and spinodal line, a nucleus is formed in the polymer solution. This nucleus together with many other nuclei will grow into droplets, until they touch each other and coalesce or until their growth stops because of solidification of the surrounding polymer solutions. The most interesting question here is: Which of the polymer phases will be nucleated when starting with a normal membrane casting solution? There are two possibilities depending on the composition of the initial polymer solution with respect to the critical point: For higher polymer concentration (ϕ_3) than the critical polymer concentration $(\phi_{cr,3})$, the nuclei consist of the PP phase, and in the other case, the nuclei consist of the (PR) phase.⁹ In our previous result,¹⁰ it was indicated that the critical polymer concentration $\phi_{cr,3}$ is mostly near 1–5 wt % in usual cases. Since a typical membrane-forming solution contains higher than 10 wt % of polymer concentration, it is expected to undergo L–L phase separation with the nucleation and growth of the PP phase.

The second kinetic process to L–L phase separation would occur if a nonsolvent could diffuse so quickly that it passed the spinodal line before nucleation could take place. For those compositions, the solution is unstable with respect to infinitesimal small concentration fluctuations. The solution then separates spontaneously¹¹ (by diffusion of molecules) into interconnected regions of high and low polymer concentration, ending up in intertwined networks of phases with compositions of PR and PP phases.

Gelation and Vitrification

Gelation can be defined as the formation of a three-dimensional network by chemical or physical crosslinking, but in membrane formation, chemical crosslinking will not be considered. The solidification of polymer solutions is frequently denoted by the general term "gelation." In membrane science, the terminology called gelation is not always clear: It is also applied to the cases of vitrification where the T_g of the PR phase becomes equal to the casting temperature and the viscosity of the PR phase increases abruptly at this point.

Physical gelation may occur by various mechanisms dependent on the type of polymer and solvent and nonsolvent. Microcrystallites, ionic interactions, hydrogen bonding, dipolar interactions, hydrophobic interactions, and solvent bridging may induce the formation of gels.¹² This gel state shows extremely high viscosity that would retard the molecular motion of polymers in solution. This is sometimes called a viscous transition.¹³ These sol–gel transitions have been observed in a semicrystalline polymer system including cellulose acetate/acetone/water¹⁴ and poly(2,6-dimethyl-1,4-phenyleneoxide)/trichloroethylene/methanol.¹⁵

But, for the amorphous polymers like PSf, polyimide, etc., there is no chance for gelation by crystallization. In these cases, vitrification is the main process of solidification of the membraneforming solution. An amorphous polymer with a high glass transition temperature shows glassy behavior at room temperature, but in the solution state, the glass transition temperature of the polymer is lower than room temperature, which means the polymer shows a rubbery behavior and the polymer chain can move with high mobility. In the immersion step, the polymer solution is quenched into a nonsolvent bath and mass transfer takes place. The ongoing loss of solvent can cause the state of the polymer solution "sol" to change into a "gel" and also change the state of the polymer "rubbery" to the "glassy" state which shows restricted mobility and, finally, fix the membrane morphology.¹⁶

EXPERIMENTAL

Materials

The PSf was Udel P-3500 purchased from Amoco Performance Products, Atlanta, GA. The polymer had an \overline{M}_n of 33,500 and an \overline{M}_w of 50,800 obtained by size-exclusion chromatography. The solvent was NMP purchased from Aldrich Chemical Co., Milwaukee, WI. The solvent was HPLC grade and used without further purification. Distilled water was used as a nonsolvent.

DSC Measurement

Samples were prepared by weighing the appropriate amount of PSf, NMP, and water in silver sample pans using a microsyringe. The amount of the polymer was about 8–10 mg. Pans were hermetically sealed and they were stored in a vacuum oven at least 2 days at 210°C to obtain a homogeneous solution. The sealed silver pan can endure 50 atm of inner pressure and there was no measurable weight loss after heat treatment. The temperature of 210°C was chosen because it is higher than the T_g of PSf (190°C). The DSC apparatus was a SEIKO Model DSC 120 equipped with cooling accessories for subambient operation. All DSC runs were carried out at a heating rate of 10°C per minute.

RESULTS AND DISCUSSION

The DSC thermogram of pure PSf is shown in Figure 2. When multiple glass transition temper-

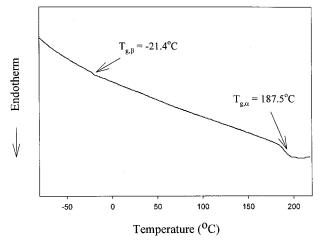


Figure 2 DSC thermogram of pure PSf.

atures are obtained, it is conventional to label the highest transition as an α -transition and labeling other transitions β , γ , etc., in decreasing order of temperature. The main-chain glass transition temperature corresponds to the α -transition. In the case of PSf, the α -transition temperature is observed at 187.5°C and the β -transition at -21.4°C is thought to be the result of phenylene group rotation.¹⁷ Since the β -transition is not relevant for the vitrification process in membrane preparation, we will consider only the α -transition in this study.

The DSC thermograms of the PSf solutions in NMP and in a mixed solvent of NMP and water are shown in Figure 3 as a function of polymer content. In the mixed solvent system, the ratio of NMP to water is 94/6 in weight. All DSC thermograms show a tendency of decreasing T_g with the addition of solvent. In the earlier study of Gaides and McHugh,⁵ they reported on the vitrification line of a PSf/dimethyacetamide (DMAc)/water system, but their experimental result shows only the pure solvent case. Their result indicated that the vitrification composition of PSf and pure DMAc is composed of 76 wt % of PSf and 24 wt % of a solvent at 25°C. The effect of solvent content on the glass transition temperature of PSf is shown in Figure 4 up to 50 wt % of solvent content. The glass transition temperature decrease with the addition of solvent is more pronounced in the concentrated region and is reduced in the dilute region.

Since membranes are generally prepared at room temperature, it is very important to know the vitrification composition in that temperature range. Figure 5 shows the relationship between total solvent content and the T_g of the PSf solution, which indicates that a linear relationship exists in the range of interest. The slope of the pure solvent case is steeper than that of the mixed solvent case. From this figure, we also estimate the vitrification composition at 25°C and it indicates a very similar polymer concentration in both pure solvent and mixed solvent cases.

Since a linear relationship between total solvent content and the glass transition temperature of PSf was confirmed in the practical temperature range, one can obtain the composition of the solution at the glass transition temperature which is summarized in Table I. We also tried to find the vitrification composition using the Kelley–Bueche glass temperature depression equation¹⁸ for ternary systems containing two diluents as described by Burghardt et al.² The equation proposed by Burghardt et al. is given as

$$T_g = \frac{R_1 \phi_1 T_{g1} + R_2 \phi_2 T_{g2} + \phi_3 T_{g3}}{R_1 \phi_1 + R_2 \phi_2 + \phi_3} \tag{1}$$

where ϕ_i are the volume fractions of the diluent 1 and 2 and the polymer 3; T_{gi} are the glass transition temperatures of pure component *i*; and R_i $= \Delta \alpha_i / \Delta \alpha_3$, with $\Delta \alpha_i$ being the difference in thermal expansivity between the liquid and glass for component *i* (component 1: water, component 2: NMP, component 3: PSf). All data needed for the calculation were found in literature sources.^{19–21} In the binary mixture of PSf/NMP, as shown in Figure 4, the R_2 value of 2.6 fitted the experimental T_g decrease very well. Based on this R_2 value, and using eq. (1), an R_1 value of 3.2 was obtained to describe the ternary mixture of the PSf/NMP/water (the ratio of NMP to water is 94/6 in weight) T_g behavior.

It is useful to include the vitrification line in the phase diagram because we can anticipate the behavior of phase separation and the solidification process. In Figure 6, empty circles represent experimental cloud points at 15°C, the dashed lines (a) and (b) show calculated binodal line at 15 and 60°C, the dash-dot lines represent the tie lines, and the solid lines (c) and (d) indicate vitrification lines at 15 and 60°C for the PSf/NMP/water system. The binodal and tie line was obtained based on Flory–Huggins thermodynamics with a concentration-dependent interaction parameter $g_{12} = 0.785 + 0.665u_2$, $\chi_{13} = 2.7$, $\chi_{23} = 0.35$ at 15°C and $g_{12} = 0.785 + 0.665u_2$, $\chi_{13} = 2.6$, and $\chi_{23} = 0.15$ at 60°C¹⁰ (u_2 is the polymer-free volume fraction of the

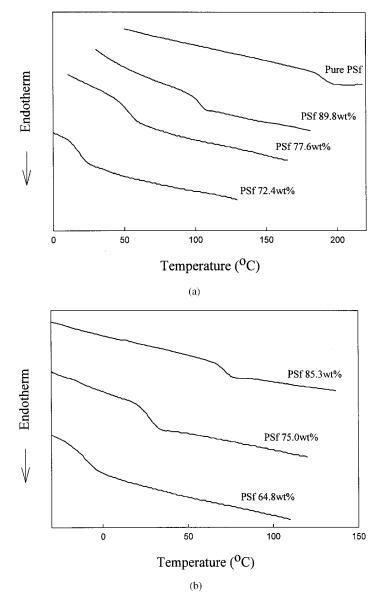
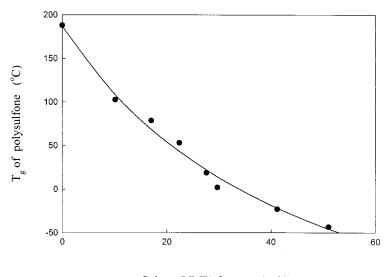


Figure 3 (a) DSC thermograms of PSf/NMP systems; (b) PSf/NMP/water system in which the ratio of NMP to water is 94/6 in weight.

solvent). At 60°C, the vitrification composition consists of 79.8 wt % of PSf and 20.2 wt % of NMP, which indicates a higher polymer concentration than in the case of 15°C. Thus, in the membrane formation at elevated temperature, phase separation can proceed further before reaching the vitrification point. Another interesting feature is the change of the slope of the vitrification lines with temperature. If the water and NMP molecules induce the same plasticizing effect, the slope should be parallel to NMP–water axes in the phase diagram. The slope decreases with the addition of water at 15°C and increases at 60°C as can be seen in Figure 6. At low temperature, the plasticizing effect is reduced due to a less favorable interaction between the polymer and the mixed solvent, which indicates that the water molecules act as a weak plasticizer for PSf. We did not find a suitable explanation for the high-temperature behavior; however we consider that the following reason could partly describe the unexpected high-temperature behavior: At low temperature such as 15°C, there exists a strong specific interaction between NMP and water due to the polar nature of both components, which gives rise to producing a polar complex of one NMP molecule and two water molecules.²⁰ At a high tem-



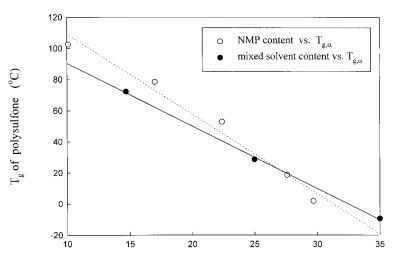
Solvent(NMP) Content (wt%)

Figure 4 Effect of the NMP contents on the glass transition temperatures of PSf and solid line indicates the fitting curve of the Kelley–Bueche equation using an R_2 value of 2.6.

perature of 60°C, the specific interaction between NMP and water is reduced and this effect leads to increasing plasticizer effects of both NMP–PSf and water–PSf, which result in increasing the slope of the vitrification line.

The most important information from Figure 6 is that we can correlate mass transfer with the vitrification phenomena. From this figure, we can estimate the amount of water to induce the vitrification and predict the time at which the vitrification begins with a proper mass-transfer model.

In this study, we considered a simplified masstransfer model having a constant ratio of polymer and solvent and only the nonsolvent is introduced into the polymer solution as indicated by solid lines (e) and (f), of which initial solution compositions are composed of 20 and 40 wt % of PSf and 80 and 60 wt % of NMP, respectively. Point W



Solvent Content (wt%)

Figure 5 T_g of PSf/NMP systems and PSf/NMP/water system in which the ratio of NMP to water is 94/6 in weight.

(composed of 5 wt % of water, 76 wt % of NMP, 19 wt % of PSf) is located at the binodal line. It indicates that, if more nonsolvent is introduced into the polymer solution, then the original solution undergoes phase separation by splitting up into two liquid phases of different composition. If the composition reaches point X (composed of 19 wt % of water, 65 wt % of NMP, 16 wt % of PSf), which is located on the tie line of the vitrification condition, vitrification can occur and is followed by fixation of the membrane morphology. In the case of point Y (composed of 14 wt % of water, 52 wt % of NMP, 34 wt % of PSf) which originates from a more concentrated solution, a lesser amount of water is needed to induce vitrification than for the case of the dilute solution. Point Z (composed of 32 wt % of water, 54 wt % of NMP, 14 wt % of PSf) represents the vitrification composition for the higher-temperature case (60°C) and it indicates that more water is needed to induce vitrification than for the case of 15°C. If we develop a more sophisticated mass-transfer model which shows the composition path during the membrane formation, then we can estimate the membrane morphology more clearly using the vitrification concept.

CONCLUSIONS

The vitrification line for the ternary system of PSf/NMP/water was determined by DSC measurement with varying compositions. In the case of PSf, the α -transition temperature is observed at 187.5°C, and the β -transition, at -21.4°C, thought to be the result of phenylene group rotation. The T_g decrease with the addition of the solvent is more pronounced in the concentrated region and less in the dilute region and there is a linear relationship between the $T_{g,\alpha}$ of PSf and

Table I Total Solvent Content (wt %) to Reach the Vitrification Temperature in PSf/NMP and in PSf/NMP/Water System

	T_{g}				
Solvent	15°C	$25^{\circ}\mathrm{C}$	30°C	$45^{\circ}\mathrm{C}$	60°C
$\begin{array}{l} \text{NMP} \\ \text{NMP} : \text{H}_2\text{O} \\ = 94:6 \end{array}$	28.0 28.6	26.3 26.2	$\begin{array}{c} 25.4\\ 24.9\end{array}$	$\begin{array}{c} 22.8\\ 21.2 \end{array}$	$\begin{array}{c} 20.2\\ 17.5 \end{array}$

The ratio of NMP to water is 94/6 in weight.

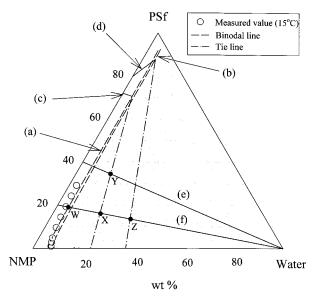


Figure 6 Ternary phase diagram for PSf/NMP/water system showing a calculated binodal line (a) at 15°C and (b) at 60°C. An experimental binodal line at 15°C, vitrification line (c) at 15°C and (d) at 60°C, tie line, and (e,f) simplified mass transfer path are also included.¹⁰

the solvent content in the range of interest, which is between 10 and 30 wt % of the solvent.

We also draw the vitrification line in the phase diagram for the ternary system of PSf/NMP/water at 15 and 60°C. As temperature increases, the vitrification line moves upward, which means a higher polymer concentration is needed to reach the vitrification condition. The vitrification composition was 72.0 wt % of PSf and 28.0% of the solvent at 15°C and 79.8 wt % of PSf and 20.2% of solvent at 60°C, respectively. We also found that the slope of the vitrification line changed with temperature and it was steep in the case of higher temperature. From the phase diagram and vitrification line, we found that a small amount of water (10-20 wt %) can induce the vitrification of polymer solution in the PSf/NMP/water system at 15°C and more water is needed to induce vitrification at the higher temperature.

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