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Effect of cellulose fibers on morphology and pure water permeation of PSf membranes

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ABSTRACT

Chemical and physical changes are necessary to improve the transport properties of polymeric membranes. Cellulose fiber pulp from *Pinus taeda* was processed in knives and balls mills in order to reduce the dimensions of the fibers for later application in polysulfone (PSf) membranes. By adding cellulosic fibers in PSf membranes, a composite membrane with improved morphological properties, permeate flux and good resistance to pressure was obtained. The fibers as well as the PSf and PSf/cellulose fibers membranes were morphologically characterized by scanning electron microscopy. Tests of pure water permeate flux were performed with pressure up to 20 bar. The addition of 0.2% (wt) of cellulose fibers in the formation of composite membranes resulted in the elimination of macrovoids, causing an increase in pure water flux (50% ± 10) when pressure was risen.

Keywords: Polysulfone membrane; Cellulose fiber; Composite membrane; Macrovoid

1. Introduction

Cellulose is the most abundant biodegradable natural biopolymer in the world. Microcrystalline cellulose (MCC) is constituted of micro-dimensional or nano-dimensional cellulose crystals that have been isolated from their natural fibers [1–3].

When Zhang et al. [4] modified PSf membranes with the addition of MCC, a casting solution of PSf/MCC blend was obtained. MCC changed the morphological structure of the membranes, by good distribution of MCC in PSf composite membrane, and thereby changed their properties regarding pure water flux and bovine serum albumin (BSA) solution retention.

Polysulfone (PSf) membranes are used in micro and ultrafiltration separation processes [5]. The use of these membranes is due not only to their mechanical and thermal properties but also to their hydrophobic properties. Regarding the morphology aspects of the formation process, membranes can be classified as dense or porous. They can also be classified as symmetric or asymmetric, depending on whether a homogeneous structure is existent or not [6].

The characteristics of these membranes can be controlled by the modification methodology with the addition of organic and inorganic reinforcing filler and definition of their application, such as nanofiltration, reverse osmosis and separation of organic mixtures [6,7].

Fan et al. [8] prepared composite membranes using polysulfone and polyaniline (PANI) nanofibers. Regarding the mechanical properties and thermal stability of

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the blended PANI/PSf membranes, elongation at break decreased 30.6% and breaking strength increased 28% when compared with PSf membranes.

Studies performed by Barzin et al. [9] to examine the morphology of PSf membranes prepared with a water/*N*,*N*-dimethyl acetamide (DMAc) system revealed the formation of macrovoids in the resulting membrane structures. In subsequent research, the authors analyzed the phase diagram from the water/inversion phase method DMAc/PES and concluded that macrovoid formation requires the existence of a significant supersaturated region within the casting solution [9].

This work assessed the effect of chemically untreated cellulose fibers on PSf membranes. The reinforcement potential of fibers processed in knives and balls mills was observed by the elimination of macrovoids. The cellulose fibers and the membranes were characterized by Scanning Electron Microscopy (SEM) and pure water flux.

2. Experimental

2.1. Materials

Cellulose pulp obtained from *Pinus taeda* wood through the kraft process was provided by Cambará S.A. (RS, Brazil). DMAc was purchased from Vetec (Brazil). Polysulfone (Mw 35.000) was purchased from Sigma-Aldrich-Chemistry (USA).

2.2. Preparation of cellulose fibers

The cellulose pulp was cut into strips, processed with a knife mill (Marconi Co., Piracicaba, Brazil) and then processed in a planetary ball mill (Sachsenwerk Dresden, Germany) for 10 h at 1345 U/min to obtain the microfibers that were sifted with 325 mesh in a granulometric stirrer.

2.3. Preparation of the PSf film containing cellulose fibers

To obtain a cellulose fiber reinforced PSf film, a specific quantity of PSf (18 wt%) was dissolved in DMAc. Then, cellulose fibers (0.2 wt% on the dry matter) were added to the polymer solution and stirred for 1 h.

The PSf films and the PSf/fiber composite membrane were cast on a glass plate using a hand-casting knife 300 μm thick and left to evaporate for 1 min. Soon after, they were immersed into a distilled water coagulation bath for 60 min to remove traces of solvent.

2.4. Scanning electron microscopy

The morphology of the films was examined by SEM (SSX-550, Shimadzu). Before the analysis, the samples were fractured in liquid nitrogen, coated with gold in a sputtering device and then transferred into the microscope chamber.

2.5. Pure water flux measurements

Pure water flux was tested according to the method described by Li et al. [10] and calculated using the following equation:

$$J_w = \frac{V}{At}$$

where V is the volume of filtered water (l), A is the area of the membrane (m^2) and t is the processing time (h).

3. Results and discussion

3.1. Fiber characterization

The dimensions of fibers after the milling process were characterized by SEM and are showed in Table 1. Subsequent to the knife-milling process, a reduction in dimensions (length and diameter) was observed, when compared to the commercial fiber. The same was observed after the ball-milling process (Fig. 1b) when compared to fibers obtained from the knife-milling process (Fig. 1a). The evidences of dimension reduction after the milling processes are elucidated by the SEM images in Fig. 1.

3.2. SEM analysis of pure PSf and composite membranes

Fig. 2 shows the SEM morphology analysis of the cross section of membranes prepared from PSf and the PSf/fiber composite membrane. It may be seen from the figure that the membranes presented an asymmetric structure consisting of a dense toplayer and a porous sublayer. The presence of macrovoids on the porous sublayer of the PSf membrane, as well as a structure of spherical pores with diameters of approximately 6 μm (Fig. 2a) was observed. Macrovoids are

Table 1
Dimensions of fibers

Fiber	Length (mm)	Diameter (μm)
Commercial	2.7 ± 0.6	50 ± 9.5
Knife mill	0.58 ± 0.1	30 ± 5
Ball mill	0.12 ± 0.03	28 ± 6

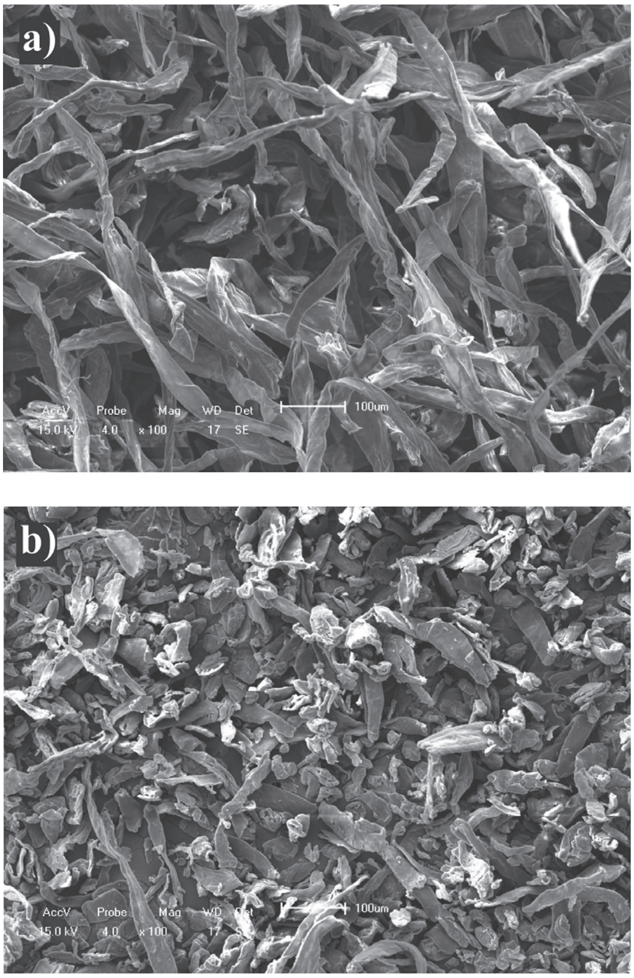

Fig. 1. SEM images of processed fibers (a) in a knife mill (100×) and (b) in both knife and ball mills (100×).

large and elongated pores which affect the permeability and mechanical strength of the resulting membranes [9]. When fibers were added, the formation of macrovoids in the sublayer did not occur, indicating that the presence of fibers influences the membrane phase separation (Fig. 2b). That happens as a result of the acceleration in the rate of water diffusion into the polymer solution caused by the fiber, which prevents the formation of macrovoids [11].

3.3. Pure water permeate flux

The effect of the addition of cellulose fibers into the pure water flux in PSf membranes was investigated and is shown in Fig. 3. It was observed that with the increase in pressure (up to 20 bar) there was a related increase in permeate flux in both membranes. This is due to the increase in effective driving force (transmembrane pressure) required for water permeation [6].

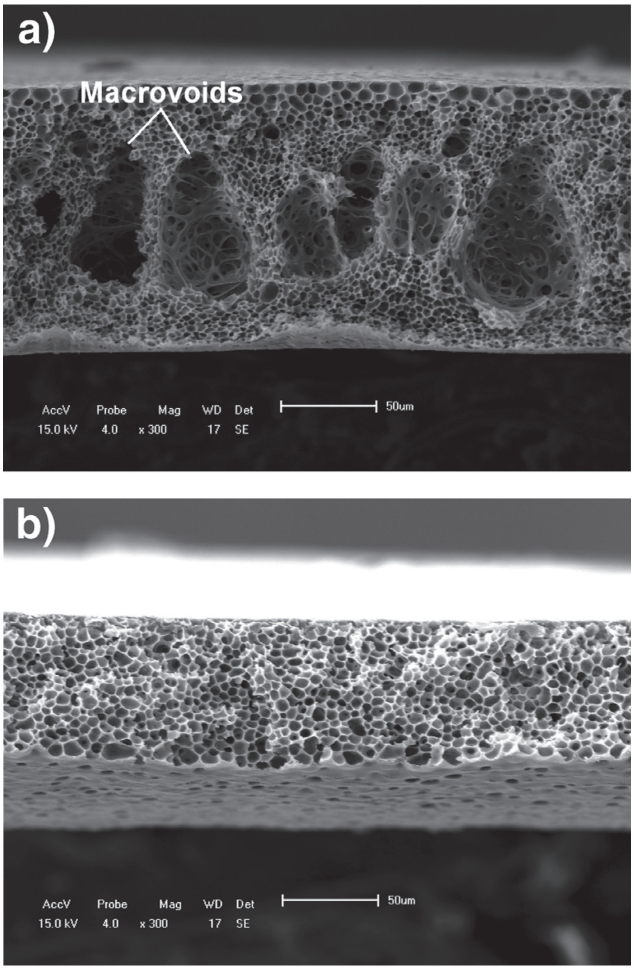

Fig. 2. SEM images of the cross section of (a) PSf (300×) and (b) PSf/fiber (300×) membranes.

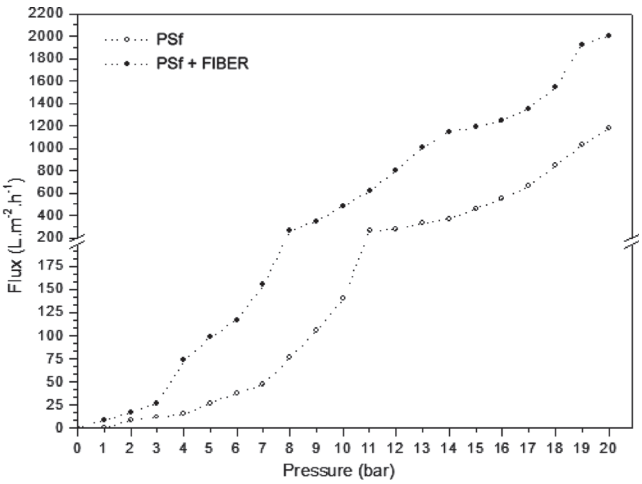

Fig. 3. Water flux of membranes with no added fiber (PSf) and composite membranes (PSf + FIBER).

The pure water flux values were higher in the PSf/fiber composite membrane at all pressures. For example, the pure water flux of the PSf/fiber composite membrane reached 618.86 l/m^2/h in comparison with 264.15 l/m^2/h for the pure PSf membrane at 11 bar. The results show that the membranes have good resistance to pressure once the permeate flux tests were conducted to pressures up to 20 bar.

The results indicate that the addition of fibers influenced the formation of the membranes porous layer, which is directly related to the increase in their permeability. The addition of cellulose fibers in PSf membranes proposed and carried out by this study increased the permeate flux. Zhang et al. [4] observed the same, though in their work the PSf membranes were prepared with the addition of MCC.

4. Conclusions

In this study, cellulose fibers were used in place of MCC to compare the efficiency of chemically untreated fibers in PSf membranes. The study showed that the membranes presented an asymmetric structure and the addition of cellulose fibers inhibited the formation of macrovoids. The addition of 0.2%wt cellulose fibers altered the membrane permeation characteristics, which improved the permeate flux of PSf membranes (±50% increase) up to 20 bar of pressure, and changed the morphological structure, revealing that the membranes are resistant to pressure.

References

[1] M. Nogi, S. Ifuku, K. Abe, K. Handa, A.N. Nakagaito and H. Yano, Appl. Phys. Lett., 88 (2006) 133124-1-133124-2.
[2] E.L. Hult, P.T. Larsson and T. Iversen, Cellulose, 7 (2006) 35–45.
[3] D. Klem, B. Heublen, H.P. Fink and A. Bohn, Angew. Chem. Int. Ed., 44 (2005) 3358–3393.
[4] L. Zhang, G. Chen, H. Tang, Q. Cheng and S. Wang, J. Appl. Polym. Sci., 112 (2009) 550–556.
[5] C.B. Spricigo, A. Bolzan, R.A. Machado, L.H.C. Carlson and J.C.C. Petrus, J. Membrane Sci., 188 (2001) 173–179.
[6] B. Chakrabarty, A.K. Ghoshal and M.K. Purkait, J. Membrane Sci., 309 (2008) 209–221.
[7] I.F.J. Vankelecom, K. De Smet, L. Gevers and P.A. Jacobs, In: Development of nanofiltration membranes, A.I. Schäfer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration—Principles and Applications; Elsevier, 2004.
[8] Z. Fan, Z. Wang, N. Sun, J. Wang and S. Wang, J. Membrane Sci., 320 (2008) 363–371.
[9] J. Barzin and B. Sadatnia, J. Membrane Sci., 325 (2008) 92–97.
[10] L. Li, S. Dong, Z. Zeng and X. Li, J. Functional Polym., 18 (2005) 42.
[11] E.H. Qua, P.R. Hornsby, H.S.S. Sharma, G. Lyons and R.D. McCall, J. Appl. Polym. Sci., 113 (2009) 2238–2247.