Phase inversion simulation of polymer PVDF membrane based on a fluid model

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Abstract
Based on the non-solvent-induced phase inversion (NIPS) membrane production process, we developed a model incorporating hydrodynamic effects and phase-field theory to simulate the phase separation process induced by concentration differences in polymer solutions. The influences of the initial polymer concentration and the composition of the coagulation bath on the film structure were studied. We found that the phase separation process starts from the top of the polymer solution layer and proceeds downwards in the layered structure. In the same system, as the initial PVDF concentration increases, the simulated morphology changes from a bi-continuous pattern to isolated droplets, thus determining the membrane morphology. Also, the validity of the model has been verified by corresponding experiments. Therefore, the model can be applied to other PVDF ternary membrane systems by modifying the material and its property parameters.

Keywords
Immersion-precipitation, polymer concentration, coagulation bath composition, delay time

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Introduction
The non-solvent-induced phase inversion (NIPS) method, also known as the immersion precipitation method, is one of the simpler methods commonly used in membrane preparation. When this method is used, the PVDF hydrophobic membranes can be prepared and modified in one step, with high performances such as large flux good hydrophobic properties, as well as high rejection and permeability.¹⁻³

The preparation typically undergoes two processes, namely, the liquid-liquid phase separation of the system and the phase transition. The film preparation is a non-equilibrium process. The thermodynamic properties of the polymer solution and the kinetic process of film formation can affect the structure and performance of the film. The film formation is actually an unsteady kinetic process. The final structure and morphology of the film are affected by both the solvent and non-solvent diffusion processes, and also by the thermodynamic properties of the system.⁴⁻⁵ In order to visualize the evolution of the membrane structure during the

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film-making process, many works have adopted computer simulation methods to explore the evolution path of the membrane morphology, and have given some important conclusions.

Termonia used the Monte Carlo particle model to calculate and simulate the membrane production process, and obtained different membrane morphological structures by changing the interaction parameters between the solvent and non-solvent.\textsuperscript{6,7} However, in their simulation system, only the diffusion dynamics are considered and the effects of fluid mechanics were ignored. Lee et al.\textsuperscript{8} established a wet casting polymer film model to discuss how the concentrations of casting solutions and the non-solvent bath interface were adjusted from the initial non-equilibrium to the equilibrium value at the double equilibrium point. This new model explained the influence of the casting solution thickness on the occurrence of macropores. Lin et al.\textsuperscript{9} established a new dissipative particle dynamics (DPD) simulation method to study the influence of the interphase mass transfer between the casting liquid and the non-solvent bath on the membrane formation process and membrane morphology. They concluded that frequent non-solvent interaction and increased mass transfer strength could lead to strong phase separation. However, this research was based on a hypothetical system composed of parameters such as polymer, solvent, and non-solvent particles, some of which may be idealized to the extent that they reduce the degree of compliance with the actual film production conditions. Tree et al.\textsuperscript{10} developed a multi-fluid model for ternary polymer solutions using Doi and Onuki’s Rayleigh form to quantitatively predict the fastest growth model obtained from the simulations, and to analyze the phase separation processes related to microstructural evolution in ternary polymer solutions. However, the model ignores some physical effects such as elastic stress and thermal fluctuations. Using the continuum and phase-field model of the terpolymer solution, Tree et al.\textsuperscript{11} studied the mass transfer driving the non-solvent-induced phase separation and found that the time required for the non-solvent to diffuse to the bottom of the film is a pivotal time scale. However, this model does not include heat fluctuations and cannot explain the nucleation phenomenon.

It is worth noting that, during the PVDF membrane formation process, the membrane structure is influenced by many factors, with the skin layer and sub-layers having different phase separation behaviors, which are influenced to varying degrees by thermodynamics and kinetics. Although certain idealized states have been used in existing simulation studies, for example, some of which consider the diffusion dynamics while ignoring the effects of fluid mechanics, and this does not conform to the real situation. In this paper, a model incorporating hydrodynamic effects and phase-field theory is developed to simulate the phase separation process induced by concentration differences in polymer solutions. It is proposed that the velocity field and energy are shared by all phases, and a set of momentum equations were constructed to solve the polymer diffusion during the simulated film formation process. The influences of the initial polymer concentration and the composition of the coagulation bath on the film structure were studied. The effects of different polymer concentrations and solvent systems on the film structure were studied.

### Method

#### Model

**Establishment of the model.** The established fluid model simulates two or more fluids by solving a set of momentum equations, and tracks the volume fraction of each fluid throughout the computational domain. The fluid model is constructed to track the free surface according to the function $\phi_f$, which is the volume occupied by the fluid in the grid unit at each time.\textsuperscript{12} The model is built on a two-dimensional Cartesian coordinate system, and the governing equations are the mass conservation equation, momentum conservation equation, and energy conservation equation of fluid flow. The mass and energy transfer produced by the phase change process are added to the conservation equations in the form of source terms, and solving for it using ANSYS 19.1.

The parameters involved in the control equations in the model and their meanings are shown in Table 1.

| Table 1. Parameter meaning. |
|-------------------------------|
| **Symbols** | **Meaning** | **Unit** |
| $U$ | Rate | m/s |
| $t$ | Time | s |
| $\rho$ | Density | kg/m$^3$ |
| $n$ | Time step | s |
| $P$ | Pressure | Pa |
| $g$ | Gravitational acceleration | m/s$^2$ |
| $\mu$ | Viscosity | Pa s |
| $\phi$ | Phase volume fraction | % |
| $F$ | Interface power source project | N/m$^3$ |
| $\sigma$ | Surface tension coefficient | N/m |
| $k$ | Curvature | 1/m |
| $\bar{n}$ | Unit normal | |
| $E$ | Energy | J |
| $T$ | Temperature | K |
| $k_{\text{eff}}$ | Effective thermal conductivity | $\lambda$ |

The mass conservation equation is defined as:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho U) = 0 \quad (1)$$

The density of the mixed system is defined as:

$$\rho = \phi_p \rho_p + \phi_s \rho_s + \phi_{ns} \rho_{ns} \quad (2)$$
\(\phi\) is the volume fraction of each phase, and the subscripts \(p, s, ns\) represent polymer phase, solvent phase, and non-solvent phase, respectively. \(\rho_p = 1.78g/cm^3, \rho_{ns} = 1.0g/cm^3, \rho_{DMC} = 1.1g/cm^3, \rho_{DMAC} = 0.909g/cm^3, \rho_{DMF} = 0.994g/cm^3\).

The volume fraction of each phase is defined by:

\[
\phi_p + \phi_s + \phi_{ns} = 1 \tag{3}
\]

The equation of the volume fraction for multiple phases is solved to track the phase interface. The volume fraction continuity equation is:

\[
\frac{\partial}{\partial t} \phi_i \rho_i + \nabla \cdot \left( \phi_i \rho_i U_i \right) = 0 \tag{4}
\]

The volume fraction equation can be discretized as follows: \((i = p, s)\)

\[
\frac{(\phi_i \rho_i)^{n+1} - (\phi_i \rho_i)^n}{\Delta t} V + \sum_f \left( \phi_{i,f} \rho_i U_i \right)^{n+1} = 0 \tag{6}
\]

where:

\(n\) and \(n + 1\) represent the previous and current time steps, respectively. Accordingly, \(\phi_i^n\) and \(\phi_i^{n+1}\) represent the volume fraction value of the grid cell body centers at the time steps of \(n\) and \(n + 1\), respectively, while, \(\phi_{i,f}^n\) and \(U_i^n\) represent the volume fraction value and the velocity of the grid cell face center at the time step of \(n + 1\), respectively. \(V\) represents the volume of the grid cell.

At each current time step, the phase volume fraction is the function of other phase variables. Therefore, it is necessary to iteratively solve the phase volume fraction equation when solving the volume fraction of a phase at any time step.

The model obtains the velocity field by solving a set of momentum equations in the entire computational domain, and the velocity field is shared by all phases. The momentum conservation equation is:

\[
\frac{\partial \rho U}{\partial t} + \nabla \cdot \left( \rho U \right) = -\nabla P + \nabla \cdot \left[ \mu \left( \nabla U + \nabla U^T \right) \right] + \rho g + F \tag{7}
\]

In this simulation, \(P\) is the static pressure, \(F\) is the source term, which is the surface tension, \(\mu\) is the dynamic viscosity, and \(T\) is the surface stress tensor caused by the surface tension. The viscosity of the mixed system is defined as follows:

\[
\mu = \phi_p \mu_p + \phi_s \mu_s + \phi_{ns} \mu_{ns} \tag{8}
\]

The physical property parameters Density \(\rho\) and Viscosity \(\mu\) in the momentum conservation equation depend on the volume fraction of all phases.

In this model, the surface tension is used as the source term of momentum equation (7), which is given by:

\[
F = \sigma \left[ \frac{\rho_p k_p \nabla \phi_p + \rho_s k_s \nabla \phi_s + \rho_{ns} k_{ns} \nabla \phi_{ns}}{\left( \frac{1}{13} \left( \frac{\rho_p + \rho_s + \rho_{ns}}{3} \right) \right)} \right] \tag{9}
\]

In equation (9), \(\sigma\) is the surface tension coefficient; \(k\) is the droplet surface curvature defined by the divergence of unit normal \(\vec{n}\), which is obtained by the following equation13:

\[
k_p = \nabla \cdot (\vec{\vec{n}}_p) k_s = \nabla \cdot (\vec{\vec{n}}_s) k_{ns} = \nabla \cdot (\vec{\vec{n}}_p)
\]

\(\vec{n}\) is defined as the divergence of interface normal:

\[
\vec{n}_p = \frac{\nabla \phi_p}{|\nabla \phi_p|}, \vec{n}_s = \frac{\nabla \phi_s}{|\nabla \phi_s|}, \vec{n}_{ns} = \frac{\nabla \phi_{ns}}{|\nabla \phi_{ns}|}
\]

According to the divergence theorem, the force at the surface can be converted to volume force. This volume force is the source term added in the momentum equation.

The energy equation is:

\[
\frac{\partial \rho E}{\partial t} + \nabla \cdot \left[ \rho (E + P) \right] = \nabla \cdot (k_{\text{eff}} \nabla T) + S_k \tag{10}
\]

Energy is also shared by all phases, as shown below, where \(E\) and \(T\) represent energy and temperature, respectively, and they are all variables based on the average of mass,

\[
E = \frac{\phi_p \rho_p E_p + \phi_s \rho_s E_s + \phi_{ns} \rho_{ns} E_{ns}}{\phi_p \rho_p + \phi_s \rho_s + \phi_{ns} \rho_{ns}} \tag{11}
\]

In the formula, each phase \(E_i\) is the function of the specific heat capacity and phase temperature; the density \(\rho\) and effective thermal conductivity \(k_{\text{eff}}\) are shared by all phases. The source term \(S_k\) includes radiation and other volumetric heat source terms.

**Model parameters.** The unknown parameters in the established fluid model are set according to the existing parameters and determined by the built-in algorithm of the fluid software. However, some values cannot be determined accurately, which will be worked on in future research. Among them, the bi-directional diffusion coefficient of solvent-non-solvent is set based on previous research results14 and are shown in Table 2.
Experiment

Experimental materials and reagents. PVDF raw materials were purchased from Shanghai Sanaifu New Material Technology Co., Ltd., model FR904. N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO) were purchased from Tianjin Comio Chemical Reagent Company, all analytical grade. The non-solvent was deionized water. The parameters of the three solvent systems are shown in Table 2.

We verified the accuracy of the model through experiments. Three groups of PVDF with different volume fractions were selected for experimental verification. The specific compositions are listed in (Table 3).

Before the experiment, PVDF was dried in an oven at 60°C for 24 h to remove excess water, and an appropriate amount of solvent was measured using an Erlenmeyer flask. A certain amount of pure water was weighed and mixed in the solvent, then dispersed ultrasonically. Then a certain amount of PVDF was weighed and stirred in the mixed solution at a constant temperature in a 60°C-water bath for 10 h until PVDF was completely dissolved. The final solution was ten-stood in a 60°C water bath to defoam for 12 h. The casting solution was scraped on the glass plate with a spatula (choose a thickness of 200 μm), and was immersed immediately in a pure aqueous solution at room temperature of about 20°C for phase inversion. The water was changed every 8 h for the first 3 days, and once a day for the next 4 days. Seven days after, the membrane was deemed to have completed the phase inversion, and it was stored in pure water for later use.

A field emission scanning electron microscope was adopted to observe the morphology and the structures of the upper and lower surfaces as well as the end surfaces of the film (SEM, DSa100, Hitachi, Japan). A wide-angle X-ray diffractometer was employed to analyze the crystal structure and crystallinity of the film (Rigaku, Dnax-rA). The porosity of the membrane was measured by the dry and wet weight method . The phase-inverted membrane was removed from the pure water; the surface moisture of the membrane was wiped off; and its wet weight was denoted as . Then the membrane was placed in an oven at 60°C for the complete treatment. After drying, its dry weight was measured at denoted as . Three samples were tested with the same ratio of the film, and the average value of was calculated as the test result according to the following formula.

\[
e = \frac{(m_w - m_d)/\rho_w}{(m_w - m_d)/\rho_w + m_d/\rho_p} \times 100\%,
\]

in which the density of water at 20°C is 0.998 g/cm³, and the density of PVDF is 1.765 g/cm³.

The high-pressure flat membrane test machine was rinsed with pure water to test the membrane’s pure water flux . After rinsing, the membrane was pressurized at 0.25 MPa for 30 min, and then the pressure was adjusted to 0.2 MPa. After the standby was running stably, 1000 mL of filtrate is collected and the elapsed time, water temperature, room temperature, and other conditions were recorded. Test three samples with the same ratio of the film, and the average value of was calculated as the test result.

\[
J = \frac{V}{A \cdot t \cdot \Delta p}
\]

In the formula, is the initial pure water flux of the pollution-free membrane \( L \cdot m^{-2} \cdot h^{-1} \cdot atm^{-1} \); is the

| System     | \( \mu (Pa\cdot s) \) | \( D_{5.0W} \times 10^6 (cm^2/s) \) | \( D_{0.5W} \times 10^6 (cm^2/s) \) |
|------------|-----------------|---------------------|---------------------|
| H₂O/DMSO/PVDF | 40.0            | 10.7                | 6.9                 |
| H₂O/DMAc/PVDF | 8.4             | 9.1                 | 16.8                |
| H₂O/DMF/PVDF  | 6.5             | 10.2                | 17.1                |

| Case | PVDF, wt% | Solvent type | Solvent, wt% | Non-solvent type | Non-solvent, wt% |
|------|-----------|--------------|--------------|-----------------|-----------------|
| A    | 0.20      | DMSO         | 0.75         | H₂O             | 0.05            |
| B    | 0.20      | DMAc         | 0.75         | H₂O             | 0.05            |
| C    | 0.20      | DMF          | 0.75         | H₂O             | 0.05            |
| D    | 0.15      | DMAc         | 0.80         | H₂O             | 0.05            |
| E    | 0.10      | DMAc         | 0.85         | H₂O             | 0.05            |
volume of filtered water $L$; $A$ is the effective area of the membrane, $m^2$; $t$ is the filtration time, $h$; $\Delta p$ is the membrane penetration pressure, $atm$.

**Results**

During simulation, the initial conditions and related parameters need to be modified to adapt to the described immersion precipitation process. The fluid model focuses on the polymer solution part while modeling a small part of the coagulation bath to provide the correct immersion precipitation environment.

In addition, during the phase inversion process of the immersed precipitation membrane, the initial conditions present two layers (coagulation bath and polymer solution), which result in a large gradient difference, so the solvent and non-solvent gradient difference serves as the driving force for diffusion.

**Simulation of PVDF membranes with different solvent systems**

In the process of preparing membranes by the immersion precipitation phase inversion method, the solution system generally involves three components: polymer, solvent, and non-solvent. In the phase separation process, the solvent-non-solvent diffusion rate significantly affects the membrane structure. The key to the immersion-precipitation phase separation process is the bi-directional diffusion of solvent and non-solvent, which is influenced by many factors, most notably the concentration of the film-forming polymer, the coagulation bath, etc.

The size of the simulation area is $125\,nm \times 250\,Vnm$; the discrete grid points used in the simulation are $150 \times 300$; and the time step $\Delta t = 10^{-6}$. In order to correctly present the submerged precipitation environment, we used most (70%) of the simulation domain to simulate the coagulation bath, and the polymer solution formed by the membrane only accounts for less than 30% of the simulation domain. In the simulation, the time steps are all in seconds ($s$).

The two initial conditions for the simulation of the systems A, B, and C are determined as:

1. **Polymer solution layer**: $\phi_p = 0.2, \phi_s = 0.75, \phi_{ns} = 0.05$;  
2. **Coagulation bath**: $\phi_p = 0.01, \phi_s = 0.01, \phi_{ns} = 0.98$.

The morphological evolution is shown in Figure 1 (variation of polymer volume fraction ($\phi_p$) with time).

Figure 1 shows the evolution diagrams of the volume fraction of the polymer PVDF with DMSO, DMAc, and DMF serving as the system solvent over time. For visual comparison, the initial volume fractions of the same polymer and solvent were controlled, and the graph of the change during the same period was intercepted. As can be seen, the changes of the three systems are roughly the same. The mutual diffusion of solvent and non-solvent is fast, but the polymer is almost stationary in the polymer solution area, and the coagulation bath is blue constantly (low polymer volume fraction). The phase separation process starts from the top of the polymer solution layer and proceeds downward in the layered structure, which is resulted from the interactions of uniform energy and gradient energy driven by the planar interface between the polymer solution and the gel bath. It is similar to the “short-wavelength composition wave” described by Allen and Cahn in the iron-aluminum system.

Over time, the spin amount decomposition proceeds in the entire layer, and then the particles are cooled to continuously reduce the total free energy. As the diffusion progresses, we can clearly observe the uneven distribution of the volume fraction of PVDF, which also verifies that the final morphology of the PVDF film is asymmetric with a dense skin layer, which is similar to experimental observations. The simulation results are shown in this figure. At a certain stage of coarsening, the top layer is broken, indicating that the top layer is destroyed during the diffusion process. This is because there is no clear setting for the final equilibrium concentration during the diffusion, which will also be worked on in our next research.

During the film formation process, the polymer solution is divided into two phases, a polymer-rich solid phase and a solvent-rich liquid phase, with the polymer-rich solid phase forming the membrane skeleton and the solvent-rich liquid phase forming the membrane pores. The volume fraction distribution of the polymer in the simulation is used to determine the membrane formation, that is, the grid with the larger polymer volume fraction is considered as the membrane skeleton and the grid with the smaller polymer volume fraction is considered as the membrane pores. The DMSO system has the largest membrane pore size, the DMAc system has the most pores, and the DMF system has the least pores but slightly larger pore size compared to the DMAc system. Therefore, it can be predicted from the simulation graph that among the three systems in terms of pure water flux, the order of solvent influence on membrane performance is: DMSO > DMAc > DMF. The lamellar structure of DMAc and DMF systems is more obvious. At the same time, in the polymer solution layer, the degree of polymer dispersion gradually increases, and the blue part appears gradually, that is, the volume fraction of polymer in the grid is smaller in the time step, and the schematic representation of each color can be seen in Figures 1 to 3. The proportion of the blue part appears
in the order: DMSO ≈ DMAc > DMF, which indicates that the diffusion rate of polymer in DMSO and DMAc system is faster than that in DMF system.

Figure 2 shows the electron micrographs of films formed by three different solvent systems. The system can be ranked as DMAc > DMF > DMSO in terms of the stability. Generally, unstable systems are prone to instantaneous phase separation and form porous membranes, while stable ones tend to delay phase separation and form relatively dense membranes. Therefore, based on the PVDF film formation mechanism studied by Cheng et al., the membrane structures change from

![Figure 1](image1.png)

**Figure 1.** Volume fraction of polymer ($\phi_p$) with time. Red represents the maximum volume fraction of polymer at each time step, and blue represents the minimum volume fraction of polymer at each time step. Other colors are between the two ((a) DMSO, (b) DMAc, and (c) DMF).

![Figure 2](image2.png)

**Figure 2.** SEM photos of membranes prepared by PVDF casting solution with different solvents ((a) DMSO, (b) DMAc, and (c) DMF) ((a) and (c) are 500 times magnification, and (b) is 1300 times magnification).
a porous one with mainly instantaneous phase separation to a dense one with predominantly delayed phase separation in the order of DMSO, DMF, and DMAc systems. For the DMSO and DMAc system sublayers, transient liquid-liquid phase separation occurs, and crystallization has little effect on the kinetic process, resulting in a sublayer with low crystallinity, high connectivity, and mainly large pores. The sublayer of the DMF system has delayed liquid-liquid phase separation, and crystallization has a great influence on the kinetic process, resulting in a honeycomb-like porous structure sublayer with high crystallinity.

The analysis of the membrane structure morphology from the kinetic process shows that the system with fast solvent/non-solvent diffusion is prone to instantaneous phase separation to form a porous membrane. In contrast, the system with slow diffusion is prone to delay phase separation and forms a relatively dense membrane. The structure of the membrane should be changed from a denser membrane based on delayed phase separation to a porous membrane based on liquid-liquid phase separation in the order of DMSO, DMAc, and DMF.

Table 4 shows the measured porosity and water flux of the three different solvent systems after membrane formation. The simulation predictions were verified experimentally, and the order of solvent effects on membrane performance in terms of pure water flux was DMSO > DMAc > DMF.

Table 4. Properties of membranes prepared by different solvent system.

| Case | Porosity (%) | Water flux (L·m⁻²·h⁻¹·atm⁻¹) |
|------|--------------|-------------------------------|
| A    | 51.62        | 463.25                        |
| B    | 57.22        | 211.34                        |
| C    | 54.34        | 183.61                        |

In this experiment, all three types of membranes were formed with an asymmetric membrane skin prior to the sublayer, which prevents the solvents in the membrane sublayers from exchanging with non-solvents in the coagulation bath, and has a significant impact on the formation of sublayers.

**Simulation of initial concentration on PVDF membrane**

Next, for the H₂O/DMAc/PVDF system, the initial composition of the polymer solution was changed to study its effect on the membrane morphology.

Figure 3 shows the ternary phase diagram and simulation results combining the three systems B, D, and E in Table 3. The black dots represent the different initial conditions simulated in the (Table 3) series. The simulated change diagrams of the three polymer systems with different concentrations of B, D, and E are roughly the same. Among them, the simulation diagram with a diffusion time ($t = 8.0 \times 10^{-5}$) is selected for comparison.

It can be seen that during the diffusion, as the volume fraction of PVDF in the polymer solution increases from a lower level, the top layer of the polymer solution layer does not break during the coarsening process but rather break when the fraction reaches a certain level, and the polymer volume fraction in the coagulation bath increases first then stayed consistent. As the volume fraction of the polymer is increased, the resulting morphology will change from a bi-continuous mode to an isolated droplet, showing that the fraction determines the morphology as it determines the spinodal position of the system and the ratios of the two phases.

From the simulation results in the figure, it can be seen that as the initial polymer concentration increases, breaking the laminar flow structure of the polymer solution layer, the membrane pores become more porous and the pore size becomes larger, and it can be seen that the pure water flux decreases in the order of the three system fluxes.

Figure 4 shows the SEM photograph of the membrane prepared by the three systems in Table 3. As the polymer concentration increases, the dense surface layer of the membrane will thicken and the permeability of
the membrane will decrease, thus reducing the porosity, the interconnection between pores, the pore size,24,25 and the formation of macroporous structures.26 For porous membranes, instantaneous liquid-liquid phase separation occurs at different polymer concentrations, but for high-concentration polymer membrane-forming liquids, the polymer concentration at the film/gel bath interface is higher, which will result in higher porosity. With a low porous surface layer, the water flux of the formed membrane is also small.

Table 5 shows the porosity and water flux after film formation for three different polymer concentration systems. The simulation predictions were experimentally verified, both water flux and porosity increased sequentially with decreasing polymer concentration.

### Discussion

As shown in Section 3.1, according to the maximum volume fraction of the polymer in the red part of each time step, draw the trend chart (Figure 5). As can be seen from this figure, the increasing trend of curve c is flatter than curves a and b. In the early stage, curve a has greater growth rate than curve b, but as diffusion proceeds, curve b exceeds a until the two curves overlap. Throughout the process, curves b and c show almost linear growth, while curve a shows a shallow s-shaped growth.

The situation shown in Figure 5 is analyzed as follows: the viscosity of the solution affects the exchange rate of the solvent–non-solvent pair. Table 1 shows the viscosities of the three systems. When the solvent changes from DMF to DMAc and to DMSO, the viscosity of the casting liquid increases and the delay time is prolonged.

In the DMSO solvent system, the casting liquid has the highest viscosity, so the delay time of the skin liquid and solid phase separation is longer. The formation of the skin layer hinders the mutual mass transfer between the sublayer and the coagulation bath. In addition, in the DMSO solvent system, the diffusion coefficient from solvent to non-solvent \( D_{\text{S-W}} \) is greater than that from non-solvent to solvent \( D_{\text{W-S}} \) (Table 1), proving

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**Figure 4.** SEM photos of membranes prepared with different volume fractions of polymer PVDF ((a) 20%, (b) 15%, and (c) 10%) (both are 1300 times magnified images).

**Table 5.** Properties of membranes prepared with different PVDF concentrations.

| Case | Porosity (%) | Water flux (L·m⁻²·h⁻¹·atm⁻¹) |
|------|--------------|-------------------------------|
| B    | 58.22        | 211.34                        |
| D    | 61.21        | 265.67                        |
| E    | 76.32        | 356.30                        |

---

**Figure 5.** The trend graph of the maximum volume fraction of the red part of the polymer in each step ((a) DMSO, (b) DMAc, and (c) DMF).
that the amount of solvent diffusing from the lean phase nucleus toward the nucleus is greater than the amount of non-solvent diffusing in the same direction. Compared with the DMSO solvent system, the DMAc solvent system has lower viscosity of the casting liquid and shorter phase separation delay time of the skin layer. In addition, opposite to the DMSO system, $D_{S-W} < D_{W-S}$ in this system. This showed that the amount of solvent that diffuses from the casting solution to the lean phase nucleus is less than the amount of non-solvent that diffuses from the lean phase nucleus to the casting solution, which limits the growth of the lean phase nucleus into macropores.

The DMF system has the smallest viscosity and its skin layer has the shortest delay time for phase separation. Like the above two systems, its liquid-liquid phase separation occurs in the sublayer. But its diffusion coefficient is the largest, and $D_{W-S} > D_{S-W}$. The system has the smallest viscosity and ideal stability, which are conducive to the diffusion of non-solvents to the entire liquid membrane sublayer. The sublayer separation time of this system is the longest compared to the above two systems, and the growth of macropores in it is completely inhibited. The film sublayer shows a honeycomb structure, resulting in a thicker film than the above two systems.

The film formation mechanism of PVDF can be discussed in stages. Different film layers have different phase separation behaviors, which are affected differently by thermodynamics and kinetics differently; that is, different membranes have different thermodynamic properties and kinetic processes. There were primary and secondary controls on the membrane structure during the layer formation.

Conclusions

A fluid model was developed to simulate the phase separation process caused by concentration differences in polymer solutions. The effects of the concentration of the film-forming polymer and the composition of the solidification bath on the structure and properties of the films were mainly investigated. The following conclusions were obtained by comparing the graphs of the simulation results with the experimental results and analyzing them.

The phase separation process is observed in the simulated results graph to start from the top of the polymer solution layer and proceed downward in the laminar structure. Also the influence of the solvent on the membrane pure water flux is in the order of DMSO > DMAc > DMF, where the laminar structure is more pronounced in the DMAc and DMF systems.

In the same system, as the initial PVDF concentration increases, the simulated morphology will change from a bicontinuous mode to an isolated droplet, and the higher PVDF concentration will break the laminar structure of the polymer solution layer, the membrane pores become more numerous, the pore size becomes larger, and the pure water flux decreases in the order of the three system fluxes. And the validity of the model was verified by corresponding experiments.

Modification instructions

1. For the summary was streamlined;
2. Added the interpretation of symbols in the model control equations in Table 1;
3. The source of the solvent is noted;
4. In the experimental method cited15,16 were argued;
5. Changed the formula for calculating water flux;
6. The analysis of simulation plots for different solvent systems was added, and the corresponding experimental section was advanced from the discussion section, and the simulation results were compared with experiments for verification analysis.
7. Only film pore-related properties can be observed in the simulated plots, so the data for film thickness and film crystallinity in Tables 4 and 5 have been deleted and briefly described in the table.
8. Figure 3 was revised according to the reviewer’s suggestion, as well as the order of electron microscopy photos in Figure 4;
9. The discussion of film formation for different solvent systems is streamlined, deleted reference25 from the original manuscript;
10. Revamped the conclusion section;
11. Figure 3 was redrawn, so references20,21 were partially omitted from the description of the figure.

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Author contributions

Conceptualization: Ping Fang; software: Kang Liu and Chaoyu Yang; writing – original draft preparation: Kang Liu; writing – review and editing: Ping Fang; supervision: Ruihua Shao, Yan Li, and Wei Ji. All authors have read and agreed to the published version of the manuscript.
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Data availability statement
The data presented in this study are available in the article. The other data of the relevant models used to support the findings of this study are available from the corresponding author upon request.

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