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Evaluation of the effect of clay in polyethersulfone membranes

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ABSTRACT

Polymeric membranes were produced from nanocomposites of polyethersulfone and clay, in proportions of 3 and 5% by weight of clay, by phase inversion technique using N, N-dimethylformamide as solvent. From X-ray diffraction analysis, an exfoliated and/or partially exfoliated structure was observed. From scanning electron microscopy images, it was observed that the nanocomposites membranes showed a surface free of defects, however, it was found in a cross section, an anisotropic structure, where the skin is thick and the porous support presents macropores. From water permeation flux measurements, it was found that the presence of the clay increased the flow, especially to the membrane with 5% of montmorillonite.

Keywords: Membrane; Nanocomposites; Polyethersulfone; Clay; Phase inversion

1. Introduction

Separation technologies using membranes are gaining interest for purifying macromolecules from solutions in substitution to classical routes, and have currently been used in several commercial applications. Membrane processes have several advantages, including a compact modular construction, stationary parts, low use of chemicals, absolute barriers to particles and pathogens, stable water filtration characteristics, and small system layout requirements [1].

Polyethersulfone (PES) is considered one of the most important polymeric materials for use in membrane applications [1]. It is a thermoplastic polymer having excellent chemical and thermal stability, high mechanical strength, well soluble in some aprotic polar solvents, and can conveniently be processed into a porous membrane by a simple phase inversion method. Actually, PES membrane is one of the most popular polymer ultrafiltration membranes and widely used in water purification, beverage filtration, protein separation, pretreatment of reverse osmosis, etc. [2].

Despite the advantages of PES as a membrane material, it is not enough hydrophilic and the water permeability of PES membrane is not satisfactory for practical application. Furthermore, pure PES membrane has serious problems of fouling, leading to the gradual decrease in permeation flux and frequent

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need membrane washing. The PES membrane often needs to be modified to improve its hydrophilicity, antifouling ability, and filtration properties before its practical use [2].

In recent years, inorganic materials have received more and more attention in membrane modification. By introducing inorganic materials into the polymer membrane matrix, the obtained organic–inorganic hybrid membranes combine the basic properties of organic and inorganic materials and shows excellent in separation performance, antifouling ability, good thermal and chemical stability, and adaptability to the severe conditions [1,3–5]. Several inorganic materials such as nanoparticle [6,7], carbon nanotube [1,8], and graphene oxide [9] have been incorporated into PES membrane to prepare the organic–inorganic hybrid membranes. The studies indicate that the addition of inorganic materials improved the water permeability and fouling resistance of polymer membrane. Recently, polymer-clay nanocomposites have achieved a great attention due to the enhancement of a broad range of properties of the organic matrix when incorporated with the nanoclay, even at low filler loadings [10].

The aim of this work is to produce membranes of PES and PES/clay by phase inversion technique and evaluate the presence of clay in these membranes. The effect of the clay is to modify the hydrophilicity of the matrix and then increase the affinity of the membrane with water and enhance the flow. The intercalation of clay in the polymer occurred through the intercalation solution.

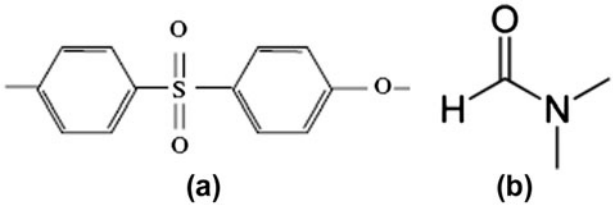

Fig. 1. (a) Molecular structure of PES and (b) DMF.

2. Experimental

2.1. Materials

The polymer matrix used was a PES in the form of powder, with particle size close to 150 μm, commercially called Veradel® 3000P, obtained from Solvay, with molecular structure showed in Fig. 1(a). For the preparation of membranes, N, N-dimethylformamide (DMF), anhydrous, 99.8%, was used as solvent. Its molecular structure is showed in Fig. 1(b) and was suplied by Labsynth Laboratory Products Inc. The montmorillonite (MMT) clay was used as nanofiller, Brasgel PA, provided by Northeast Bentonit Union (BUN), located in Campina Grande/PB/Brazil, in the form of powder and passed in a sieve ASTM 200 mesh. The average particles size of this clay is 5.93 μm and presents 24.61% of weight with particle size below 2 μm, according to Costa et al. [11].

2.2. Membrane preparation

The polymer PES was dried at 80°C for 24 h to eliminate adsorbed water and stored in a desiccator.

For the composition of the pure polymer, the solvent is poured directly with the polymer, leaving under stirring for 45 min, using a Ultra-Turrax stirrer at 16,000 rpm. For compositions containing clay, the solution was first prepared by adding clay and solvent. So this solution is stirred for 45 min with Ultra-Turrax mixer at 16,000 rpm. The compositions of the systems with polymer, clay, and solvent are presented in Table 1. As a representative example, for the PES/MMT 2 wt.%, a mixture of 90 g of DMF, 0.3 g of MMT, and 9.7 g of PES was used to prepare the composition.

The flat membranes were obtained according to the procedure used by Habert et al. [12], where the solution was spread on a glass plate using a casting knife with an opening height of 0.250 mm and was exposed to atmospheric air for 1 min, so that the

Table 1
Composition of the membranes

			Solid components = Polymer + Clay (10 wt.%)	
Samples	Solvent (wt.%)	Solid components (wt.%)	Polymer (wt.%)	Clay (wt.%)
Pure PES	90	10	100	0
PES/MMT 3 wt.%	90	10	97	3
PES/MMT 5 wt.%	90	10	95	5

selective layer (skin) was formed. Then, the plate was immersed in a bath of nonsolvent to precipitate the solution and form the membrane.

2.3. Membranes characterization

2.3.1. X-ray diffraction (XRD) analysis

XRD analysis for clays and for flat membranes was conducted on a Shimadzu XRD-6000 instrument, using copper Kα radiation, 40 kV of voltage, current 30 mA, scanning from 2 to 30 with a scan rate of 2°/min.

2.3.2. Scanning electron microscopy (SEM)

To analyze the morphology of flat membranes, the surface and cross section were evaluated. Both analyses was performed on the Superscan 550 SSX-Shimadzu equipment, operating at 15 kV. For the cross-section analysis, the samples were fractured in liquid nitrogen to avoid plastic deformation. All samples were gold sputtered.

2.3.3. Contact angle

The system used for the analysis of the contact angle was composed of a digital photo camera Nikon D5000, positioned in front of a platform, where the membranes were placed and a drop of deionized water was deposited on the surface of the film.

2.3.4. Permeation flux with distilled water

To evaluate the permeation flux with distilled water, a filtration cell was used, with an effective area of about 13.0 cm^2 and a pump model with 1/5 HP of power, coupled to a system, which allows to circulated the fluid from the feed tank through the membrane cell. The permeate water was collected according to Fig. 2. The membranes were subjected to three pressure levels (0.5, 1.0, and 1.5 bar). For each pressure, at least three measurements were done to obtain the average values of water permeate flow.

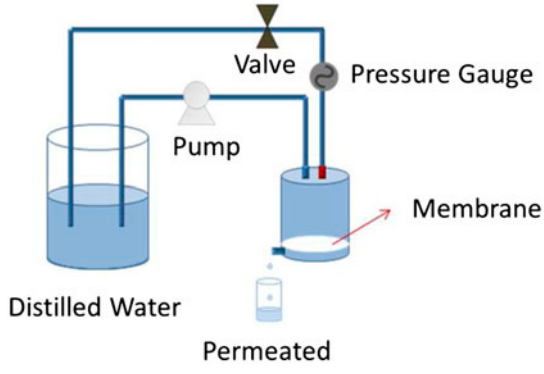

Fig. 2. Schematic representation of the filtration system used to estimate the permeate flow with distilled water.

3. Results and discussion

3.1. XRD analysis

The curves from of XRD analysis of the membranes are shown in Fig. 3 and it was observed that

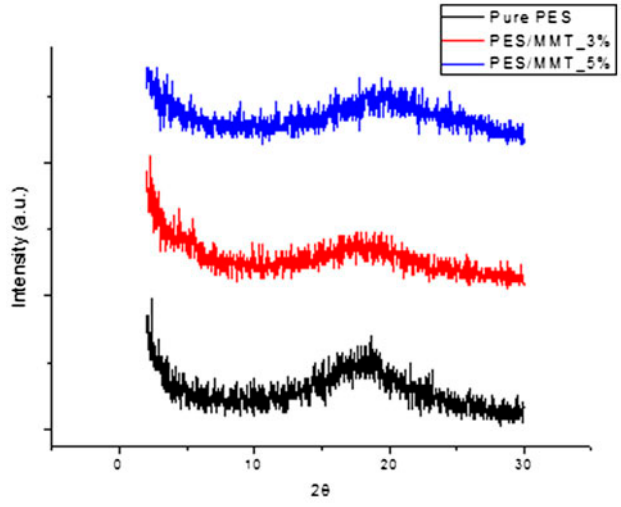

Fig. 3. XRD patterns of PES and their nanocomposites membranes.

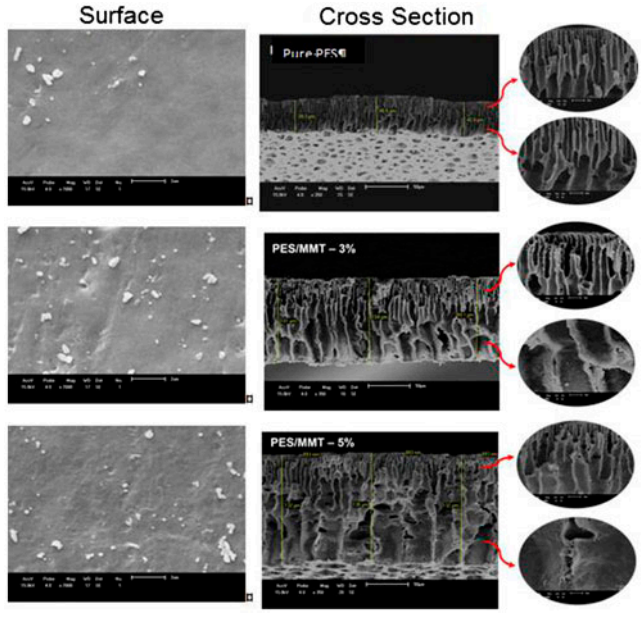

Fig. 4. SEM of the surface and cross membranes of pure PES and PES/MMT with 3% and 5 wt.%.

the curve of the pure polymer membrane refers to a noncrystalline polymer, or amorphous, and remains unchanged when compared with the XRD pattern of the pure polymer, as observed in the literature [13,14], showing that the presence of the solvent and the whole procedure for obtaining the membrane did not affect the structure of them.

It is also observed that for membranes with clay, the characteristic peaks of MMT were not detected in the curves of the membranes with its presence, indicating a possible exfoliated and/or partially exfoliated structure. According to Liang et al. [14], the non-appearance of characteristic peak of MMT can be attributed to efficient intercalation of the polymer chains between the clay layers.

Membranes with exfoliated structures were also observed by Ghaemi et al. [13] and Wang et al. [15]; in these cases, the clay mineral layers were dispersed in DMF and soon after were added to the PES/DMF solution. Delaminated clay mineral layers were adsorbed to the polymer chains as the solution is stirred. When the film was immersed in the nonsolvent bath, the solvent was continuously exchanged by water (nonsolvent) with a decrease in diffusion rate. The layers of clay, filled with polymer chains, are linked up forming the intercalated/exfoliated

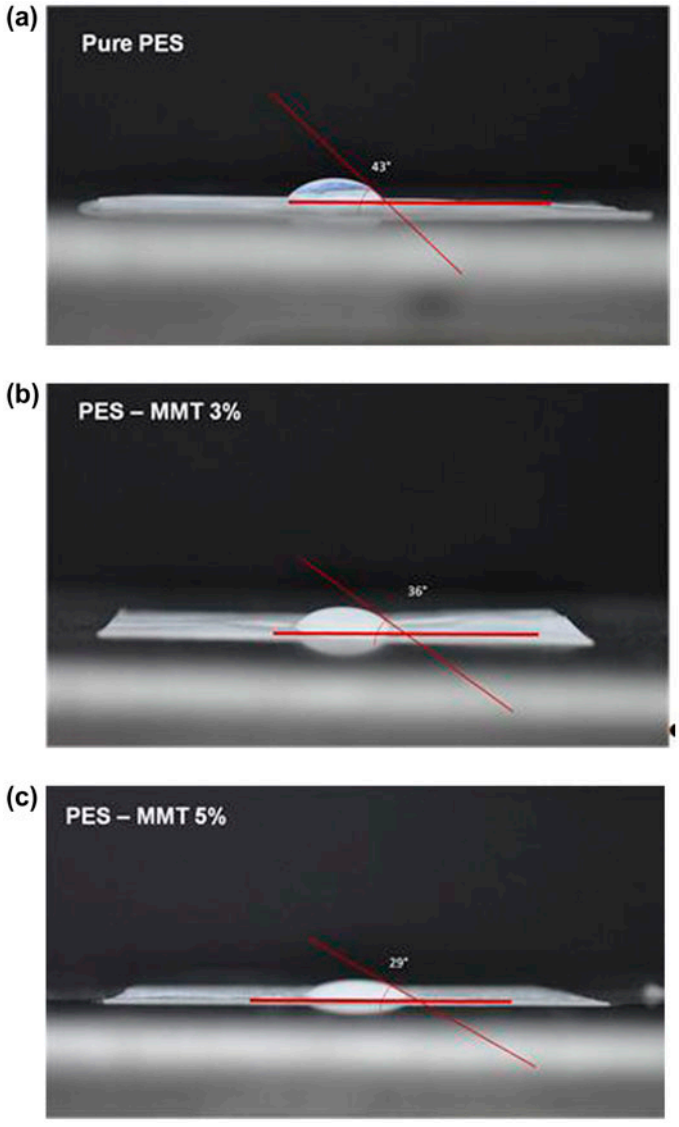

Fig. 5. Contact angle of a drop of distilled water on the membrane surfaces: (a) pure PES, (b) PES-MMT 3%, and (c) PES-MMT 5%.

structures and once diffusion was reduced by the coagulated surface [13].

3.2. SEM

The SEM images of the surface and cross section of the pure PES flat membranes and nanocomposites with MMT clay in proportions of 3 and 5% are shown in Fig. 4.

The pure PES membrane presents a surface with porous structure and apparently without much surface roughness when compared with the membrane with 3 and 5% of MMT. All compositions showed particles on the surface, indicating possibly undissolved polymer and/or clay particles, as also observed by Wang et al. [15]. In some parts, large agglomerates of these particles were observed. According to Liang et al. [14], the presence of these particles can be attributed to poor adhesion between PES and inorganic fillers (MMT), due to hydrophobic and hydrophilic character.

As for the cross section that is observed in general, all membranes present similar behavior with an anisotropic structure, where there is a selective, dense top layer and a porous support. The selective layer is very thin (less than 1 μm) which is interesting, because it facilitates the flow. To support, macropores are observed in the "fingers" format, with internal pores interconnected. This morphology was also observed by Ran et al. [16], Saedi et al. [17], Wang et al. [18], and Mierzwa et al. [19] for pure PES membrane.

At a higher magnification, as illustrated with arrows near the top of the dense layer of the membrane, there is connectivity between the two layers. This microstructure is desired, because of reducing the transport path of the solute in the separation process. Probably, the presence of clay affects the hydrophilicity property of the casting solution and altered membrane formation during phase inversion process. Through a qualitative visual analysis, it is possible to identify changes in the internal pore structure due to the addition of the clay. There is a change in the structure formation of macropores, which internally has a sponge-like morphology. Accordingly, Mierzwa et al. [19] in their study with PES/(clay + sodium hexametaphosphate) said that sponge-like structures can increase the resistance to water permeability and act as a filter.

3.3. Contact angle

Fig. 5 shows the contact angle of a drop of distilled water on the membrane surfaces for pure PES, PES-MMT 3%, and PES-MMT 5%. It was observed that the contact angle with water on the membrane surface decreases with increasing clay content, changing from 43° to pure PES membrane, to 36° for PES-MMT 3% and to 29° for the PES-MMT 5%. The inclusion of clay affect the morphology and increases the hydrophilic character of the membranes and may contribute to an improvement of the water permeation through the membrane.

3.4. Permeation flux with distilled water

To better evaluate the permeate flow with distilled water on the membrane, all compositions were analyzed at three different pressures (0.5, 1.0, and 1.5 bar).

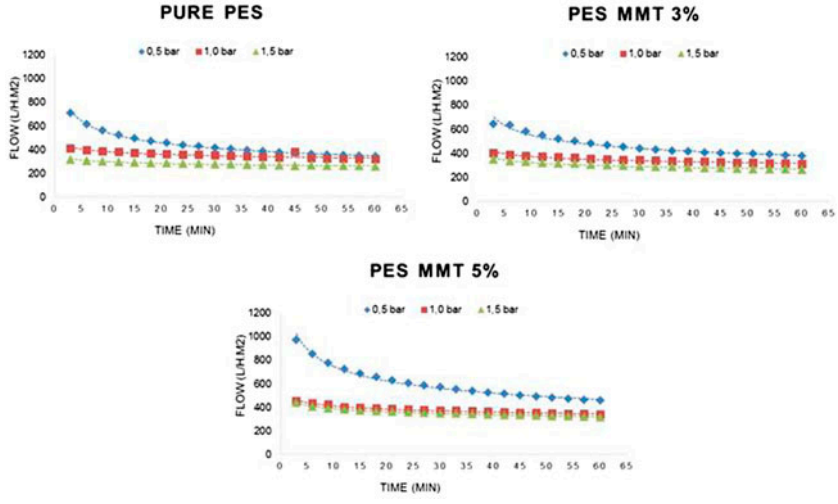

Fig. 6. Distilled water permeate flow vs. time for pure PES membrane and its nanocomposites.

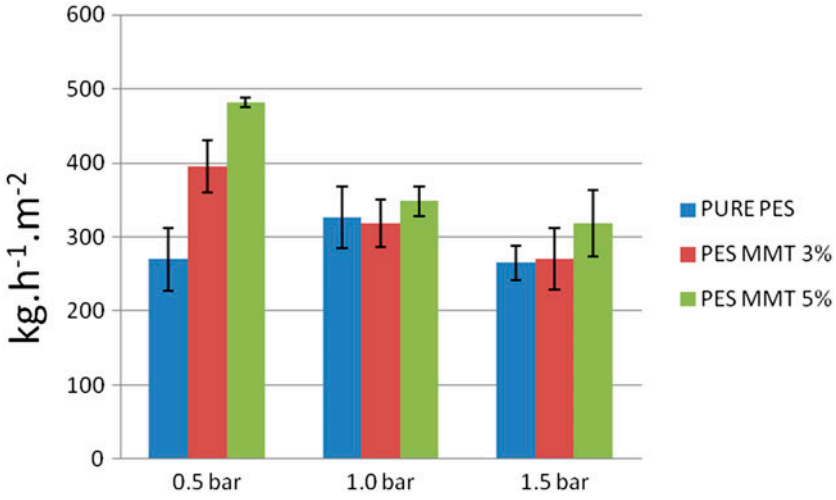

Fig. 7. Stabilized distilled water permeate after 1 h of experiment for pure PES membrane and its nanocomposites.

The graphs of permeate flow vs. time are shown in Fig. 6 for the pure PES membrane and its nanocomposites.

It was observed that all compositions have the same tendency to flow, which begins quite high and then stabilize over time. In all membranes, the optimal pressure at which stabilization was obtained with higher flow was 0.5 bar. In other pressures, flows were lower, probably because at high pressure, there is a relatively high compression of the membrane, reducing the flux. In Fig. 7, it was observed that the flux for the pure PES membrane at 0.5 bar stabilizes at 465 kg/h m^2 after 1 h of experiment, which is considerably above the flow (214 kg/h m^2) obtained by Liu et al. [20] to this polymer membrane.

The highest stabilized flow after 1 h was for the PES-MMT 5% membrane (477 kg/h m^2) when compared with pure PES and PES-MMT 3% membranes. It is interesting that this fact occurs only for the membrane with 5% of clay. From SEM images, the PES-MMT 5% membrane surface did not show discrete pores with a magnification of 7,000×. So, this increase in permeate flow can be attributed, probably, to the interaction between the polymer/clay that affected the hydrophilicity of the membrane.

4. Conclusion

PES membranes and its nanocomposites were successfully obtained. From XRD analysis, it can be seen that the nanocomposites membranes had exfoliated and/or partially exfoliated structures. From SEM, it was possible to conclude that the membranes showed a surface apparently without pores and a cross section with anisotropic structure. All compositions showed the same trend of permeate flux with distilled water and presented higher flux with 0.5 bar of pressure. The incorporation of clay modified the hydrophilicity of the membranes and increased the permeate flow with distilled water.

Acknowledgments

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