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Phase separation analysis of Extem/solvent/non-solvent systems and relation with membrane morphology

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ABSTRACT

The phase separation behavior of Extem/water/solvent systems for various solvents and Extem/NMP/non-solvent systems for different types of coagulants was investigated. Ternary phase diagrams of studied systems were constructed based on cloud point data obtained by titration at room temperature. In the first part, N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were employed as solvent and water was used as coagulant. The cloud point curves from these systems showed that Extem/NMP/water and Extem/DMSO/water has the smallest and largest demixing gap, respectively. Subsequently, water, methanol, and glycerol were employed as coagulants and NMP was selected as solvent. The obtained results indicated that water and methanol had the strongest and weakest coagulant power, respectively. The linearized cloud point and precipitation value were applied to identify the strength of the non-solvent for casting solution (Extem/NMP) with a certain concentration. The solubility curve of Extem was obtained using the Hansen solubility parameter, calculated by a group contribution method. In order to evaluate the influence of different solvents and non-solvents on the final structure of the resulting membranes, scanning electron microscopy (SEM) was used. The morphology of the membranes prepared from Extem/solvent/water systems (except Extem/DMSO/water) showed a finger like sub-layer, while a sponge-like structure was observed for the Extem/DMSO/water system. Using methanol as coagulation medium resulted in a thick dense layer over a macroporous sub layer, while a fully sponge like structure with microporous skin layer was obtained for the Extem/NMP/glycerol system. In order to find the source of these unexpected observations, thermodynamic and kinematic aspects such as binary interaction parameters, heat of mixing, viscosity and diffusion rate were discussed thoroughly.

1. Introduction

Phase inversion (phase separation), as a well-known method, is used for the preparation of polymeric membranes that can be applied in various processes and applications such as gas separation, water treatment, the biochemical and pharmaceutical industry, etc. The preparation of asymmetric membranes can be accomplished by several techniques which non-solvent induced phase separation (NIPS) is the most industrially used method [1–5]. In NIPS, a homogeneous polymer solution containing a polymer and a relevant solvent is first casted as a flat film on a suitable support, shortly exposed to air, then immersed in a coagulation medium that acts as a non-solvent for the membrane casting solution. The so formed membrane typically has an asymmetric structure including a thin, selective top layer over a porous sublayer. It should be noted that if water vapor is absorbed by the casting solution, phase separation can take already place, as applied in the so called vapor-induced phase separation (VIPS) technique [6–8]. Generally, structure of the membrane is controlled by both the thermodynamic and the kinetic aspects of the membrane forming system. The thermodynamic part of the system is defined by the phase equilibrium between components while the kinetic part is related to the mutual diffusion between components [9–11].

The ternary phase diagram plays a key role in defining the final morphological and microstructure of the membrane. Since a phase diagram is constructed based on thermodynamic characterization of the system, it shows a qualitative description of the thermodynamic features of the membrane formation process. In addition, ternary phase diagrams can clearly demonstrate whether a certain polymer/solvent/non-solvent system forms a membrane with specific structure [12,13]. Therefore, in order to improve asymmetric membranes, a comprehensive analysis of the phase separation behavior of a casting solution in the presence of a non-solvent is essential. Fig. 1 shows the

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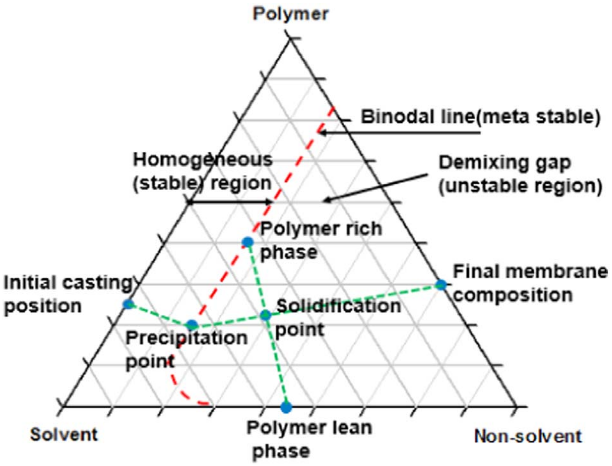

Fig. 1. Schematic phase diagram of the ternary system during membrane formation.

ternary phase diagram and composition path of the polymer solution during precipitation process. The ternary diagram is divided into two regions by the cloud point curve: a homogenous stable region where all species are present in a single phase, and a two phase region where the system is divided into separate phases, a polymer rich and a polymer lean phase, which are in thermodynamic equilibrium.

In a ternary system, every composition on the cloud point curve (meta-stable region) demixes into two separate phases (of course with different compositions) but that are in equilibrium. The membrane formation is tracked from the initial casting solution to the final solid structure through the composition path. The precipitation point is the point that the polymer precipitation starts. As the precipitation continues, the polymer viscosity increases to becomes high, and is considered a solid. Composition of polymer, solvent and non-solvent in each separated phase at equilibrium state can be determined by a tie line passing through the solidification point. Thus, the initial composition of the polymer solution, the position of the binodal line and the composition pathway have a profound effect on the membrane morphology [14,15]. It should be noted that in macromolecular systems, equilibrium always does not occur, while as mentioned above the phase diagram presents an equilibrium state. Hence, the phase separation in these systems is affected by kinetic parameters as well [16,17]. Although kinetics of transport process influence the membrane final structure, thermodynamic analysis of phase separation is still the main interest of many researchers. For example, Kim et al. [18] evaluated the phase separation and corresponding membrane structure of Matrimid/DMSO/water and Matrimid/NMP/water systems at room temperature. They determined the ternary phase diagram including the binodal and spinodal curves, gelation point, and tie-lines. The cloud point curve of Matrimid/DMSO/water system was much closer to the polymer-solvent axis compared to Matrimid/NMP/water. The opposite result was observed by SEM images. A finger-like structure was obtained for Matrimid/NMP/water system while the Matrimid/DMSO/water system exhibited a sponge-like (free macrovoid) membrane. It was found that in the Matrimid/DMSO/water system, the membrane morphology is determined at an earlier stage than in the Matrimid/NMP/water system, resulting in a sponge-like structure. Wang and Teo [19] analyzed the phase separation behavior of Ultem/solvent/non-solvent systems for different solvents and non-solvents through the measurement of precipitation values (PVs) at temperatures between 20 and 50 °C. The hollow-fiber membranes prepared from a solvent with higher PV showed a dense skin layer, while a porous skin layer was observed from a solvent with much lower PV. Leblanc et al. [20] experimentally determined the ternary phase diagram of a fluorinated polyimide (6FDA-mPDA) by using different solvents and non-solvents at 20 °C. They also evaluated the morphology of membranes prepared from a 6FDA-mPDA/solvent/non-solvent systems by SEM to examine the correlation with the membrane morphology. The comparison of SEM images showed that the local polymer concentration is the most important factor for membrane formation, which is directly related to the thermodynamic and kinetic parameters. Barzin and Sadatnia [21] investigated the phase separation and membrane morphologies of PES/DMAc/water and PES/NMP/water systems at room temperature. An instantaneous liquid-liquid demixing was induced for both systems; this typically results in macrovoids occurrence. Despite the lower miscibility (higher interaction parameter) between water/NMP compared to water/DMAc, the membranes prepared from the water/NMP system showed less sponge-like structures. They discovered that the type of macrovoid structures is significantly affected by the position of vitrification and gelation boundaries. Yin et al. [22] analyzed theoretically the phase behavior of three systems including polyamic acid (PAA)/DMAc/water, PAA/DMAc/ethylene glycol (EG) and PAA/DMAc/ethanol. The surface and cross-section structures of the fibers were also investigated by SEM. This indicated that an increasing DMAc amount in the coagulation bath generates sponge-like with rough surfaces, while further increasing the DMAc concentration led to porous structures.

In the current study, we attempted to comprehensively analyse the phase separation behavior of Extem/solvent/non-solvent systems with various solvents and non-solvents and to relate thermodynamic and kinetic parameters of the studied systems with their membrane morphologies. To the best our knowledge, no research is available in the literature on the phase separation behavior of Extem/solvent/non-solvent systems. Thermodynamic phase diagrams of Extem/solvent/non-solvent systems for different solvents and coagulations were constructed by cloud point measurement at room temperature. The solubility region (solubility envelope) of Extem was identified based on Hansen solubility parameters, calculated through group contribution. In order to identify the non-solvent strength for the casting solution (Extem/NMP), the linearized cloud point (LCP) and PV were employed. The morphology of asymmetric flat sheet membranes was examined by SEM to evaluate the effect of various solvents and coagulants on the final structures of membranes. The reason for selecting Extem as the polymer is that it is a relatively new aromatic polyetherimide with ether (–O–), isopropylidene ($-C(CH_3)_2-$) and sulfone (S=O) groups, which has an excellent performance up to high temperatures with a superior resistance to chemicals including organics and acids, a high thermal-oxidative stability and good processability [23]. This makes it a good candidate for membrane processes like gas separation, organic solvent nanofiltration and pervaporation in harsh environments. The structure of Extem is shown in Fig. 2.

2. Experimental

2.1. Choice of solvents and non-solvents

In phase inversion process, the choice of a solvent/non-solvent combination has a profound effect on the morphology, mechanical properties and separation performance of asymmetric membranes [5,24]. The choice of a solvent is actually depends on the selection of the polymer, since the polymer must readily dissolvable or dispersible in the selected solvent.

NMP, DMF, DMAc, and DMSO were employed as the solvents for the dope formulation due to their high miscibility with water; they have a different degree of interaction with the polymer (Extem). However, it is not easy to evaporate those solvents from the casting solution due to their poor volatilities. Therefore, vacuum evaporation, high temperature evaporation, or a prolonged evaporation period should be applied.

Before the selection of the coagulants, it should be noted that the solvent and the non-solvent must be completely miscible. Deionized water was used as an inexpensive and environmentally safe coagulant. Methanol and glycerol were also selected as non-solvents due to their

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