Characterization of Polyamide 66 Membranes Prepared by Phase Inversion Using Formic Acid and Hydrochloric Acid Such as Solvents

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The membranes properties prepared from water/formic acid (FA)/ polyamide 66 (PA66) and water/hydrochloric acid (HCl)/polyamide 66 (PA 66) systems has been studied. The different solvents interact distinctly with the polymer, affecting the membrane morphology. The asymmetric structure of the membranes showed a dense top layer and a porous sublayer. The membranes M-HCl prepared from HCl/PA 66 system showed a larger dense layer (around 23 µm) in compared to those prepared from FA/PA 66 system (M-FA) (around 10 µm). The membrane morphology was a determinant factor in results of water absorption, porosity and pure water flux. The lower thickness of dense layer in M-FA membranes resulted in a higher water absorption and, consequently, porosity, approximately 50%, compared with M-HCl membranes, approximately 15%. The same trend was observed to permeate flux, the lower thickness of dense layer higher pure water flux.

Keywords: *polyamide 66, porous membrane, asymmetric membranes*

1. Introduction

The preparation and application of polymeric membranes obtained by phase inversion method is reported in the literature by many authors[1-7]. The mechanism of phase inversion is a determinant factor in the membranes morphology and in understanding the phenomena involved in their synthesis. The conditions for the membranes preparation (polymer concentration, type of solvent, time and temperature of casting and composition of coagulation bath) may directly influence their morphology and transport properties. The choice of these conditions determines the formation of symmetric or asymmetric membranes with diverse pore structures and the characteristics of transport properties[8].

Young et al.[9], evaluated the effect of temperature on the membranes formation from polyamide 66 (PA 66) and found that slight alterations on solvent evaporation temperature also affected the morphology and crystalline structure of the membrane.

The composition of the coagulation bath, which has a direct effect on the mass transfer rate between solvent and non-solvent[10], the use of additives in the polymer solution[11-15] and the effect of different solvents and non-solvents[16] cause significant modifications on morphology and permeability of polymeric membranes. In our previous work[15] was showed that the addition of a second polymer with high molecular weight (polyvinyl pyrrolidone) in PA 66 membranes enhanced the morphological structure, decreasing the thickness of dense layer and increased permeate water flux.

The miscibility, crystallinity and morphology of membranes from polyamide/poly(vinylalcohol) (PVA) blend materials were studied by AI-Rawajfeh et al.[4,5]. The PVA addition had a positive effect on increasing hydrophilicity and in morphology of nanofiltration and reverse osmosis application. By Lin et al.[10] membranes with nanometer-scale crystalline morphology were obtained by varying the composition of the polymer solution (non-solvent/solvent/polyamide 66) and the coagulation bath (non-solvent and solvent). Yao et al.[3] prepared membranes of polyamide 6 using hydrochloric acid as solvent and found that the change in non-solvent, different morphological structures were obtained resulting in variations of pure water flux. Using the most basic solutions to the water, such as pyridine and ammonium hydroxide, the finger pore structure was formed and using alcoholic solutions the sponge-like structure was obtained.

Membranes prepared from polyamide/ formic acid are usually described in literature[4,5,7,10,17,18], but few studies[3] and our previous works[15,19] have reported the preparation of membranes from PA 66/ hydrochloric acid. This paper aims to show that the solvent has an important role in the preparation of polymeric membranes and the characteristics of each solvent impose different morphologies. The membrane-forming systems consisting of water/formic acid/PA 66 and water/hydrochloric acid/PA66 were used for obtaining the polymeric membrane. The resulting membranes were characterized by scanning electron microscopy (SEM), water content, porosity and pure water flux.

2. Experimental

2.1. Materials

Commercial PA 66 from Alfa Chem. Co., Brazil, Mw 161,000 g.mol⁻¹, was received in pellet form. The hydrochloric acid (HCl) (Merck Brazil, 37%) and formic acid (FA) (Merck Brazil, 98%) was used as the solvent and used as received. Distilled-deionized water was used as the nonsolvent for PA 66.

2.2. Membrane preparation

Polymer solutions of 20 wt. (%) of PA 66 in FA and HCl were cast at room temperature (± 23°C) on glass plates with a uniform thickness of 0.3 mm by a casting stainless steel knife. Different conditions at the evaporation stage have been tested in accordance with Table 1, which will be discussed in section 3.1. The solvent was evaporated and the glass plates were immersed in a coagulation bath

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Table 1. Preparation conditions of PA 66 membranes.

Membrane	Solvent	Evaporation conditions		Coagulation conditions	
		Time (minutes)	Temperature (°C)	Time (minutes)	Temperature (°C)
M-FA	HCOOH	5	20	120	15
		60	60	120	15
M-HCl	HCl	5	20	120	15
		60	60	120	15

M-FA= PA 66 membrane/formic acid (HCOOH), M-HCL = PA 66 membrane/HCl.

containing deionized water. Immediately after the contact with water, a variation in film color occurs, from clear to white, followed by the detachment of the film from the glass plate surface. After polymer coagulation, the prepared membranes were transferred to a second bath containing fresh distilled water to remove any residual solvent and then they were dried in air.

2.3. Scanning electron microscopy (SEM) analysis

The samples were initially fractured in liquid nitrogen and then gold-coated in a sputtering developed by laboratory of SEM (University of Caxias do Sul), for 1.5 minutes. The cross section morphology of the membranes was obtained by a Shimadzu SSX 550 scanning electron microscopy operated at 15 kV.

2.4. Water content

The membranes with an area of 1 cm^2 were placed in closed flasks containing 50 mL of distilled water for 24 hours at a temperature of 23 °C. The experiments were carried out in triplicate. The excess water on the surface of the wet membranes was removed with filter paper and the samples were weighed. Then, the samples were oven dried at 60 °C for 24 hours and weighed once again. In order to minimize the experimental errors, the water content of each sample was measured three times and the results were reported in average. From the results obtained from weighing the samples in wet and dry conditions, the amount of water absorbed by the membrane was calculated with the Equation 1:

$$(\%) \ water = \frac{W_w - W_d}{W_d} \times 100 \tag{1}$$

where, W_w is the weight of wet membranes (g) and W_d is the weight of dry membranes (g).

2.5. Porosity

Porosity of the membranes was determined as follows[12]:

$$P(\%) = \left[\frac{W_w - W_d}{\rho_w}\right] \times \frac{100}{Ah} \tag{2}$$

where, ρ_w is the density of pure water at room temperature (g.cm^{-3}), A is the area of membranes (cm^2) and h is the thickness of membranes (cm). This method of measuring porosity can only indicate overall porosity and is unable to discriminate the porosity of the skin layer from that of the porous sub-layer.

2.6 Pure water flux measurements

Pure water flux of the polyamide membranes were measured with a parallel flux type cell (area 0.0016 m^2) at 101 kPa and J_w values were calculated using Equation 3[12]:

$$J_w = \frac{V}{A\Delta t} \tag{3}$$

where, V is the volume of the permeate (L), A is membrane area (m^2) and Δt is the sampling time (hours).

3. Results and Discussion

3.1. Membranes preparation conditions through the use of different solvents

The system that forms the membranes (polymer/solvent/ non solvent) needs to be studied in detail in order to determine its best preparation conditions. Variations relative to preparation conditions are important factors that influence on the morphology and consequently on the membrane performance[8,16].

The purpose of this work was to show that the use of different solvents during the preparation of polyamide 66 membranes resulted in different preparation conditions. In other words the solvent determined the best condition for the membrane preparation.

Most of the works[7,10,18] utilize immersion precipitation when they use polyamide and formic acid. The membrane prepared through 5 minutes evaporation at 20 °C and posterior immersion into non solvent, showed a characteristic structure with the formation of the top layer and the porous sublayer (the membrane morphology will be discussed in the following section). The membrane formed at a temperature of 60 °C for 60 minutes showed a fragile structure that breaks off easily and at the same time it didn't show any pores formation that could be noticed all along its cross section (not shown here).

When HCl was used as solvent and evaporated for 5 minutes at 20 °C, there did not appear the homogenous polymeric layer formation when immersed into non solvent. The prepared membrane morphology with 60 minutes evaporation at 60 °C and posterior immersion into non solvent was the condition where the polymeric film was obtained.

3.2. Surface morphological analysis

In a polymer/solvent/non-solvent system, the characteristics of phase separation determine the membrane structure. The membrane properties, which are correlated with morphology, are strongly influenced by the interaction between polymer and solvent[20]. Different solvents used in this work interact distinctly with the polymer, affecting the preparation conditions and the membrane morphological characteristics.

Formic acid is a weak organic acid whereas hydrochloric acid is a strong inorganic acid regarded as corrosive. However, the use of a strong acid, such as HCl, does not change the chemical structure of polyamide as demonstrated in our previous work[19].

The top surface of the membranes (Figure 1a and 1d featured a non-porous dense layer containing polygonal grains, as also observed on membranes studied by Shih et al.[18], which increases resistance to the flux. The formation of these grains on the membrane surface is due to the increase of polymer concentration in the interface between
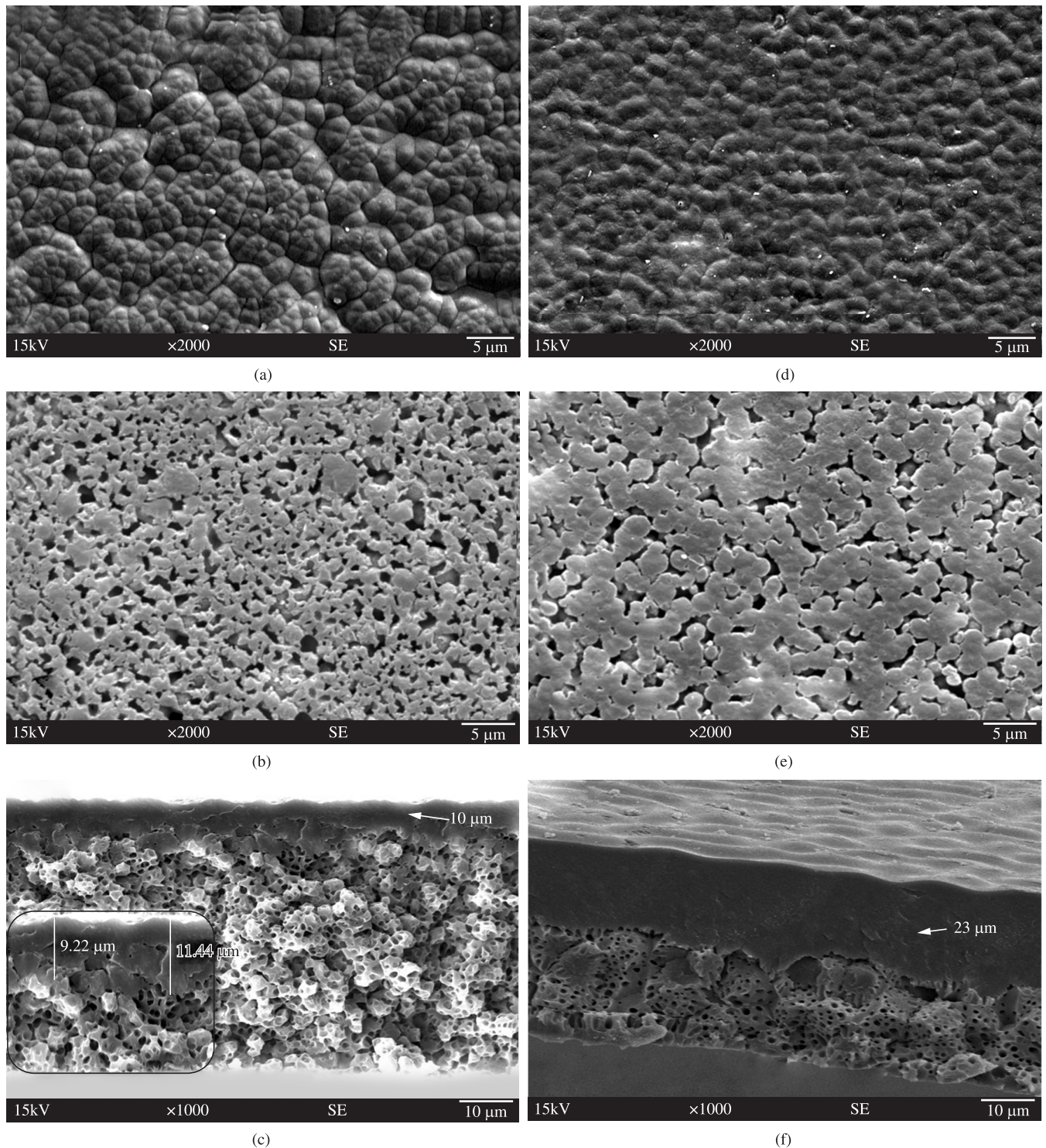
Figure 1. Morphology of membrane M-FA: a) top surface; b) bottom surface; c) cross section and morphology of membrane M-HCl; d) top surface; e) bottom surface; and f) cross section.

the coagulation bath and the polymer solution soon after contact with water[10], which is a fast coagulant for the polymer.

The morphology of the bottom surface of both the membranes is presented in Figure 1b and 1e. A large number of liquid micelles have to nucleate directly on the surface of the glass plate. As a result of the structure formation against the glass plate, the production of pores seems to have been interrupted and the feature observed is of a flattened surface.

As observed in Figure 1c and 1f, the cross section of the asymmetric membranes shows a porous substructure and a dense top layer. The morphology found in the membranes prepared in this work with FA is very similar morphologies described by the earlier authors[7,10]. The thickness of the dense layer of membranes was measured by one a software tool of microscope. In membranes prepared in formic acid, the thickness of the dense layer was 10.3 ± 1.5 µm, whereas in the M-HCl membrane was around 23.1 ± 1.2 µm.

3.3. Formation mechanisms of PA 66 membranes structures

The dense top layer and the porous sublayer are formed by different mechanisms, generating different morphologies. As soon as the polymer solution is immersed into the coagulation bath, the top layer formed first on the interface between the coagulation bath and the polymer solution, as a result of the high polymer concentration on the interface.

According to Chuang et al.[21], during the formation of the sublayer, the precipitation of the top layer creates an additional barrier to the mass transfer between sublayers and the coagulation bath. Subsequent to the formation of the dense layer, the solvent outflow rate to the coagulation bath is reduced. At that moment, the coagulant diffuses through the top layer down to the sublayers for the formation of the nuclei that correspond to the polymer-lean phase. The nuclei grow, originating pores, and their walls are formed from the polymer-rich phase. Thus, the cellular morphology found occurs in the membrane sublayers supporting the dense top layer during its formation process.

In regard to the membrane prepared with HCl, it was necessary to evaporate the solvent (in the present case 60 minutes) before the immersion in the coagulation bath. Such fact suggests that during evaporation there is a greater concentration of polymer on the surface, increasing the thickness of the dense layer. When FA is used, the membrane is formed by immersion into the non-solvent (immersion precipitation) without an evaporation stage, resulting in a thin dense layer.

However, the casting solution prepared from PA66/HCl (M-HCl) is evaporated to film formation, suggesting that this long stage of evaporation (60 minutes) favors the formation of thick dense layer compared with the M-FA membrane, which is evaporated for 5 minutes.

3.4. Water content and porosity

The water content is an important parameter for the membrane characterization and it is indirectly related to the hydrophilicity degree and directly related to the porosity of the membrane[11]. The percentage values of water absorbed in 24 hours are reported in Table 2. The membranes prepared in formic acid showed greater water absorption and greater porosity. The M-FA membrane absorbed approximately 60% of water, whereas M-HCl membrane absorbed just about 20%. In parallel to those results, the total porosity of the membranes was approximately 50% in M-FA membrane and approximately 15% in M-HCl membrane.

The pores in the sublayer are responsible for accommodating water molecules in the membranes[12]. The lower value of water absorption and, consequently, of porosity may be a result of the morphology of the membrane prepared with HCl, in which the thickness of dense layer is relatively high, as observed in the microscopy shown in Figure 1.
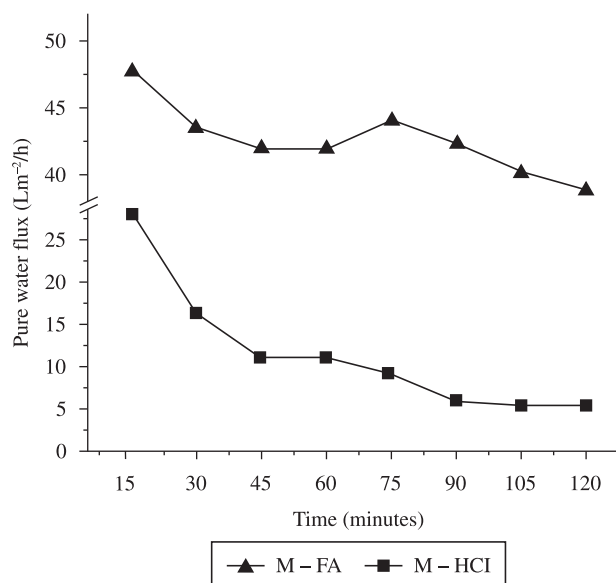
3.5. Pure water flux

The membranes are subjected to water permeation carried out for 2 hours at a constant transmembrane pressure of 101 kPa. The water permeation of PA 66 membranes was investigated, as shown in Figure 2. The membranes showed a stable behavior with small variations in pure water flux.

It is shown that the flux declines gradually due to hydraulic compaction with time. This is due to the fact that walls of pores become closer, denser and uniform resulting in reduction in pore size as well as the flux during compaction[11,12]. The pure water flux value of 39 Lm^{-2}/h was obtained for M-FA membrane and 5.5 Lm^{-2}/h for M-HCl membrane in the end of 120 minutes. This lower value may be attributed to the higher thickness of dense layer, as discussed

Table 2. Parameters for PA 66 membranes characterization.

Membrane	Water content (%)	Porosity (%)	*Pure water flux ($Lm^{-2}h^{-1}$)
M-FA	63 ± 3	53 ± 3	39
M-HCl	22 ± 4	15 ± 2	5.5

* Flux value in the end of 120 minutes.

Figure 2. Pure water flux of M-FA and M-HCl membranes.

previously. According to Mulder[22], increasing the thickness of dense layer increases the resistance to the water flux.

Morphology and structure of membranes (top layer and sub layer) also play a key role in this regard. Lastly, the solvents (FA and HCl) may also be considered as important factor in the membranes preparation, because they strongly affect the morphology and properties of a membrane.

4. Conclusions

The conditions established for the preparation of PA 66 membranes through the process of phase inversion strongly influence the membrane final structure. The use of FA and HCl as the solvents for the PA 66 showed that the morphology obtained in the films is an asymmetric structure, but presented a significant difference in thickness of the dense layer.

The greater thickness of dense layer in membranes prepared with HCl directly influenced as to result the lower water absorption, total porosity and pure water flux when compared to membranes prepared with formic acid.

When comparing the best solvent among the membranes, the use of FA resulted in membranes with the thinnest dense layer and smallest resistance to water flux. Nevertheless, these results are not sufficient to exclude the use of HCl as solvent for PA66 in the preparation of membranes.

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