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Variation of the physicochemical and morphological characteristics of solvent casted poly(vinylidene fluoride) along its binary phase diagram with dimethylformamide

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ABSTRACT

Poly(vinylidene fluoride), PVDF, films and membranes were prepared by solvent casting from dimethylformamide, DMF, by systematically varying polymer/solvent ratio and solvent evaporation temperature. The effect of the processing conditions on the morphology, degree of porosity, mechanical and thermal properties and crystalline phase of the polymer was evaluated. The obtained microstructure is explained by the Flory–Huggins theory. For the binary system, the porous membrane formation is attributed to a spinodal decomposition of the liquid–liquid phase separation. The morphological features were simulated through the correlation between the Gibbs total free energy and the Flory–Huggins theory. This correlation allowed the calculation of the PVDF/DMF phase diagram and the evolution of the microstructure in different regions of the phase diagram. Varying preparation conditions allow tailoring polymer microstructure while maintaining a high degree of crystallinity and a large β crystalline phase content. Further, the membranes show adequate mechanical properties for applications in filtration or battery separator membranes.

1. Introduction

Membrane technology is widely used in biomedical [1], chemical [2], filtration [3] and energy storage [4] applications, among others. Each application imposes specific membrane characteristics such as porosity, pore size distribution, roughness and permeability, among others [5,6].

Fluoropolymers are particularly interesting for the preparation of porous membranes for different applications and, in particular, poly(vinylidene fluoride), PVDF, and its copolymers are appealing due to their suitable mechanical properties, high dielectric response, high thermal stability, chemical inertness and hydrophobic properties [7–10].

The hydrophobic characteristic of PVDF is essential for membrane distillation applications, for example. PVDF is soluble in most aprotic solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO) and triethylphosphate (TEP) [5,11].

PVDF membranes can be prepared by phase inversion processes such as thermal evaporation, immersion precipitation, non-solvent separation and electrospinning [12–16]. The membrane formation is influenced by the polymer concentration, solvent temperature evaporation, solvent type, non-solvent content in the solution and coagulation bath [17,18].

A wide variety of porous morphologies can be obtained through the combination of these processing parameters [5]. The selection of the solvent is critical in order to tailor the porous structure, as it controls the pore growth kinetics and the crystallization behavior of the polymer.

The morphologies of the membranes can be predicted by analyzing the phase diagram of the system. The phase diagram for a two or three component system (polymer, solvent and non-solvent) shows the regions of miscibility and the regions where the phase separation occurs [19]. The formation of pores – cellular or finger-like – in the membrane can be obtained in the liquid–liquid event (binodal line in the phase diagram) whereas interlinked crystalline phase prevails in solid–liquid phase [11]. In particular, the mechanical properties of the membranes are strongly dependent on porosity and pore size and polymer membranes with high degree of porosity and large pores often does not show adequate properties to be used in demanding membrane applications.

Large values of porosity are obtained with a high level of miscibility between solvent and non-solvent, which will influence the demixing rate and therefore the final microstructure [6]. Another critical parameter is the polymer concentration as it affects the solution thermodynamic properties such as the binodal line. Most often the polymer concentration when a sample is prepared by solvent casting is between 15 and 25 wt.%. Increasing polymer concentration in the solution results in membranes with lower porosity and higher interface between polymer and non-solvent [20]. Finally, temperature also strongly affects membrane

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formation. The viscosity of the solution and the exchange rate of solvent and non-solvent during phase inversion can be controlled through temperature [21,22]. Through temperature variations it is also possible to determine the cloud-point that represents an approximate boundary when liquid–liquid demixing occurs.

Microporous membranes of PVDF have been prepared by precipitation from 1-octanol/DMF/PVDF and water/DMF/PVDF systems. It was verified that as the temperature increases, the gelation region contracts significantly more than the liquid–liquid demixing region. Cellular asymmetric morphologies were obtained at high temperatures [21].

PVDF membranes were also produced from DMA/water and DMA/C1–C8 alcohols solvent/non-solvent pairs, concluding that high casting solution temperatures play an important role in membrane formation due to the effect of increasing liquid–liquid demixing rate on the crystallization [17].

Polymer membranes were also achieved from PVDF/DMSO/water [23] and PVDF/DMAc/water systems [18]. Membranes show low degree of crystallinity and the presence of both α- and β-phases in the surface layers when precipitated at high temperatures.

The microstructure of PVDF can be also modified by crystallizing from binary systems, such as PVDF/DMF at different temperatures, the solvent evaporation playing a critical role for obtaining porous membranes based on PVDF [14].

In this sense, PVDF membranes with TEP as a solvent have been prepared for micro- and ultra-filtration, showing that symmetric and asymmetric structures with bi-continuous inter-connected pores can be effectively controlled by tuning PVDF concentration [11].

Computer simulation of the polymer structure (“mesoscale structure”) is very important for predicting and understanding the microstructure formation at different points of the phase diagram in binary or ternary systems [24]. The morphology is obtained through mesoscale modeling of the polymer/solvent interaction [25].

Despite the aforementioned efforts in modifying PVDF microstructure, a systematic approach along binary phase diagrams is still needed, being nevertheless the simplest way to obtain specific microstructure in a systematic and reproducible way. In the present work, PVDF membranes were prepared by solvent casting from a binary system with N, N dimethylformamide (DMF) as a solvent varying polymer/solvent relative content and evaporation temperature.

The effects of polymer concentration and solvent evaporation temperature were thus systematically studied and the phase diagram of the polymer solution was analyzed according to the Flory–Huggins theory. The microstructure of the PVDF/DMF binary system in different points of the phase diagram was simulated through mesoscopic models. Membranes with different microstructures, degree of crystallinity, crystalline phase content, porosity and mechanical properties have been obtained.

2. Experimental

2.1. Materials

PVDF (Solef 1010 with Mw = 352,000 g/mol) was supplied by Solvay. The solvent N,N-dimethylformamide (DMF, 99.5%) was purchased from Merck.

2.2. Membrane preparation

The PVDF concentration in solution ranged between 5 wt.% and 20 wt.%. The polymer was dissolved in DMF at room temperature using a magnetic stirrer until a homogeneous solution was obtained. After total dissolution of the polymer, flexible films of ~50 μm were obtained by spreading the solution on a clean glass substrate followed by isothermal evaporation in a temperature range between room temperature and 80 °C within an air oven of Binder during the maximum 15 days. The samples produced were called (x PVDF y) where x represents the polymer concentration and y represents the evaporation solvent temperature.

2.3. Sample characterization

The porosity of the samples (Ø) was measured with a pycnometer by the following procedure: the weight of the pycnometer filled with ethanol was measured and labeled as (W_1); the mass of the sample was measured (Ws) and immersed in ethanol. After the sample was soaked in ethanol, additional ethanol was added to complete the volume of the pycnometer. Then, the pycnometer was weighted and labeled as (W_2) and the sample filled with ethanol was taken out of the pycnometer. The residual weight of the ethanol and the pycnometer was labeled (W_3). The porosity of the membrane was calculated according to [26]:

$$\phi = \frac{W_2 - W_3 - W_s}{W_1 - W_3}. \tag{1}$$

The mean porosity of each membrane was obtained as the average of the values determined in three samples and the error is given as the standard deviation of the values.

The morphology of the PVDF membranes was analyzed by scanning electron microscopy (SEM) (Cambridge, Leica) with an accelerating voltage of 15 kV. Previously the samples were coated with a thin gold layer using a sputter coating (Polaron, model SC502 sputter coater).

The polymer phase within the porous membranes was determined by Fourier Transformed Infrared Spectroscopy (FTIR) performed at room temperature with a Perkin-Elmer Spectrum 100 apparatus in ATR mode from 4000 to 650 cm^{-1}. FTIR spectra were collected after 32 scans with a resolution of 4 cm^{-1}.

The thermal behavior and degree of crystallinity of the PVDF membranes were analyzed by differential scanning calorimetry (DSC) measurements with a Mettler DSC 821 (Mettler-Toledo) apparatus. The samples were cut into small pieces, placed into 50 μl aluminum pans and heated between room temperature and 200 °C at a heating rate of 10 °C/min. All experiments were performed under a nitrogen purge. The temperature accuracy of the thermal analyzer is ±0.1 °C.

Mechanical tests were carried out at room temperature through stress–strain measurements in the tensile mode of a TST350 setup from Linkam Scientific Instruments and a strain rate of 15 μm/s. The tensile force range of the instrument ranges from 0.01 N to 20 N with a force resolution of 0.001 N.

The estimated error in the FTIR, DSC and mechanical tests was calculated taking into account the precision of the equipment and the least squares method.

3. Mesoscale simulation method

The phase separation phenomena in the polymer mixture were described by phenomenological mesoscopic models based on dynamic density functional.

The concept behind the mesoscale model is the Gibbs free energy, F, described as a functional:

$$F = F^{id} + F^{mf} \tag{2}$$

where F^{id} is the ideal free energy function and F^{md} is the mean field free energy.

The dynamic density functional model consists on representing the total functional free energy in order of time. This model is represented by the diffusion equation of the time-dependent Ginzburg–Landau model [27]:

$$\frac{\partial c(r,t)}{\partial t} = \frac{M \nabla^2 \delta F}{\delta c(r,t)} + \eta(r,t) \tag{3}$$