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On the initiation of macrovoids in polymeric membranes – effect of polymer chain entanglement

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ABSTRACT

The present work investigated the mechanism of macrovoid initiation in polymeric membranes, with focus on the initiation position of macrovoids. The results show that where macrovoids were initiated strongly depended on the polymer concentration in casting solution and the solvency for polymer of the solvent used. Comparing the results with the rheological properties of casting solutions, we observed a close relationship between the initiation position of macrovoids and the degree of polymer-chain entanglement in the casting solution. High degree of chain entanglement helped to suppress the occurrence of macrovoids. And low quality solvent enhanced chain entanglement and brought about environment not favored for macrovoid initiation. We also obtained results showing that the time needed to induce the phase separation of casting solution played an important role in initiation of macrovoids. A model was developed to take into account the effects of the degree of chain entanglement and the time needed to induce phase separation, by using the chain relaxation time to characterize the effect of chain entanglement and the time constant of the movement of phase separation front to quantify the time needed for phase separation. The model can quantitatively describe the relationship between the initiation position of macrovoids and the polymer concentration in casting solution for the polymeric membranes prepared in the present work.

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1. Introduction

The wet phase inversion process, also called immersion precipitation, has been widely used to prepare porous polymeric membranes [1]: cast films of homogeneous polymer solution are immersed in coagulation bath (usually water bath) to bring about phase separation of the films and formation of porous structure. During the process, the homogeneous solution demixes to form polymer-rich and polymer-poor phases. The polymer-rich phase turns into the matrix of membranes and the space occupied by the polymer-poor phase becomes pores after the solvent and coagulant are removed from the precipitated solution. Though the process has been used for decades to prepare commercial membranes, it still attracts much research attention [2–4].

An interesting research topic related to the phase inversion process is the formation of macrovoids in polymeric membranes. Macrovoids are elongated pores in membranes that can sometimes span the cross-section starting from the membrane surface

till the bottom [1]. The existence of macrovoids lowers the flow resistance when the membranes are applied to membrane filtration processes. However, they weaken the mechanical strength of membranes and may result in structure collapse under high transmembrane pressure. Researches have been performed to get insight into how the macrovoids are initiated and how it can grow to a length on the order of 100 μm [5].

Several mechanisms were proposed for the formation of macrovoids. Some researchers [6,7] believed that the interfacial instability caused by the surface tension gradient on the cast film was the reason for the initiation of macrovoids. Strathmann et al. [8] argued that the shrinkage of polymer-rich phase after phase separation caused rupture of the surface of cast films. And then through the rupture points the capillary force drove the flow of coagulant into casting solution to form macrovoids. Smolders and his co-workers [9] proposed that instantaneous demixing of casting solution resulted in nuclei of polymer poor phase that could later imbed the solvent in casting solution to grow into macrovoids. They pointed out that the concentration difference between the macrovoid nuclei (polymer-poor phase) and the casting solution was the driving force for the nuclei to grow. The

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mechanism was later modified by McKelvey and Koros [10] to explain why macrovoids can grow to a length covering the whole membrane cross-section. To further explain the fast growth of the nuclei of macrovoids, Krantz and his co-workers [11–14] proposed that the growth of macrovoid nuclei was driven by solute-capillary convection.

Though the formation of macrovoids has been investigated for a long time, a unanimous mechanism has not yet been obtained. In addition to the mechanisms discussed above, several other mechanisms [15–18] have been proposed to explain new observations on the formation of macrovoids. Some stressed the important role of polymer gelation in macrovoid formation [16]. Other works [18,19] pointed out that macrovoids could be initiated by viscous fingering, a hydrodynamically unstable phenomenon occurring when a less viscous fluid displaces a more viscous one. And a mechanism based on the competition between viscous fingering and phase separation was proposed to reason the macrovoid initiation [19]. Some of the proposed mechanisms reported in the literature are not consistent. For example, though instantaneous demixing caused by fast exchange of solvent and coagulant was recognized as an important factor for initiation of macrovoids [2,20], some other research results indicated that fast phase separation of casting solution helped to suppress the occurrence of macrovoids [19,21]. To resolve the inconsistency and to unify the theories on macrovoid formation, more researches are still needed.

A point that has not been elaborated in the literature is the role of phase separation mechanism. Casting solution can phase separate via the mechanism of nucleation and growth (NG) or spinodal decomposition (SD), depending on the solution composition at which phase separation occurs [1]. The mechanism is NG if the phase-separation composition is in the meta-stable region, and the mechanism is SD if the composition is in the unstable region. As the solution phase separates via NG, the formation of macrovoids can be explained by the classic theory proposed by Smolders and his co-workers [9]: phase separation results in nuclei of polymer-poor phase that can grow into macrovoids. However, as the solution phase separates via SD, phase separation generates continuous polymer-poor phase but not nuclei-type. Under the circumstance, one needs to use other mechanisms, instead of phase separation, to account for the initiation of macrovoids. The focus of the present work is to investigate macrovoid initiation as the casting solution demixes via SD.

Phase separation via SD requires fast exchange of solvent and nonsolvent, so that the solution composition stays in the meta-stable region for only a short period and there is thus not enough time for phase separation to occur via NG (formation of nuclei takes time). For membrane formation systems that the exchange of solvent and nonsolvent is fast enough to bring about spinodal decomposition, evidenced by forming membranes with bi-continuous (lacy) structure, a characteristic to be reported in the present work is that macrovoids may not occur right at the membrane surface, but occur at deeper positions, with a distance to the membrane surface. In the present work we systematically investigated the initiation positions of macrovoids in membranes containing bi-continuous structure and then developed a model based on the obtained results to get insight into the mechanism of macrovoid initiation.

2. Experimental

2.1. Materials

Polysulfone (PSF50800, Udel[®] P-3500, $M_w=50,800$ g/mol, $d=1.24$ g/cm³) was purchased from the Amoco Products Inc. (Ridgefield, CT, USA). PMMA (poly(methylmethacrylate), $d=1.18$ g/cm³, $M_w=120,000$ g/mol) was purchased from Sigma-Aldrich. And PI (polyimide, $d=1.03$ g/cm³, $M_w=119,035$ g/mol) and PEI (polyetherimide, $d=1.27$ g/cm³, $M_w=17,098$ g/mol) were provided by Taiwan Textile Research Institute. N-methyl-2-pyrrolidinone (NMP, $d=1.03$ g/cm³) of reagent grade was purchased from Riedel-de Haën (RDH 15780) and 2-pyrrolidinone (2P, $d=1.12$ g/cm³) of reagent grade was purchased from Sigma-Aldrich. The de-ionized water was used as the coagulant to prepare membranes and as the nonsolvent additive in some of the casting solutions.

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2.2. Membrane preparation

Polysulfone (PSF) was dissolved in three kinds of solvent: N-methyl-2-pyrrolidinone, 2-pyrrolidinone, and 2-pyrrolidinone with water (0.5 wt%). They are referred to as NMP, 2P, and 2P/water, respectively. The dissolution temperature was controlled at 60 °C. For each kind of solvent, homogeneous polymer solutions with different PSF concentrations were prepared. The PSF solutions were cast into thin films on glass plates. In the following, if without specific description, the casting thickness was 200 μm. The cast films were then immediately immersed into coagulant (water) bath and stayed there for about 24 h to allow of polymer precipitation and complete exchange of solvent and coagulant, after which the precipitated films were peeled off from the glass plates and dried to form membranes in the air at room temperature. With the same method, PMMA, PI, and PEI membranes were prepared by immersing PMMA/NMP, PI/NMP, and PEI/NMP solutions into water bath.

2.3. Scanning electron microscopy (SEM)

The membrane samples were fractured in liquid nitrogen and coated with platinum. The membrane structures were then examined by using a Hitachi (S-4800) scanning electron microscope. With the SEM photos, the positions where macrovoids started to occur were located and their distance to membrane surfaces was determined.

2.4. Measurement of solution viscosity

The viscosities of the polysulfone solutions were measured by using a Brookfield viscometer (DV-1+; Brookfield Engineering Labs. Inc., Stoughton, MA). The measurement temperature was constant at 25 °C. The solution viscosities at different shear rates were obtained. Extrapolation of the data to 0 s⁻¹ gave the zero-shear viscosities. All the viscosity data of PSF solutions are zero-shear viscosities. And the viscosities of PMMA/NMP, PI/NMP, PEI/NMP solutions were measured at the shear rate of 10 s⁻¹.

2.5. Observation on the moving of phase separation front

A drop of casting solution was introduced into the space between two slides that separate with a gap of 15 μm. Afterwards the slides and the solution were placed under an optical microscope (Olympus BHT-M-113D). Coagulant (water) was then introduced through the gap to contact with the casting solution to bring about phase separation. The moving of the phase separation front was observed with the microscope and videotaped. The videotaped images were further analyzed by using commercial software (Optimas 5.1, Bioscan). The positions of the phase separation front at different times were identified and recorded.

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