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Influence of relative air humidity and casting time on the permeation properties of PSf nanofiltration membranes

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ABSTRACT

In this study, polysulphone (PSf) membranes were manufactured in different conditions to establish the influence of manufacturing factors on the permeation properties of PSf nanofiltration membranes. PSf membranes were prepared by diffusion-induced phase inversion in N-methyl-pyrrolidone (NMP) as solvent and deionized water as coagulant. The influence of the relative air humidity and casting time of the polymer in the manufacturing process were studied. All the polymeric solutions were prepared at 30 wt% PSf in NMP and a thin film of 250 μm thickness was cast on a support wetted with NMP, to tamp the pores from the support. The influence of these factors on the permeation properties of PSf membranes was investigated in a series of filtration experiments, and by contact angle measurements and SEM observations. The results show an important influence of the relative air humidity and casting time on the permeability properties and reproducibility of the membrane performance.

Keywords: Nanofiltration; Influence factors; Membrane synthesis

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1. Introduction

Membrane filtration is an important alternative for wastewater treatment and was developed after the eighteenth century following Abbé Nollet's discovery of water permeation through a diaphragm, a phenomenon called osmosis [1].

Membrane water treatment process was applied first in the US and Middle East, but has expanded dramatically in the present: drinking water production relies on membranes all over the world [2]. Membrane technologies are used at a large scale in many industries, including the food industry, the chemical industry and the water industry [3].

The membrane properties may vary depending on the fabrication steps [4]. A widely used method for polymeric membrane's preparation is phase inversion.

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The attraction of this approach is partly related to its versatility, for example, mixing with hydrophilic components is applied to improve the hydrophilicity of the polymer, and chemical modifications of the surface are common [5] to improve the fouling resistance of the membrane [6]. The phase inversion process itself also allows for optimization; many synthesis factors have an influence on the membranes properties. The most important factors are the polymer concentration, the relative air humidity, solvent selection and the use of additives in the polymeric solution or in the non-solvent bath [7,8], the temperature of the non-solvent bath [9,10] and the initial casting film thickness [11].

The adjustment of two key parameters, polymer concentration and the solvent ratio, can determine the viscosity of the dope solution [12]. A higher polymer concentration reduces the formation of the macrovoids in the skin layer and decreases the porosity and pore size. These effects reduce the water flux but the separation capability of the membrane will be increased. Another important parameter is the relative air humidity, studied by K. Boussu [13]. Increasing the relative air humidity the permeation properties increase. In general, in the fabrication process, room humidity is used because a high humidity is difficult to control and have additional cost.

Another parameter that is important to take into consideration is the use of nanoparticles as additives in membrane structure [14]. The most used type of nanoparticles is TiO_2 [15–19]. With the addition of TiO_2 nanoparticles, it was found that the hydrophilicity and porosity of the membranes were increased [20]. Recently, ZnO nanoparticles were used, with better results in term of rejection and water permeation [21,22]. The effect is mostly related to the hydrophilicity of the nanoparticles, but morphological aspects may also play a role.

The objective of this study is to elucidate the role of two parameters, the relative air humidity and the casting time, which are assumed to play a role and may be interrelated.

2. Experimental

2.1. Materials

The support layer, Viledon FO2471, for the membrane manufacturing was obtained from Freudenberg (Weinheim, Germany). The polymer used was polysulphone (PSf) supplied by Solvay (Belgium). As solvent, 1-methyl-2-pyrrolidone (NMP, 99.5%) was used (Merck, Belgium).

2.2. Membrane preparation

PSf membranes were manufactured with a concentration of 30 wt% polymer in N-methyl-pyrrolidone (NMP) as solvent using phase inversion induced by immersion precipitation. The casting solution was obtained by adding PSf into NMP and mixing for 24 h under mechanical stirring at 200 rpm and room temperature. On the polyester support, a thin film of the polymer solution with a thickness of 250 μm was cast with a filmograph (K4340 Automatic Film Applicator, Elcometer) in an atmosphere with controlled relative air humidity, at room temperature. Deionized water was used as non-solvent.

2.3. Membrane characterization

2.3.1. Filtration experiments

The water flux and the permeability of the prepared membranes were studied using a dead-end filtration device (Sterlitech HP4750 Stirred Cell). A constant pressure of 10 bar was used as a reference value to study the water flux and a differential pressure between 2 and 15 bar was used to study the permeability. The variation of flux with time was established recording at regular intervals of the time obtained for 5 ml of permeates.

2.3.2. Scanning electron microscopy

To study the membrane structure, scanning electron microscopy (SEM) was used; a Philips XL30 FEG instrument was used with an accelerating voltage of 20 keV. Membrane samples were prepared by fracturing the membranes in liquid nitrogen, to keep the pore structure. The samples were sputtered with gold to have a clear image of the membrane structure.

2.3.3. Water contact angle

An important property of the membranes is the hydrophilicity/hydrophobicity. This property is important to understand the results of the permeation experiments. To study the hydrophilicity of the membranes, a drop shape analysis system (DSA) 10 Mk2 was used. The membrane samples were dried before testing. The contact angle between the membrane surface and a droplet of 2 μl of water was calculated for every type of membrane.

3. Results and discussion

3.1. Influence of the relative air humidity

3.1.1. SEM analysis

The influence of the relative air humidity to the membrane morphology is shown in Fig. 1.

Fig. 1 shows that the number of macrovoids just below the top layer increases when the relative air humidity increases. The process of exchange between solvent from the casting solution and the water vapour is faster at higher air humidity, and therefore, the number of macrovoids close to the top layer increases. However, the penetration depth of water vapour during casting is limited, and therefore, the membrane structure deeper in the membrane matrix looks similar for all relative air humidities.

3.1.2. Pure water flux and permeability

The influence of the relative air humidity on the permeation properties is shown in Fig. 2 and was studied testing eight different membranes obtained at 22, 32, 42, 52, 62, 72, 82 and 92% of relative air humidity. The pure water permeability increases when the relative air humidity increases. This represents a remarkable effect, in which the permeability is more than doubled.

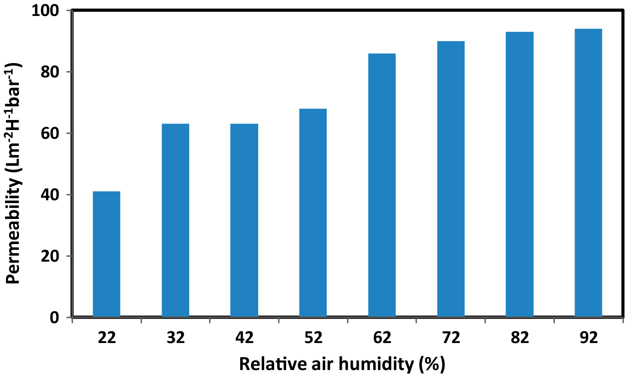

Fig. 2. Influence of the relative air humidity on the membrane permeability.

The permeability increase is thought to be related to the membranes becoming more porous when, during the casting of the polymer film, the humidity increases [9]. Phase separation occurs when the polymeric film is immersed in the non-solvent bath. By

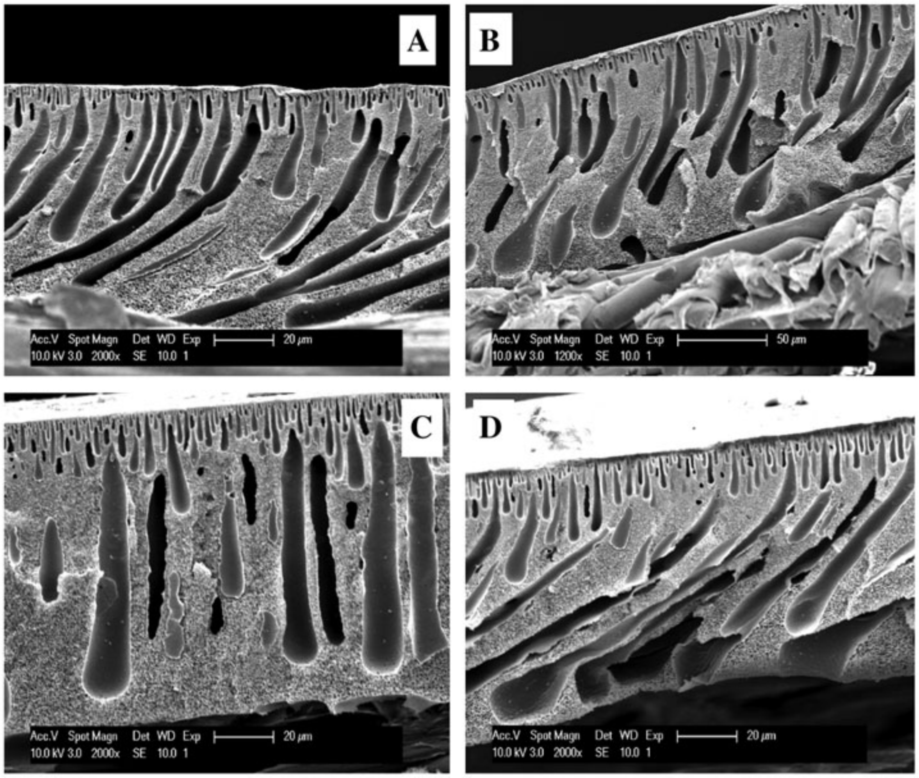

Fig. 1. Cross-sectional SEM images of membranes at different relative air humidity (A) 32%, (B) 52%, (C) 62% and (D) 92%.

increasing the relative air humidity, however, water already diffuses into the polymer solution before the actual casting process; at very high humidities, the separation phase may even already start before immersing [13]. This increase of permeability was also observed when TiO_2 nanoparticles [23] and ZnO nanoparticles [24,25] were added in the polymeric solution. This indicates a strong effect of thermodynamics on the phase separation.

3.1.3. Hydrophilicity and contact angle

The influence of relative air humidity on the hydrophilicity of membranes is shown in Fig. 3.

It can be seen in Fig. 3 that the hydrophilicity of the membranes increases when the relative air humidity increases (contact angles decrease). This is a remarkable effect, which is often overlooked in studies of membrane synthesis. Because the polymer is exactly the same in all cases, the effect shown in Fig. 3 is a morphological effect. The changes can be explained by the larger number of macrovoids close to the top layer and more water can penetrate though membrane surface, which indeed may influence the contact angle. These results are in concordance with permeation properties. Thus, it is demonstrated that changes in contact angle are closely related to changes in morphology.

3.2. Influence of the casting time of the polymer

The eventual aim is to understand how the influence factors can be tuned to obtain membranes with better properties, to increase the reproducibility and to have uniform properties on the entire membrane. For example, the permeability is measured as an average value of the results obtained from different parts of a membrane sheet (Fig. 4). By taking a large membrane area, permeabilities are averaged, but small-scale lab measurements reported in the literature often describe local values obtained with small and sometimes non-representative samples.

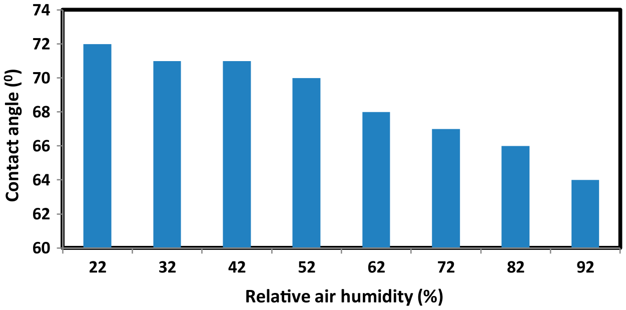

Fig. 3. Infuence of the relative air humidity on the membranes hydrofilicity.

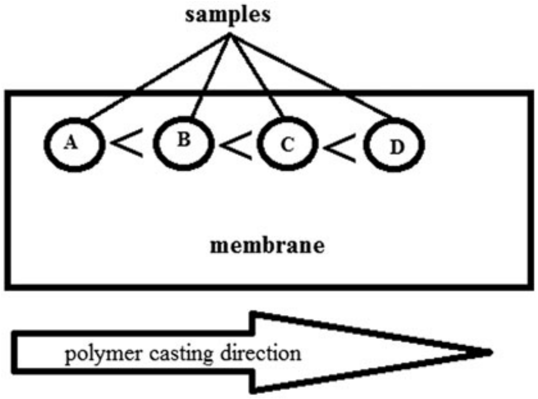

Fig. 4. Establish the permeability function of polymer casting direction.

When the results are obtained from different parts, it will be observed that the permeability is different. This difference may not be random: there might be an increasing trend in the polymer casting direction (Fig. 4).

These different results obtained for different parts of the membrane sheet can be attributed to the influence of the casting time of the polymeric solution on the support layer until the membrane is immersed in the non-solvent bath.

The time needed for the deposition of the polymeric film is 15 s for the synthesis procedure used in this study, representing the time of point A of the membrane until immersing the membrane. From point A to point D the time decreases to 3 s.

To establish the influence of the casting time, seven membranes with different casting time were prepared. All membranes were manufactured at the same concentration of polymer, i.e. 30 wt% PSf. The immersing time was varied, i.e. 20, 40, 60, 80, 100 and 120 s. The membrane obtained in normal condition was noted with time 0 and the results obtained are shown in Table 1.

Comparing the results, a substantial influence of the casting time on the permeation properties can be observed. The permeability increases when the casting time decreases. Furthermore, the membranes obtained at 100 and 120 s have the same properties on the entire surface.

The influence of the casting time on the membrane permeability is shown in Fig. 5.

In view of these results, it can be concluded that the casting time of the polymer film has a great

Table 1
Permeability values for membranes obtained at different casting time

Casting time	Sample A Lm^{-2} H^{-1} bar^1	Sample B Lm^{-2} H^{-1} bar^1	Sample C Lm^{-2} H^{-1} bar^1	Sample D Lm^{-2} H^{-1} bar^1
0	68	69	71	72
20	66	67	67	68
40	62	63	64	65
60	59	59	60	61
80	57	57	58	58
100	57	57	57	57
120	57	57	57	57

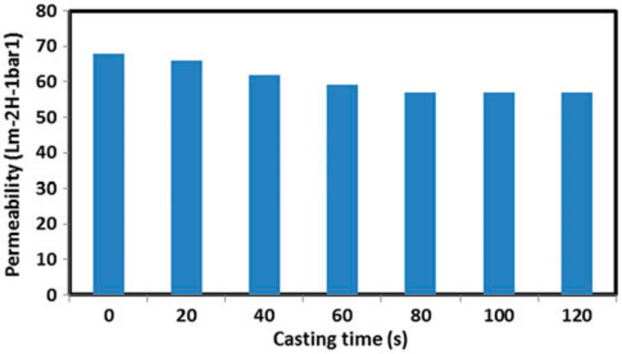

Fig. 5. Influence of casting time on the permeability.

influence on permeability. At the same setting for the casting time, the difference of time for different parts of the same membrane leads to different permeability values in different parts of the membrane. This variation becomes smaller at longer casting times, but these membranes were found to have a lower permeability. Thus, in order to obtain high permeability membrane and with the same properties throughout its entire surface, it is necessary to reduce the casting time of the polymer film as well as its uniformity on the entire surface of the membrane. This aspect is usually not considered and may lead to misinterpretations in membrane synthesis studies.

4. Conclusions

Increasing the membrane's permeability is an important issue for researchers, because this leads to a decrease in the operational cost for applications. The relative air humidity was shown to have an important influence on the permeation properties of PSf membranes. The permeability increases from 40 Lm^{-2} h^{-1} bar^1 for membranes obtained at 22% of air humidity to 85 Lm^{-2} h^{-1} bar^1 for membranes obtained at 92% air humidity. These results are explained by the membrane morphology: the number of macrovoids close to the top layer increases when the relative air humidity increases. The casting time of the polymer has an important influence on the permeability but, more importantly, on the reproducibility. Increasing the casting time, the permeability decreases from 68 Lm^{-2} h^{-1} bar^1 for membranes obtained at normal casting time to 57 Lm^{-2} h^{-1} bar^1 for membranes obtained after 120 s. At a given casting time, the membrane samples have the same permeability over the entire sample when the casting time exceeds 80 s.

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