Journal of Membrane Science 507 (2016) 143–153

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Understanding the thermally induced phase separation process via a Maxwell–Stefan model

Han-han Lin [a], Yuan-hui Tang [a,b,*], Tian-yin Liu [a], Hideto Matsuyama [c], Xiao-lin Wang [a,**]

[a] Beijing Key Laboratory of Membrane Materials and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China
[b] School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, PR China
[c] Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, Kobe 657-8501, Japan

ARTICLE INFO

Article history:
Received 11 November 2015
Received in revised form
15 January 2016
Accepted 27 January 2016
Available online 4 February 2016

Keywords:
Thermally induced phase separation
Polymeric microporous materials
Maxwell–Stefan model
Mass transfer
Heat transfer

ABSTRACT

A Maxwell–Stefan model was firstly established to describe the mass and heat transfer in the air gap and coagulation bath stages via thermally induced phase separation (TIPS) process. A cylindrical configuration was considered with the polyvinylidene fluoride-diphenyl carbonate system. The model results showed that firstly, in the air gap, a polymer concentration gradient was induced in the polymer solution due to the diluent evaporation, and with an increase in the evaporation time, the gradient increased gradually. When the initial polymer concentration decreased, the polymer concentration gradient increased while the concentration gradient depth decreased due to a reduction in the diffusion coefficient. Secondly, the temperature of the polymer solution declined rapidly when it was immersed in the coagulation bath, which resulted in a temperature gradient in the solution. The temperature gradient diminished as the quenching time increased because of the heat transfer at the polymer solution–coagulation bath interface. In addition, with the initial polymer concentration decreasing, the solution heat transfer coefficient raised a little, which caused a slight rise in the temperature gradient. Finally, the model results were validated by the experiments to obtain a beneficial reference for the formation of polymeric microporous materials via TIPS.

1. Introduction

Thermally induced phase separation (TIPS) proposed by Castro in 1980s [1] has been regarded as one of the most important methods to prepare polymeric microporous materials that are widely applied as foams [2,3], tissue engineering scaffolds [4,5] and membranes [6,7]. During the materials preparation via TIPS, a homogeneous polymer solution at an elevated temperature is immersed in a coagulation bath that always contains water to induce phase separation and polymer solidification after passing an air gap. In the previous work of our group, the effects of the mass and heat transfer across the polymer solution–coagulation bath interface on the phase separation and the resultant polymeric microporous structure have been studied by a method based on the dissipative particle dynamics simulation [8–11]. The results have shown that the microporous structures are directly controlled by the dynamics of the TIPS process, which are strongly influenced by the mass and heat transfer. Since the transport phenomena are greatly affected by the evaporation during the air gap and the quenching during the coagulation bath [12–15], for the purpose of optimizing the performance of the polymeric microporous materials, both experimental and theoretical studies have been conducted to describe the transport phenomena and their effects on the phase separation mechanism of the TIPS process.

Some experimental studies have been conducted to analyze the effects of the air gap distance and the coagulation bath temperature on the morphologies and properties of the resultant polymeric microporous materials [12–14]. The experimental results showed that in the air gap, the evaporation rate of diluent was a key factor in determining the porosity of the resultant fibers. Since the diluents can evaporate from the outer surface of the hollow fiber, a dense layer on the outer surface can be formed by increasing the air gap distance. Besides that, the mean pore sizes and porosity increased with the increasing bath temperature because the phase separation morphology had longer coarsen time to develop. However, the details of the TIPS process can hardly be

---

[*] Corresponding author at: Beijing Key Laboratory of Membrane Materials and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China.
[**] Corresponding author.
E-mail addresses: tangyuanhui@126.com (Y.-h. Tang), xl-wang@tsinghua.edu.cn (X.-l. Wang).

http://dx.doi.org/10.1016/j.memsci.2016.01.049
0376-7388/© 2016 Elsevier B.V. All rights reserved.

directly observed by the macroscopic experimental methods since the polymeric microporous materials formation process via TIPS is so fast.

Theoretical studies have also been carried out to investigate the transport phenomena and their effects on the phase separation mechanism of TIPS process [16–19]. Several one-dimensional transport models based on Fick's law combining mass transfer and heat transfer have been built since 1990s to describe the macroscopic transport phenomena, and the results demonstrated that concentration and temperature profiles would be induced by the transport phenomena, which affected the final porous structures of the materials. It was proved that the anisotropic structure was formed by the evaporation of diluent from the atmosphere–polymer solution interface [20]. In addition, the calculated temperature profiles during the coagulation bath could be used to facilitate the analysis of the phase separation mechanism [21] and the crystallization in the TIPS process [22]. Nevertheless, these models on the basis of Fick's law only relate the diffusional fluxes to the component change and are limited to the binary systems [20–22].

Maxwell–Stefan equation [23,24] proposed in 1870s is a general constitutive equation covering more driven forces of fluxes for describing the transport phenomena in multicomponent systems [25–27]. It has provided a facile basis for explaining various transport phenomena involving simultaneous heat and mass transfer in different areas, such as the permeation and separation for membranes [26,28,29]. However, the application of Maxwell–Stefan equation in the polymeric microporous materials preparation has hardly been reported.

As mentioned above, the mass and heat transfer between the polymer solution and the environment (air or coagulation bath) have an important effect on the phase separation. In order to get a deeper and more accurate understanding on the phase separation, a Maxwell–Stefan model is constructed to study the influence of the mass and heat transfer on the TIPS process in this work. Since hollow fibers have been acknowledged to possess large surface area per unit volume of the fiber to provide a great potential for the commercial application, the Maxwell–Stefan model is developed in cylindrical coordinates. In the following part, the polymer concentration and temperature gradients in the polymer solution, resulting from the mass and heat transfer in the air gap and the coagulation bath stages of the TIPS process, are firstly calculated based on the Maxwell–Stefan model. Then the effects of the evaporation time corresponding to the air gap distance, quenching time and initial polymer concentration on the profiles are investigated. Finally, the polymeric microporous materials are prepared to validate the model results.

2. Model and analysis

2.1. Basic description of Maxwell–Stefan equation

The Maxwell–Stefan equation was originally proposed to describe the multicomponent diffusion in ideal gases [23,24]. Afterwards it was extended to a generalized Maxwell–Stefan equation for the multicomponent diffusion in gases, liquids or solids, covering a comprehensive set of driving forces (e.g., chemical potential, pressure, electric field). The generalized Maxwell–Stefan equation [25–27] with the chemical potential as the driving force is

$$\frac{x_i}{RT}\nabla\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{1}{C_t}\frac{x_iN_j - x_jN_i}{D_{ij}} \qquad i = 1, 2, \ldots\ldots n{-}1 \tag{1}$$

where the subscript i and j denote the component i and j, respectively. μ_i is the chemical potential of the component i. x_i represents the mole fraction of the component i. The mole flux N_i for the component i is given by $N_i = J_i + C_i v$, where J_i represents the mole diffusional flux of the component i. D_{ij} is the mutual diffusion coefficient between the component i and component j. C_t is the total mole concentration of the solution.

For a multicomponent system undergoing phase changes (e.g., evaporation) involving simultaneous heat transfer and mass transfer, the latent heat will cause the energy transfer to be dependent on the mass transfer, resulting in the coupling of the temperature and concentration fields. The Maxwell–Stefan equation can be introduced to the diffusion term of the conservation equations and the boundary conditions of both the heat transfer and mass transfer, thereby the aforementioned fields are obtained.

Taken a cylinder as an example, if the transport phenomena in the radial direction are merely considered, the continuity equation can be expressed as

$$\frac{\partial\rho}{\partial t} + \frac{1}{r}\frac{\partial(\rho r v)}{\partial r} = 0 \tag{2}$$

Then, the local conservation equation of mass for the component i in the solution can be given by

$$\frac{\partial\rho_i}{\partial t} + \frac{1}{r}\frac{\partial(r\, n_i)}{\partial r} = 0 \tag{3}$$

where n_i is the mass flux for the component i.

The mass boundary condition of the component i at the interface of phase α and β is expressed as

$$\left(n_i - \rho_i v\right)^{\alpha} = \left(n_i - \rho_i v\right)^{\beta} \tag{4}$$

where v represents interfacial velocity. ρ_i^{α} and ρ_i^{β} are the densities of the component i at the phase α side and the phase β side of the interface, respectively.

With regard to heat transfer, on the basis of Fourier's law, the heat flux is defined as $q = -k(\partial T/\partial r)$, where k is the thermal conductivity of the solution. The constitutive equation of energy is

$$E = -\,k\frac{\partial T}{\partial r} + \sum_{i=1}^{n}\frac{n_i}{M_i}\bar{H}_i \tag{5}$$

where $\overline{H}_i$ is the partial molar enthalpy of the component i.

The local conservation equations of energy in the polymer solution is expressed as

$$\frac{\partial \sum_{i=1}^{2}\frac{\rho_i\bar{H}_i}{M_i}}{\partial t} = -\frac{1}{r}\frac{\partial E}{\partial r} + H_v \tag{6}$$

where H_v represents the rate of the energy input from the external power sources per unit volume.

The energy boundary condition at the interface of phase α and β can be expressed as

$$\left(E - \sum_{i=1}^{n}\frac{\rho_i v\bar{H}_i}{M_i}\right)^{\alpha} = \left(E - \sum_{i=1}^{n}\frac{\rho_i v\bar{H}_i}{M_i}\right)^{\beta} \tag{7}$$

The n_i consisted in Eqs. (3)–(7) can be obtained by the Maxwell–Stefan equation.

2.2. Model development

During the TIPS process, the mass transfer and heat transfer usually happen simultaneously. In this section, the application of Maxwell–Stefan equation is extended to the description of the transport phenomena during the TIPS process as reported in the preceding work [15,30,31]. A Maxwell–Stefan model derived from