



# The prediction of polymeric membrane characteristics prepared via nonsolvent induced phase separation by the apparent coagulation time



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## ABSTRACT

Model cellulose acetate (CA) membranes were prepared by casting their solutions containing different polymer compositions and formamide (cosolvent) to acetone (solvent) ratios (FAR) followed by their precipitation in a water bath. The selected system provided the opportunity of changing the membranes morphology systematically via phase separation by nucleation and growth of polymer lean phase, spinodal decomposition and nucleation and growth of polymer rich phase mechanisms. The membranes morphological analysis by scanning electron microscopy confirmed their phase separation by various mechanisms leading to finger-like, sponge-like and sintered bead-like structures, respectively. The solution polymer concentration increase at constant FAR decreased the membranes porosity and pure water permeability, while enhanced their thicknesses, whereas it's FAR increase at constant polymer concentration raised the aforementioned characteristics. The application of simple phenomenological  $\eta_0\Delta P^{-1}$  model where  $\eta_0$  and  $\Delta P$  stand for the solution zero shear viscosity and the nonsolvent based osmotic pressure difference, respectively, well-predicted the membranes porosities and thicknesses. The model corresponded the apparent coagulation time, which its capabilities further proved by well-predicting the membrane thicknesses of three selected sets of experimentally found literature data representing the effects of polymer additive, cosolvent and polymer concentration.

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## 1. Introduction

Immersion precipitation is still the most popular method of preparing polymeric membranes. The product forms as a thin film experiencing nano-structuring through its solution casting followed by immersion precipitation in a nonsolvent bath. Morphology is a key characteristic affecting membrane properties, which its manipulation deserves a very intricate job due to many material and process based variables involved [1]. Therefore, many research groups have set their main goal to achieve design guidelines for membrane preparation with finite morphology and its predictability since 1970. Strictly speaking, the research works dedicated to the membrane structure prediction can be divided into two main categories. The first group has engaged in solving the mass transfer equations for extracting the solution composition evolution path (or the phase separation path) on a ternary phase diagram [2–8]. This challenging job leads to the threshold

composition of phase separation onset. The second group, however, has focused on developing simple phenomenological models based on sound foundations. The phenomenologist's actually started earlier if the pioneering work of Schulz [9] is considered who obtained an empirical relation between polymer solution concentration ( $C$ ) and precipitant concentration ( $\xi$ ) at the onset of phase separation:

$$\log C = a + b\xi \quad (1)$$

where  $a$  and  $b$  are constants. Later,  $K = C\gamma^n$  correlation was presented for prediction of membrane structure [10].  $C$  and  $\gamma$  were polymer solution concentration and required precipitant volume to activate phase separation, respectively. In addition,  $K$  and  $n$  represented precipitation constant and polymer–solvent interaction parameter, respectively. Membranes with high  $n$  exhibited fine porous structures.

High and low rates of casting solution precipitation usually correspond instantaneous and delayed demixing, respectively, leading to finger-like structure in the former and sponge-like structure in the latter [11]. Ternary phase diagram of nonsolvent/

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solvent/polymer system with large two-phase region requires less nonsolvent for the onset of liquid–liquid phase separation and corresponds to finger-like void formation [12]. Accordingly, the relative size of two-phase region,  $\Phi$ , was estimated by the following equation and used to predict membrane structure [13]:

$$\Phi = \frac{\Delta\delta_{P-S}\Delta\delta_{P-NS}}{\delta_P\Delta\delta_{S-NS}} \quad (2)$$

where  $\Delta\delta_{P-S}$ ,  $\Delta\delta_{P-NS}$  and  $\Delta\delta_{S-NS}$  are the solubility differences between polymer–solvent, polymer–nonsolvent, and solvent–nonsolvent, respectively while  $\delta_P$  stands for polymer solubility parameter. The increase of  $\Phi$  dictates finger-like structure while its decrease leads to sponge-like structure formation.

Precipitant (coagulant or nonsolvent) diffusion rate into casting solution is also a determinant key parameter in demixing type. A linear correlation was found between the square of nonsolvent penetration depth ( $L^2$ ) and the coagulation time ( $t$ ) by superimposing experimental data by the Fick's second law [11]. The extracted correlation was proposed as a simple tool for membrane structure prediction [14–16]. Similarly, the square of wet membrane thickness ( $d^2$ ) over its coagulation time ( $\tau$ ) is nominated as the apparent diffusion coefficient,  $D_a$ , which is proportional to the square of precipitant diffusion depth ( $L^2$ ) over the precipitation time ( $t$ ) [17]:

$$D_a = \frac{d^2}{\tau} \propto \frac{L^2}{t} \quad (3)$$

The application of  $D_a$  led to the correct porosity estimation for several prepared membranes [17]. By emphasizing on the solvent–nonsolvent exchange rate as a key factor in controlling membrane final morphology, the average in-diffusion nonsolvent velocity into the casting solution was also proposed as a phenomenological simple model for predicting membrane characteristics [18].

The mixing free energy change between casting solution and precipitant along with solution viscosity were also used simultaneously to modify the membrane structure estimation [19]. The former and the latter were respectively reported as the major motive for and resistance against macrovoid formation. Membrane systems with higher heat of mixing between solvent and precipitant also found susceptible to finger-like morphology [11]. Nonsolvent osmotic pressure difference between precipitant and polymer lean phase nucleus of casting solution was also nominated as a key factor manifesting macrovoid formation [20]. In other words, higher nonsolvent osmotic pressure difference causes fast precipitant diffusion and instantaneous demixing of casting solution leading to macrovoid formation. A phenomenological criterion for delineating nonsolvent affinity toward spinning solution,  $X$ , was also combined with dope on-line viscosity,  $\eta$ , to predict the as-spun fiber porosity with some successes [21]:

$$X\eta^{-1} = \frac{\Delta\delta_{P-S}^2\Delta\delta_{P-NS}^2}{\eta\Delta\delta_{S-NS}^2} \quad (4)$$

Later, nonsolvent affinity toward casting solution was substituted by the more exact quantity of components mixing free energy change [22]. Accordingly, the nucleus growth inside membrane precursor after its instantaneous nucleation by polymer lean phase was modeled and corresponded with  $\Delta P\eta_0^{-1}$ .  $\Delta P$  and  $\eta_0$  were nonsolvent osmotic pressure difference between the coagulation bath and solution and zero shear viscosity of solution, respectively. Well correlated  $\Delta P\eta_0^{-1}$  with dimension of inverse time and the membrane porosity was found [22]. Interestingly,  $\Delta P\eta_0^{-1}$  behaves similar to  $K_{os}\eta_0^{-1}$  parameter of Endo et al. [23].

They studied solution phase separation under shear flow and found  $K_{os}\eta_0^{-1}$  as key controlling parameter, which  $K_{os}$  represented the solution osmotic modulus. In other words, solution phase separation under shear flow corresponds to immersion precipitation by nonsolvent intrusion. Indeed,  $K_{os}\eta_0^{-1}$  represents apparent diffusion coefficient ( $D_{app}$ ) [24] in phase separated systems via spinodal decomposition. In other words,  $K_{os}$  represents the second derivative of Gibbs free energy of mixing (thermodynamic motive), while  $\eta_0^{-1}$  stands for diffusivity or molecular mobility [25]. Seifollahi et al. [22] also pointed out the equivalence of  $\Delta P\eta_0^{-1}$  with  $D_{app}$ . Nonetheless,  $\Delta P$  in their model represented the first derivative of Gibbs free energy of mixing (thermodynamic motive). Several simple membrane characteristics: Thickness, turbidity, porosity and pure water permeability were also used to quantify the phase separation path of solution approaching its phase boundary [26,27].

In this research work, the porosity and thickness of model CA membranes developed by various phase separation mechanisms were estimated correctly based on a simple phenomenological model,  $\Delta P\eta_0^{-1}$ . The first derivative of Gibbs free energy of mixing,  $\Delta P$ , performs as thermodynamic driving force of coagulant intrusion, while solution zero shear viscosity,  $\eta_0$  behaves as a resistive force. The former was calculated by the compressible solution model of Mayes [28,29], while the latter was measured experimentally. The model application was also successful in predicting the membranes thicknesses of three sets of experimentally found literature data.

## 2. Experiments

### 2.1. Materials

Cellulose acetate (CA) with acetyl content of 39.8 wt%,  $M_n = 30,000$  g/mol, density of  $1.39$  g/cm<sup>3</sup> and purity of more than 99% was purchased from Aldrich. Acetone and formamide were supplied by Merck and used as received. Tap water was used as coagulant.

### 2.2. Preparation of polymer solutions

Polymer was mixed with acetone and formamide with different compositions in sealed glass bottles according to the prescribed recipes, Table 1. The mixtures were left for 24 h at 40 °C and then homogenized using a magnetic stirrer. The prepared solutions were then stored at room temperature for another 24 h to allow the removal of entrapped air and temperature equilibration.

### 2.3. Rheological characterization

Brookfield viscometer (model RVT-ESER: 55162) was used to determine the shear viscosity of the polymer solutions at ambient temperature ( $21 \pm 1$  °C). The measured viscosities of various solutions were then extrapolated to zero shear rates to extract  $\eta_0$ . Experimental error margin was at most 10%.

### 2.4. Membrane preparation

The polymer solutions were cast as thin films, 200  $\mu$ m in thickness, on smooth glass plates. The membrane precursor was then quickly immersed into a vessel containing 9 L of stagnant tap water at  $21 \pm 1$  °C. Maximum evaporation period of the cast solutions in air was  $5 \pm 1$  s. After polymer precipitation, the peeled off membrane was transferred into a larger vessel containing tap water and left for a week before performing characterization.

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