DEVELOPMENT OF MEMBRANES WITH REGIONS WITH DIFFERENT CHARACTERISTICS BY PHASE INVERSION TECHNIQUES

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Abstract

Separation membrane cells comprising membrane sections with different characteristics can be the base for new separation processes. Hybrid membrane cells require new membranes with regions with different characteristics. In this paper we present numerical and experimental approaches to develop such membranes by the phase inversion technique. The two main steps of the phase inversion technique, the evaporation step and the immersion precipitation step, are studied by numerical methods. The numerical approach is based on the solution of the mass transport equation to predict the film composition after the evaporation step and in the solution of the Cahn–Hilliard equations to predict the structure of the membrane after the immersion precipitation step. The equations are solved by finite difference methods. The numerical simulations are used to predict the influence of several experimental parameters (temperature, composition of the initial polymeric solution, evaporation time, precipitation time, immersion bath composition) in the structure of the membrane. The experimental approach is based on the manipulation of the experimental conditions to produce regions of different characteristics in the same membrane. An experimental method to create different regions from two different initial polymeric solutions is presented.

Introduction

Membrane separation processes are used to fractionate mixtures, concentrate and purify components. The efficiency of separation of this kind of processes is limited by the increase of solute concentration along the bulk of the retentate and by the formation of concentration boundary layers over the membranes, commonly referred as concentration polarization. This phenomenon is a desirable state of high components separation but it also leads to a decrease of the driving force across the membrane, thus to a decrease of the permeate flux.

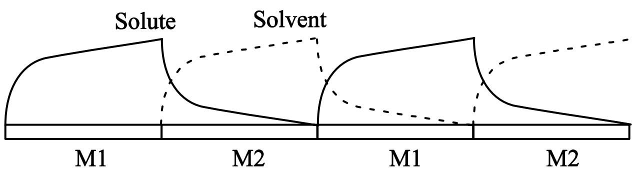


Figure 1 – Mass boundary layers of the solvent and solute in an hybrid membrane cell which combines solvent removal (M1) and solute removal membranes (M2).

In order to constrain the undesirable effects of concentration polarization without destruction of the separation created by this phenomenon, hybrid membrane cells (Figure 1), comprising different membrane sections and performing different functions, are a promising alternative. Examples are cells comprising semi and fully-permeable membrane sections (Miranda and Campos, 2007), cells comprising reverse osmosis and pervaporation membrane sections and cells comprising hydrophobic and hydrophilic membrane sections. Advantages of these cells include reduction of concentration polarization, control of the membrane surface concentration and increase of the separation selectivity. Hybrid membrane cells require new membranes with regions with different characteristics. In this work we present numerical and experimental approaches to develop such membranes by phase inversion technique.

Theory

The two main steps of the phase inversion technique, the evaporation step and the immersion precipitation step, can be studied by numerical methods. The numerical approach is based on the solution of the mass transport equation to predict the film composition after the evaporation step. The solvent distribution in the membrane after the evaporation step can be predicted by solving the mass transport equation for the domain represented in Figure 2 a) considering periodic boundary condition in boundaries I and III and zero flux across boundaries II and IV. The structure of the membrane after the immersion precipitation step can be predicted by the Cahn–Hilliard equations for the domain represented in Figure 2 b):

$$\frac{\partial \varphi_s}{\partial t} = M_{ss}\left[\nabla^2\left(\frac{\partial f}{\partial \varphi_s}\right) - K_{ss}\nabla^2\nabla^2\varphi_s\right] + M_{sp}\left[\nabla^2\left(\frac{\partial f}{\partial \varphi_p}\right) - K_{pp}\nabla^2\nabla^2\varphi_p\right] \quad (1)$$

$$\frac{\partial \varphi_p}{\partial t} = M_{ps}\left[\nabla^2\left(\frac{\partial f}{\partial \varphi_s}\right) - K_{ss}\nabla^2\nabla^2\varphi_s\right] + M_{pp}\left[\nabla^2\left(\frac{\partial f}{\partial \varphi_p}\right) - K_{pp}\nabla^2\nabla^2\varphi_p\right] \quad (2)$$

In these equations, φ_s is the volume fraction of the solvent, φ_p the volume fraction of the polymer, $M_{i,j}$ the mobility of species *i* due to a gradient in species *j* chemical potential, $K_{i,j}$ a gradient penalty coefficient and *f* the homogeneous free energy density (Zhou and Powell).

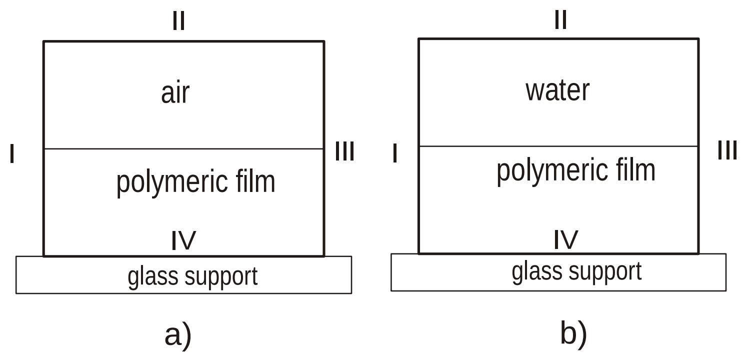


Figure 2 – Numerical domains: a) evaporation step; b) immersion step.

The equations are solved by finite difference methods. The numerical simulations are used to predict the influence of several experimental parameters (temperature, composition of the initial polymeric solution, evaporation time, precipitation time, immersion bath composition) in the structure of the membrane.

Experimental

The materials used to prepare the casting solution were cellulose acetate (acetyl content of 40 % wt) from Sigma Chemical Co., acetone with a minimum purity of 99.5 % from VWR, magnesium perchlorate from VWR and water. Hybrid membranes were prepared from two casting solutions with different compositions. An adapted film applicator from Elcometer with two solution chambers (see Figure 3a) was used to cast the membrane. The polymer solutions were fed to the applicator, each one to the respective chamber. A 100 μm thick film was cast in a glass plate at room temperature. After a period (30 seconds) of partial evaporation of the solvent, the membrane plate assembly was immersed in an ice-water bath for about one hour. Once this period was over, the membrane, which detached during the gelation step, was removed from the bath and submitted to a heat post treatment. The heat treatment consists in the immersion of the membrane in water at 70 ºC for 5 minutes.

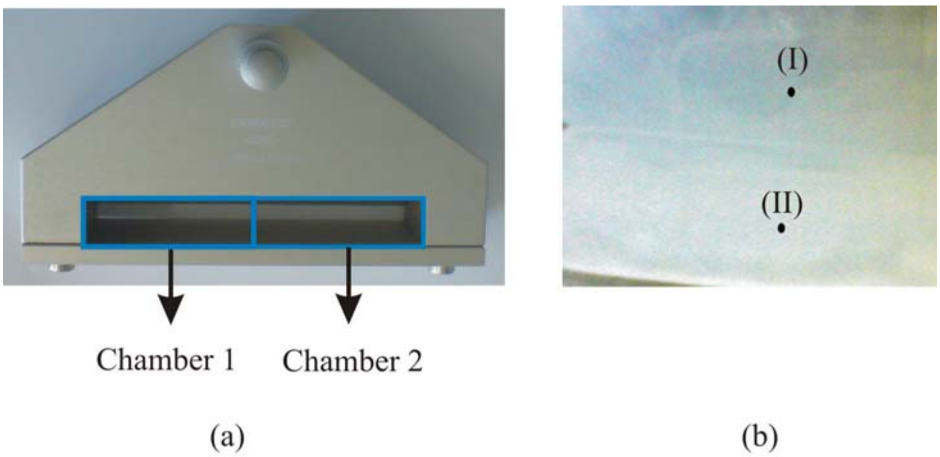
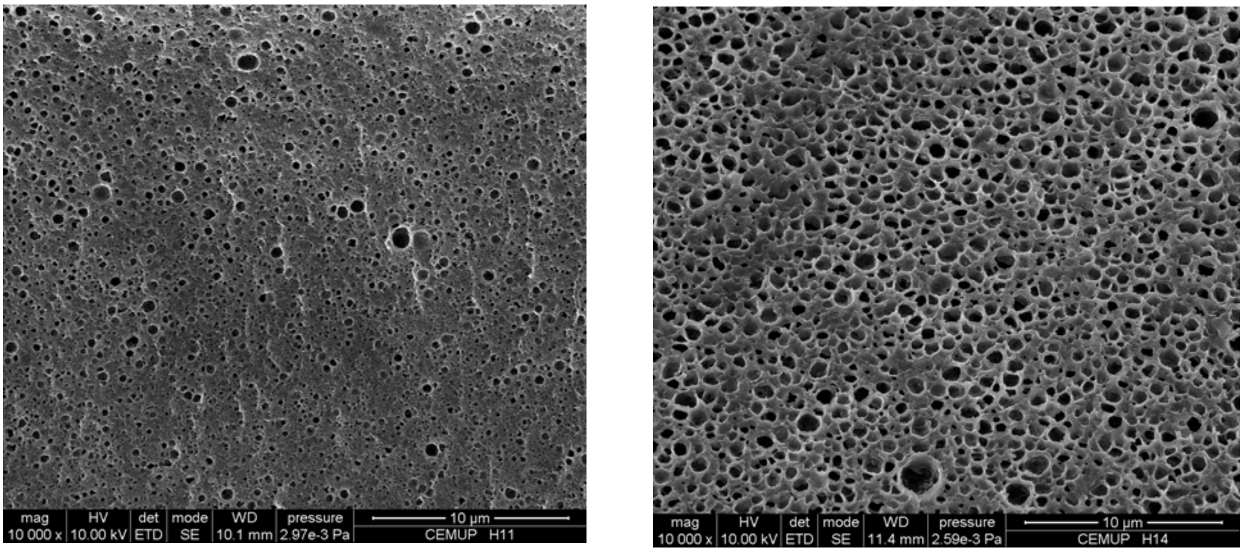


Figure 3 – Casting of an hybrid membrane: a) schematic representation of the film applicator used in the procedure; b) picture of a hybrid membrane presenting two sections. The compositions of the sections are: (I) – 20 % (w/w) in CA and (II) – 15 % (w/w) CA.

Results and discussion

The hybrid membranes obtained by phase inversion technique exhibited two observable segmented sections that can be recognizable by bare eye (Figure 3b). It could also be identified an interface where the solutions of different compositions contact. Both sections of the membrane were studied by electron microscopy (SEM) using the equipment FEI Quanta 400 FEG / EDAX Genesis X4M at high vacuum. Figure 4 shows the SEM images of a hybrid membrane obtained by casting a solution of 20 % (w/w) in CA and another of 15 % (w/w) in CA. The spot where the samples were collected to perform SEM analysis is shown in Figure 3 b).
The section with 20 % (w/w) content in CA originated a membrane structure with pores of about 0.50 μm in diameter, while the section with 15 % (w/w) in CA originated a membrane structure with pores of about 0.90 μm in diameter.



(a) (b)

Figure 4 – SEM images of different sections of the membrane. The compositions of the sections are: (a) – 20 % (w/w) in CA and (b) – 15 % (w/w) CA.

Conclusions

A hybrid membrane was obtained by casting side by side polymeric solutions with different compositions. SEM images of the two regions of the membrane show that the pore size is higher for the region produced from the polymeric solution with the lower concentration of CA. The procedure can be used to produce membranes with heterogeneous surfaces. In the future other approaches to produce these membranes will be studied. A numerical study of the evaporation and immersion steps is under way.

References

JM Miranda, JBLM Campos, 2007. Numerical study of a hybrid membrane cell with semi and fully permeable membrane sub-sections, Chemical Engineering Science, 62, 1215 - 1229

Bo Zhou and Adam C. Powell, 1984. Phase field simulations of early stage structure formation during immersion precipitation of polymeric membranes in 2D and 3D Journal of Membrane Science, 268, 150-164.