Modeling of pore formation in phase inversion processes: Model and numerical results

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ABSTRACT

Various theories about the mechanism of pore formation in porous polymer membranes have been proposed in the past. Here, we predict pore structure formation, based on density-gradient theory, where surface tension is included as part of the gradient of the chemical potential. A simplified thermodynamic model, assuming a fluid mixture with symmetric miscibility gap, is used. Based on this model we conclude that the development of finger pores as well as of sponge pores is due to diffusive mass transport.

The evolving picture of pore formation is as follows: At contact of polymer solution and coagulation bath, a counter-diffusion of polymer, solvent and non-solvent occurs until the miscibility gap is reached. Then, nuclei are formed and the polymer solution phase separates, while the locus of nucleation moves in the direction of the polymer solution by continuing counter-diffusion of polymer and non-solvent, when solvent concentration is constant. As a result, we observe a moving precipitation front. Different morphology develop, depending on polymer mass fraction and velocity of the precipitation front. The results are in qualitative agreement with experimental observations.

1. Introduction

Porous polymer membranes are used in many different processes [1,2]. Depending on the process, different morphological properties of the polymeric separation layer are required for an efficient separation process, determining selectivity, permeability and mechanical stability.

Most of the commercial porous polymer membranes are prepared by a phase inversion process. A polymer-solvent mixture is brought into contact with a non-solvent and, due to a thermodynamic miscibility gap, the mixture separates into a polymer rich and a polymer lean phase. The polymer rich phase forms the polymer matrix and the polymer lean phase forms the pores of the membrane. The phase inversion process for reverse osmosis membranes was pioneered by Loeb and Sourirajan [3].

1.1. Theories of asymmetric membrane formation

The formation of the morphology of asymmetric membranes depends on the interaction of thermodynamics and precipitation kinetics during the phase separation and subsequent solidification process. In the last 50 years comprehensive experimental studies on the formation of polymer membranes have been reported [4], correlating morphology, thermodynamics and kinetics. Thermodynamic studies enlarged the knowledge, e.g. concerning the impact of polymeric additives [5]. Kinetic studies were focused on diffusive transport of polymer, of solvent and of non-solvent in a homogeneous polymer solution and coagulation bath [6–8].

Several theories on the origin of different pore structures, like macrovoids or sponge and finger pores have been published. Strathmann et al. [9] postulated shrinkage and cracks in the polymer rich phase due to mechanical stress as origin of finger pores. Matz [10] and Frommer & Messalam [11] proposed that variations in the surface tension due to different solvent concentrations initiate and promote macrovoids. Reuvers & Smolders [12,13] proposed to distinguish between spontaneous and delayed demixing to differentiate between finger and sponge pores. Ren et al. [14] reported experiments on flat sheet membranes between two parallel glass plates and concluded that viscous fingering is responsible for the formation of macrovoids. Recently, Yu et al. [15] presented experiments that indicate macrovoids inside the polymer solution. They proposed that there are local density variations during phase separation and compaction or shrinkage of the polymer rich phase, which could result in density-driven convection. A major obstacle in understanding the details of pore formation results from the lack of time- and spatially-resolved measurements of the fast

kinetics of precipitation and the small size of the nuclei during the onset of pore formation. As an alternative to experiments, numerical simulations shall be used to study the formation of pores, based on detailed mathematical modeling of the phase inversion process.

Published models for phase inversion processes can be classified into quasi-homogeneous 1D and heterogeneous 2D/3D models. 1D models do not resolve the spatial details of phase separation. Instead they are based on effective diffusive mass transfer in a homogeneous mixture of polymer solution and coagulation bath. The first model of this type was proposed by Cohen et al. [6] and successively improved by Reuvers et al. [7], Tsay & McHugh [16], Cheng et al. [17] and Lee et al. [18,8]. The models are based on thermodynamics for polymers (Flory-Huggins-equation of state) and Maxwell-Stefan diffusion. The aim of these models is to calculate a fictitious composition path in the phase diagram during contact of polymer solution and coagulation bath, by identifying the intersection of binodal and spinodal and by considering the time delay, before phase separation occurs. By comparison with experiments, the developing morphology can be correlated with the diffusive mass transport in the polymer mixture. But since the models do not consider phase separation of the polymer solution in detail, they are unable to predict a developing morphology.

Heterogeneous 2D/3D models on the other hand consider the details of diffusive mass transfer in a phase separating polymer solution, which is initially unstable, e.g. inside the miscibility gap. The models are based on the mass balance equations, where surface tension is included in the gradient of the chemical potential. This leads to a fourth-order partial differential equation, known as the Cahn-Hilliard equation [19], which is commonly used to model phase separation of mixtures. The first models of this type were proposed by Akthakul et al. [20] using the *Lattice Boltzmann* method and Zhou & Powell [21] using the *Finite Volume* method to study immersion precipitation. Both observe qualitatively similar morphology (sponge pores) and a compaction of the membrane, which is in qualitative agreement with experimental observations. The same model was recently used by Mino et al. [22] to study thermal-induced phase separation. A mesoscopic model based on the *Dissipative Particle Dynamics* method was proposed by Wang et al. [23–27]. Instead of using a Cahn-Hilliard equation, different forces between coarse-grained particles are used to describe phase separation.

In the phase inversion process, polymer solution and coagulation bath initially mix by diffusion of solvent from the polymer solution and non-solvent from the coagulation bath. When, at a certain location in the polymer solution, a composition beyond the binodal is reached, nuclei originate. Due to continuing diffusion of solvent and non-solvent, new nuclei will be formed further inside the polymer solution. This leads to a moving precipitation front. But in none of the 2D/3D models finger pores have been predicted which grow into the polymer solution and produce asymmetric membrane structures. The reason is that the authors initially assume an unstable polymer solution instead of a moving precipitation front. Actually, they implicitly model an infinitely fast precipitation front.

1.2. Liesegang patterns

Recently, Foard & Wagner [28] analyzed a mathematical system of similar to immersion precipitation. Their model is based on the Cahn-Hilliard equation and, in contrast to previous studies, they consider a moving precipitation front and are able to predict sponge and finger pores with the same model. Based on diffusive mass transport, they showed that different kind of morphology in the wake of an enslaved phase-separation front, similar to so-called Liesegang patterns [29], are formed.

Liesegang patterns are periodic patterns of alternating structures. They are typically observed in systems with a moving precipitation front, e.g. in chemical reaction systems where an electrolyte E_1 with low viscosity diffuses into another electrolyte E_2 or into a gel with a higher viscosity. At the mixing front a chemical reaction takes place. Liesegang

patterns evolve with the moving reaction front and form alternating bands or rings [30]. A review of Liesegang patterns can be found e.g. in [31].

The characteristics of the above mentioned chemical reaction system are very similar to an immersion precipitation system when a non-solvent diffuses into a more viscous polymer solution and the precipitation front moves towards the polymer solution. Here we observe regular patterns of precipitate behind a moving phase separation front. This phenomena was previously investigated by Ball [32], Hantz and Biro [33], Köpf et al. [34], Foard [28,35] and the references therein. In literature, the term *Liesegang pattern* is commonly connected to alternating bands or rings but in this paper we use it to indicate different regular patterns, e.g. sponge pores, finger pores or dense lamella-like structures.

The aim of this work is to demonstrate that Liesegang pattern formation is the decisive mechanism of pore formation in porous polymer membranes during a phase inversion process and to discuss the respective basic phenomena. Therefore, we extend and apply the model proposed by Foard & Wagner for a multi-component model-fluid and study the formation of sponge and finger pores or macrovoids.

The paper is organized as follows: First we review the thermodynamics and kinetics of a phase separating system and introduce the simplified model and its numerical discretization. Then, we investigate the simulation of different morphologies and propose a characterization of morphology based on the simplified model. Finally, the limitations of the current approach are discussed. A detailed discussion of the nucleation mechanism of pores is postponed to a future article.

2. Model and method

In this section we first give a qualitative picture of membrane formation, based upon the main effects and the related interactions of thermodynamics and diffusive mass transfer, before we develop and simplify the respective model equations and discuss the modeling results.

2.1. Thermodynamics and mass transfer

The thermodynamics, describing the interactions of polymer solution and coagulation bath, were elaborated in the last decades for several systems, e.g. polyethersulfone [5]. We recap the major characteristics of a typical system of polymer solution (polymer + solvent) and coagulation bath (non-solvent). A ternary phase diagram with a miscibility gap between polymer and non-solvent is shown in Fig. 1. Solid and dashed lines indicate binodal and spinodal. The critical point cP is located at large solvent concentrations. The binodal at low polymer concentration is very close to the binary solvent/non-solvent axis, as shown in the enlarged detail in Fig. 1.

Several points in Figs. 1 and 2 are important in the following discussion. Points A and D represent the initial composition of the homogeneous bulk phases of polymer solution and coagulation bath. Point B indicates the point inside the miscibility gap where a nucleus of phase separation originates. This point is located either between the binodal and spinodal or beyond the spinodal, resulting in either nucleation and growth or spinodal decomposition. We label B as point of nucleation. The corresponding phase equilibrium is indicated by the composition of the polymer rich phase, B^1, and the polymer lean phase, B^2. Subsequently, solidification of the polymer rich phase at high polymer fraction leads to vitrification. During vitrification solvent diffuses from the polymer rich to the polymer lean phase. The point of vitrification is represented by point C^1, with the corresponding equilibrium composition of the polymer lean phase, C^2.

At contact of polymer solution and coagulation bath, an interface region is formed where solvent from the polymer solution diffuses towards the coagulation bath and non-solvent (water) from the coagulation bath diffuses towards the polymer solution. We label the