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Polyethersulfone nanocomposite membranes with different montmorillonite clays for oil/water separation

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ABSTRACT

Nanocomposites of polyethersulfone (PES)/clay with different types of clays were obtained to be applied in the development of flat membranes, prepared by phase inversion technique. An X-ray diffraction analysis verified that membranes with clay had exfoliated and/or partially exfoliated structures. The contact angle of the membranes with clay decreased in the presence of distilled water and oil. Moreover, such effect was more pronounced for montmorillonite (MMT) clay. By SEM images, a variation in the morphology of the membranes with modification of the internal pore structure due to the presence of clays was observed. In the test of flow measurements with distilled water and oily emulsion, a considerable increase in the permeated flow was observed when introducing clay. This effect is clearer when introducing MMT and Cloisite Na$^+$ clays. The best results for permeate flow were presented by membranes with Cloisites clays (Na$^+$ and 20A). All membranes had a high oil/water separation yield (all of them above 84%), where the membranes with the Cloisite clays had the best yield and it may be concluded that all membranes have great potential to treat oily effluents.

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

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1. Introduction

During oil and gas production, water is collected at the wellhead and called produced water (PW). In 2003, about 800 million m^3 of produced water were discharged to the ocean from offshore facilities throughout the world [1]. The Environment Council in Brazil has set a limit of 20 mg/L of oil in water when this material is discharged to the sea [1].

According to Motta et al. [2], the frequently used methods to remove these droplets are air flotation, hydrocyclones, coalescer bed, and gravitational separators. However, these processes have some disadvantages, such as (i) the use of chemicals, high cost, problems in handling and disposing large volumes of sludge (in the case of air flotation); (ii) high operational complexity, (iii) power consumption, (iv) investment costs, and (v) operating costs. In these circumstances, new treatment methods for PW are needed, given that oil production has increased considerably over the years. In this context, the treatment through membrane separation process (MSP) is a very attractive technology. This treatment presents a potential solution to the problem of emulsions droplets with diameters in the range of micrometers or submicrometers [3].

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MSP is an emerging technology in the treatment of water and when comparing against conventional treatments, MSPs bring better product quality and treatment plants are more compact and easy to be automated. Moreover, these processes generate less sludge and have a competitive cost also comparing with conventional treatment systems. In this way, they are potential alternatives for water treatment in area where there is restricted space available, such as in the petroleum industry [4,5].

The phase inversion is the most used method to obtain polymer membranes using immersion–precipitation technique. They are produced by precipitation of a dispersed polymer solution as a thin or extruded film as a hollow fiber, and subsequently put in a non-solvent bath that destabilizes the solution and precipitates the polymer in the membrane form. This technique allows a wide morphological modification by performing small variations in some parameters used in the membrane preparation process [4,6].

Currently, the membranes most used worldwide in MSP are those produced from synthetic polymers [7], such as polyethersulfone (PES). These membranes have good mechanical strength, thermal stability and fast precipitation. However, PES has some disadvantages in their membrane preparation, such as: low permeability and high tendency to form fouling [8]. Due to these inadequate PES properties, there is a need to add a hydrophilic agent as an additive to mitigate these limitations.

An alternative to PES is the development of membranes from polymer nanocomposites. These membranes aim to meet a demand for products with different properties compared with traditional ones, and they increase specific applications, such as energy generation and ultrafiltration membranes [9,17–19].

The preparation of some polymer nanocomposites involves the incorporation of inorganic particles into polymer matrices and this has been done first by Cho and Paul [10], and Araújo et al. [11]. Considering the dimensions of polymer chains and their crystalline assemblies, it can be said that all polymer have structure on the nanometer size scale and, further that the mechanical properties of polymer are governed by the interactions of these nanostructures. These inorganic fillers used and presented in the literature include zeolites, silicas, clays, molecular sieves of coal, activated carbon, carbon nanotubes, nanoparticles of metal oxides, among others [12].

The most commonly used particle to prepare nanocomposite is clay from the smectite group, such as montmorillonite (MMT). In this clay mineral, the silicate layers are joined through relatively weak dipolar Van der Waals forces and the cations Na^+ and Ca^{2+} are located in the interlayer [11].

The addition of inorganic nanoparticles in polymer materials to produce membranes improves their filtration properties. This technique has attracted great attention to the development of membrane science and technology. Studies by Yang et al. [13], Uragami et al. [14] and Nagarale et al. [15] showed that adding a small quantity of inorganic nanoparticles (less than 10% by weight) in a solution with polymer eliminates the formation and growth of macrovoids. Moreover, they observed that it increases the number of small pores, improving porosity, permeability mechanical properties, thermal stability, and anti-scale performance [16].

There are few works comparing the use of different clays and the effect of organophilic clay. In this context, the aim of this work is to evaluate the variation of type and amount of clay in the development of flat membranes obtained from nanocomposites polymer. This research evaluated the properties and efficiency of membranes in the water–oil separation process.

2. Experiment

2.1. Materials

For membrane preparation, the polymer matrix PES which has high molecular weight and high melt flow index, was used. It was purchased from Solvay Specialty Polymers (India), powder form, trade Veradel® 3000P. It was used as solvent, N,N-dimethylformamide-PA (DMF) produced by Labsynth Laboratory Products Inc., (Brazil) Brasgel PA clays (MMT) and Cloisite (CL Na^+ and CL 20A) were used as nanofiller, both supplied by Bentonite União Nordeste (BUN) of Campina Grande – PB/Brazil and São Paulo-SP/Brazil, respectively. For the organophilization of the MMT clay (called OMMT), the Praepagen HY® (alkyl dimethyl hydroxyethyl ammonium chloride) quaternary ammonium salt was used with 40% active material, from Oxiteno – SP.

2.2. Methods

2.2.1. Clay organophilization

The preparation of the organophilic montmorillonite with the Praepagen HY® (alkyl dimethyl hydroxyethyl ammonium chloride) quaternary ammonium salt as follows: the Na-MMT was mixed in distilled water with stirring to form a homogenously dispersed suspension. After all the clay has been added, the suspension was stirred for 20 min. Then, organic salt equivalent to 1:1 cation exchange capacity of Na-MMT was added to the dispersion. The mixture was stirred for more than 20 min. After 24 h, the mixture of montmorillonite and the salt was washed with distilled water for several times to remove the excess salt and it was dried at 60ºC for 48 h, and finally, passed in a sieve 200 mesh. The procedure is described in detail by Araújo et al. [11], de Paiva et al. [20] and Leite et al. [21].

2.2.2. Membrane preparation

Initially, the solution with PES (dried at 80°C under vacuum for a period of 24 h) and N,N-dimethylformamide-PA (DMF) was prepared, using an UltraTurrax disperser at a speed of 16,000 rpm, for 45 min. For the clay-containing compositions, dispersion was initially prepared with clay and N,N-dimethylformamide-PA, under the same conditions. After, the polymer was added to the dispersion under stirring for 45 min. The systems compositions with polymer, clay and solvent are presented in Table 1. As an example, for the PES/MMT 5 wt%, a mixture of 90 g of DMF, 0.5 g of MMT and 9.5 g of PES was used to prepare the composition. The flat membranes were obtained according to the procedure used by Leite et al. [21] and Medeiros et al. [22]. The solution was spread on a glass plate by using a casting knife with opening height of 0.250 mm. It was exposed to atmospheric

Table 1
Composition of the membranes

Sample	Solvent (wt%)	Polymer (wt%)	Clay (wt%)
Pure PES	90	10	–
MMT 3%	90	9.7	0.3
MMT 5%	90	9.5	0.5
OMMT 3%	90	9.7	0.3
OMMT 5%	90	9.5	0.5
CL Na 3%	90	9.7	0.3
CL Na 5%	90	9.5	0.5
CL 20A 3%	90	9.7	0.3
CL 20A 5%	90	9.5	0.5

air for 1 min so that the selective layer (thick) was formed. Then the plate was immersed in a bath of non-solvent (distilled water) to the precipitation of the solution and membrane formation.

2.2.3. Characterization of membranes

2.2.3.1. X-ray diffraction

The analysis of clay and membranes was conducted on a Shimadzu XRD-6000 instrument (Japan) using copper Kα radiation, 40 kV of voltage, current 30 mA, scanning from 2° to 30° and a scan rate of 2°/min.

2.2.3.2. Scanning electron microscopy

To analyze the morphology of flat membranes, the cross section was evaluated. This analysis was performed on the Superscan 550 SSX – Shimadzu equipment, operating at 15 kV. Samples were fractured in liquid nitrogen (to avoid plastic deformation) and gold sputtered.

2.2.3.3. Contact angle measurements

The contact angle measurements were obtained by the sessile drop method, using a portable instrument, Phoenix-i model of the Electro Optics – SEO Surface. The drop image was captured and analyzed in the equipment software. Five different areas were evaluated on the surface of each membrane, to obtain the average of contact angles.

2.2.3.4. Flow measurements

For the analysis of the membrane flow measurements, it was used a perpendicular filtration cell with an effective area of about 13.0 cm^2, coupled to a system, which allows the circulation of the fluid from the feed tank through the membrane cell, by a pump with 1/5 HP. The membranes were subjected to permeability tests with distilled water and oil emulsions. The measurements were performed in triplicate under a 1 bar pressure. The permeate was collected every 1 min for 1 h. The test follows the same scheme as the system performed by Medeiros et al. [22].

The synthetic effluent separation tests were performed using an emulsion with 100 ppm of commercial oil for automotive engines from Selenia Motor Oil, Petronas, in water. It is a multi-viscosity lubricating oil, viscosity SAE 10W-30. The oil-in-water emulsions were prepared at constant stirring speed of 15,000 rpm, for 30 min, using an Ultra Turrax, from IKA Works Inc., (China).

2.2.3.5. UV spectrophotometry

To measure the oil concentrations in the feed and permeate, spectrophotometer (UV) UV-VIS Biochrom Libra S60 (USA) was used. The sample preparation followed the instructions of the Petrobras Manual described by Cirne et al. [23].

The selectivity was estimated by the rejection coefficient (R%) or yield. It was calculated according to Eq. (1):

$$R(\%) = \frac{C_0 - C_p}{C_0} \times 100 \quad (1)$$

where C_p is the concentration of oil in the permeate (CP) and C_0 is the oil concentration in the feed.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction (XRD) curves of untreated clays (MMT), organophilic (OMMT), CL Na$^+$, and CL 20A. Analyzing these results, it could be observed a better efficiency of organophilization process by increasing the basal interplanar distance (d001) of treated clay (OMMT) in relation to untreated clay (MMT). The same was observed when comparing commercial Na clay to 20A clay.

The XRD pattern of the MMT and OMMT clays shows a peak at approximately 20.04° (basal spacing ≈ 4.41 Å), characteristic of the smectite (S) mineral clay, as predominant and other peaks close to 21° (basal spacing ≈ 4.20 Å) and 26.05° (basal spacing ≈ 3.33 Å), assigned to the presence of quartz (Q). Amorim et al. [24] observed similar results.

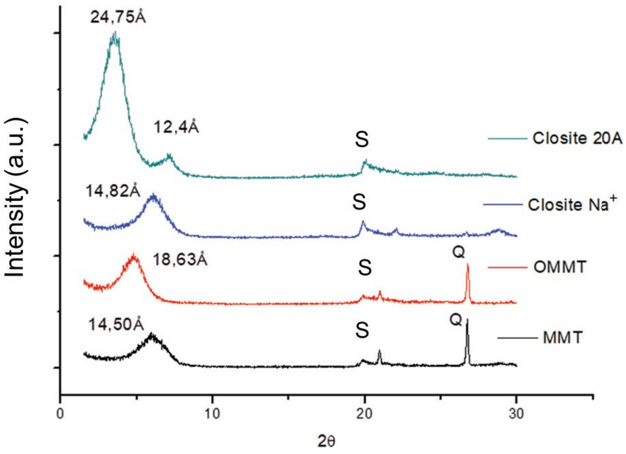

Fig. 1. XRD patterns of montmorillonite (MMT), organophilized MMT (OMMT), Cloisite Na$^+$ and Cloisite 20A. The numbers depicted in the figures means the basal interlayer spacing of the clays.

Observing the XRD pattern of the OMMT, it can be noticed displaces in peaks to smaller angles and consequent expansion of the layers to 18.63 Å. This fact may be related to an effective intercalation of the organic salt molecules among the layers of clay, which may favor the incorporation of clay into the polymer. This behavior was also observed by Araújo et al. [25], Cavalcanti et al. [26], and Barbosa et al. [27].

For CL Na^+ clay, it presents a basal distance value close to that of the MMT clay of 14.50 Å. CL 20A shows a greater distancing, around 24.75 Å, confirming that it is a commercially organophilized clay. This fact may be favorable for better dispersion in polymer. It could also be observed the presence of a second peak of 12.4 Å for CL 20A clay, related to d002 plane. Barbosa et al. [27] reported similar results citing Souza Santos about X-ray crystallography that it is not necessary to consider the reflection plane (002) and second order (001), since the planes (002) lattice are uniquely identified as any other plane (hkl).

The presence of a second peak for CL 20A was also noted in the studies reported by Giulio et al. [28], Hotta and Donald [29], Li et al. [30], Stoeffler et al. [31], and Litchfield et al. [32]. In these studies, this effect has been attributed to the reflection of planes d002. This can represent a second-order peak, since the calculated spacing value is approximately half of plane d (001) [31].

Fig. 2 illustrates the XRD patterns of the pure polymer and nanocomposites membranes. This figure shows that the presence of the solvent and the whole procedure for obtaining the membrane did not affect the polymer structure. Liang et al. [12] also observed the same effect.

For membranes containing MMT clays in both proportions and the CL Na 3%, the characteristic peak of montmorillonite clay is not evident in the curves and indicates a possible exfoliated and/or partially exfoliated structure. According to Liang et al. [12], the non-appearance of the characteristic peak of smectite can be attributed to an efficient intercalation of the polymer chains between the lamellae of the clay, generating an exfoliated and/or partially exfoliated structure. The MMT layers are well dispersed in the DMF (polar solvent) and remain well separated during the polymer precipitation in the coagulation bath immersion. Consequently, a nanocomposite membrane is obtained.

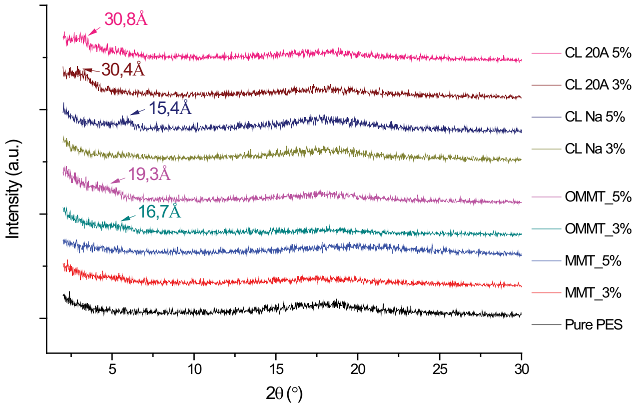

Fig. 2. XRD patterns of pure PES and nanocomposites membranes.

For the compositions with OMMT (3% and 5%) and CL 20A (3% and 5%) a shoulder is observed, with a basal distance of approximately 16.7, 19.3, 30.47 and 30.84 Å, respectively that indicates an intercalated structure and/or a microcomposite. CL 20A had greater basal spacing apparently because its dispersion in the polymer was not efficient. Different untreated clay, the organophilized clays formed coarse dispersions in DMF and the water addition, during coagulation bath immersion, favored its agglomeration and less dispersion.

Wang et al. [33] and Ghaemi et al. [34] also observed membranes with exfoliated structures. These authors attributed such effect to an entropy increase, when the clay layers are dispersed in DMF. Then when the dispersion of DMF/clay is added to the PES/DMF solution, it disturbs the arrangement of clay layers. The delaminated clay layers favor the intercalation of the polymer chains during the solution stirring. When the film is immersed in the non-solvent bath, the solvent is continuously exchanged for water (non-solvent), reducing the diffusion rate. Clay layers filled with polymer chains form intercalated/exfoliated structures where diffusion can be hampered by the precipitated surface, favoring more dispersed structures [34].

3.2. Contact angle

The results of the contact angles with distilled water and oil on the surfaces of the PES membranes and their nanocomposites are shown in Figs. 3a and 3b, respectively.

It was observed that the membrane with pure PES presents the highest contact angle (65.2º) when comparing it to other compositions. This is probably due to the presence of ether bonds in PES chains, which results in a slight hydrophilic characteristic.

The inclusion of clay increased the hydrophilicity of the membranes, being this effect more pronounced with compositions with a higher clay content. This effect can probably be attributed to the fact that clay facilitates the formation of hydrogen bonds, favoring the increase of water affinity.

The membranes with the lowest contact angles were those containing the regional clays (MMT and OMMT), probably due to the presence of quartz impurities, as well as observed in XRD. This effect was more intense for compositions with MMT clay (3 and 5 wt%) which presented angles of 60° and 58.6°, respectively. For the other clays, the contact angle increased to approximately 61°. Similar results were obtained by Mierzwa et al. [5]. In this work, the authors added hexametaphosphate and clay Na at concentrations of 1, 2.5 and 5 wt% to PES membranes.

The contact angle of membranes with synthetic oil (Fig. 3b) presents the same behavior, where the inclusion of clay decreases the contact angle. However, the affinity of membrane and oil was considerably greater, since its angle is practically half of that obtained with water. It was also found that addition of clay increases the membrane/oil affinity. However, a decrease in contact angle of membranes with clay was observed. This higher affinity can be observed for membranes with MMT clay (3% and 5%), where the contact angle of pure PES membrane was 33° and with the inclusion of clays, it reduced to 28° and to 30.8°.

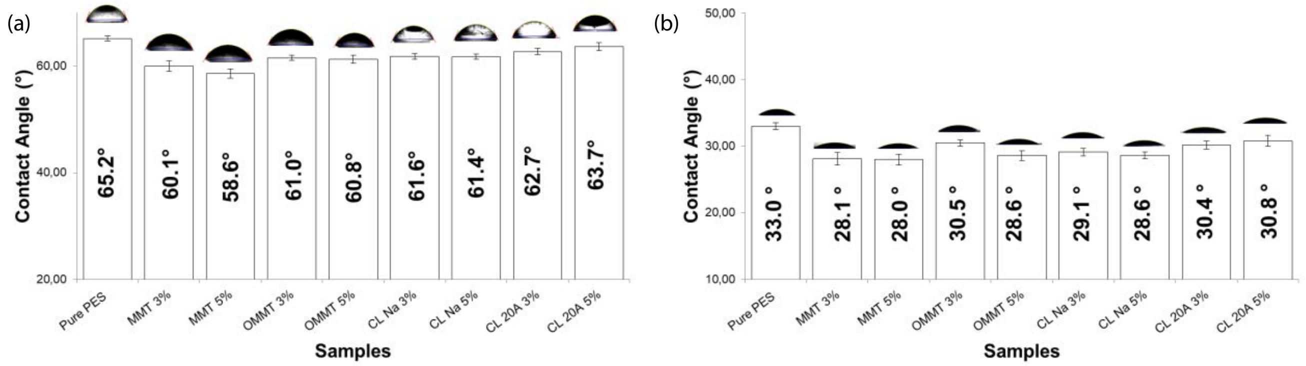

Fig. 3. Contact angle of the drops of (a) distilled water and (b) oil on the membrane surfaces.

Litchfield et al. [32] explain that PES with oil should not have chemical affinity, since the polymer contains polar groups, favoring this characteristic. However, the composition of the oil used in our study contains several additives, such as detergents, dispersants, antioxidants, antifoams and others which can increase the affinity of the oil droplet with membrane surface. Some of these additives have hybrid (polar and apolar) character that interacts with both polymer and oil.

3.3. Scanning electron microscopy

The scanning electron microscopy (SEM) images of the cross section of pure PES membranes and nanocomposites with MMT, CL Na, OMMT, and CL 20A clays, and different proportions (3 and 5 wt%) are shown in Fig. 4.

In general, the cross sections of the membranes presented an asymmetric morphology, apparently consisting of a thin skin and a large layer of porous support. According to Salahi et al. [35], the membrane morphology depends on the phase inversion kinetics and the thermodynamics involved in the solution precipitation.

In Fig. 4, it is possible to visualize that the porous support has macropores structure similar to "fingers". These pores are more elongated and they are apparently larger in the bottom surface, characteristic of the precipitation immersion method. The selective layer is apparently dense and thin. This is interesting because the flow will be facilitated in this thin layer. Similar results were also verified by Zhao et al. [36] and Medeiros et al. [22].

It can be seen that the presence of clay affects the morphology of the pores, favoring the formation of macropores, type "fingers". As observed by Guillen et al. [37], several studies propose mechanisms to describe the formation kinetics of these macropores. Strathman et al. [38] believe that it is the rate of precipitation that determines the macropore structure. Boom et al. [39] and Smolders et al. [40] explain that the diffusion of solvent evaporated from the polymer solution causes the growth of these pores. This type of pore is generally formed in systems where instantaneous precipitation occurs, except when the concentration of polymer additive and the concentration of non-solvent in the polymer solution exceed a minimum value.

The clay acts, in a certain way, as an additive. It reduces the interaction between polymer chains, which results in a delay in precipitation of the polymer solution. Another factor that may contribute to this behavior is the hydrophilic character of the clay and the formation of hydrogen bonds between clay and solvent (DMF). These factors can delay the evaporation rate of the solvent, resulting in polymer precipitation delay and higher concentration of non-solvent. Based on this, it decreases the growth of the skin layer and favored the formation of finger-shaped pores in the support [30].

The membranes with the clays presented larger total thicknesses than pure PES membranes. Besides, the increase of the content favored the increase of the membrane thickness. It can be attributed to a higher viscosity of the solution, which increases with growing clay content. Guillen et al. [37] explains that lamellar nanoparticles, such as clays, are generally used because they provide the best surface/volume relation, improving properties, and strong interfacial interactions of the nanoparticles with the surrounding polymer, favoring the increase of solution viscosity. This effect is more pronounced for MMT and OMMT clays.

According to Kim et al. [41], a higher viscosity favors a greater membrane thickness because it favors the mechanism of nucleation and growth that predominates during the membrane formation.

3.4. Flow measurements for distilled water

The stabilized permeate flows with distilled water for pure PES membrane and its nanocomposites are shown in Fig. 5. All compositions showed the same flow tendency, which starts high and then stabilizes after approximately 20 min of test. After stabilizing, its flow rate was measured and it is shown in Fig. 5.

It is observed that the flow to pure PES membranes presented a high flow with distilled water of approximately 460 kg h^{-1} m^{-2} bar^{-1}. Moreover, it is considerably higher when compared with others works that used membranes of the same polymer, such as Mierzwa et al. [5] obtained 176.4 kg h^{-1} m^{-2} bar^{-1}, while Guillen et al. [37] 21 kg h^{-1} m^{-2} bar^{-1} and Liu et al. [42] 214 kg h^{-1} m^{-2} bar^{-1}. These differences were probably due the methodology used, different solvents and mainly to the PES dope solution concentration that favored this improvement. In our study, we used a dope solution concentration of 10 wt% of PES with DMF. Mierzwa et al. [5], used 18 wt% of PES and N-methyl-2-pyrrolidinone (NMP) as a solvent. Guillen et al. [37] used 20 wt% of PES

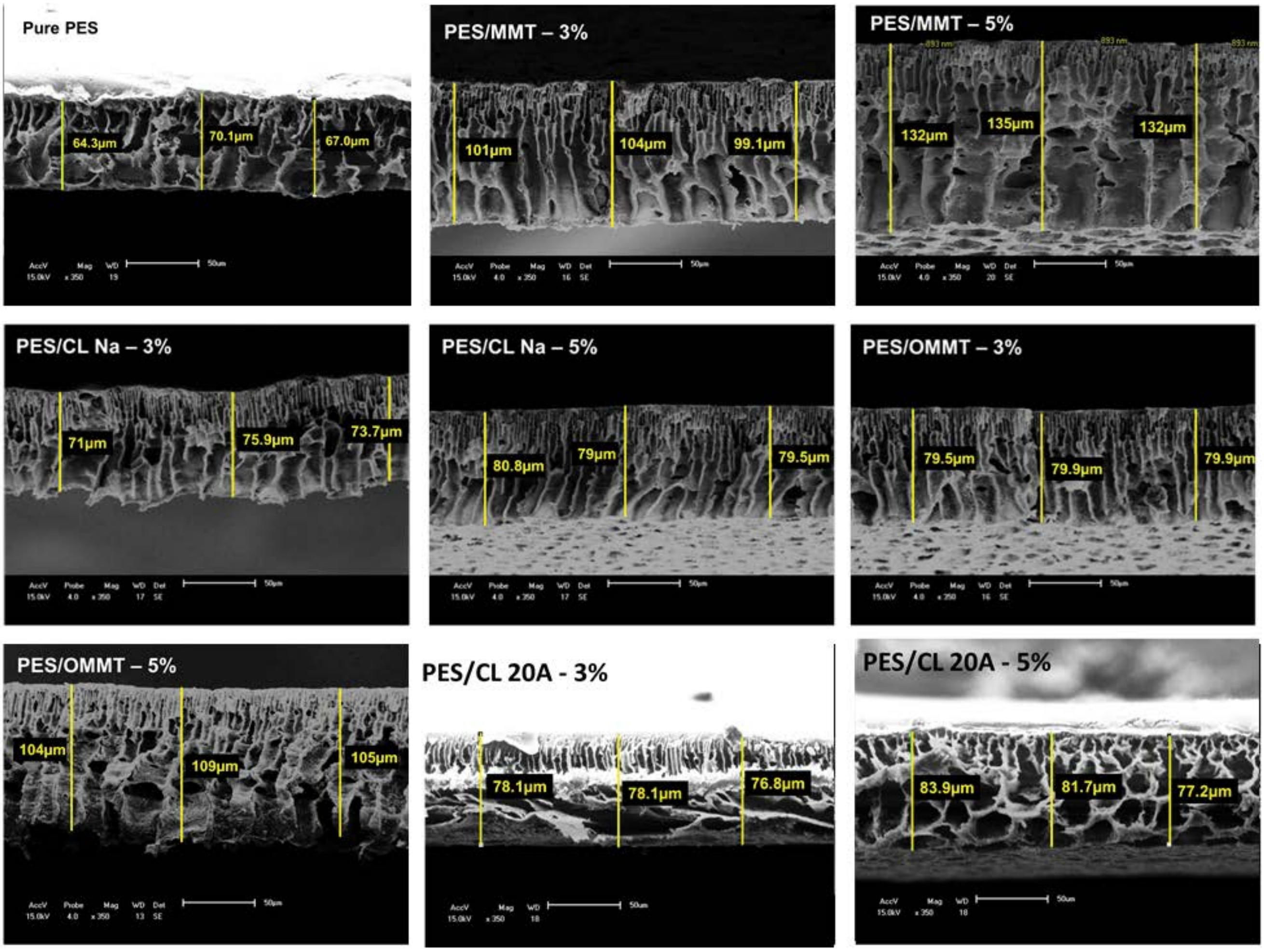

Fig. 4. SEM images of the cross section of the membranes of pure PES and PES/clays with 3% and 5% wt.

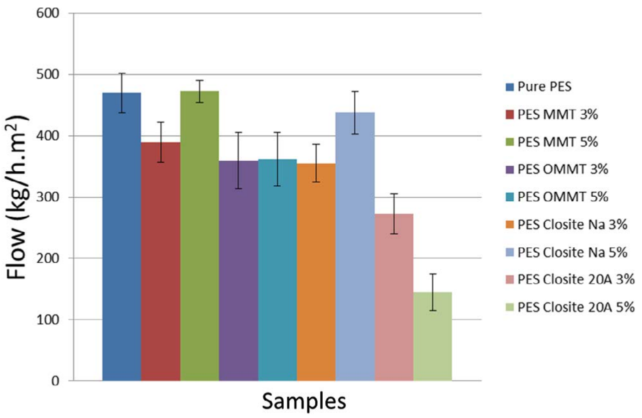

Fig. 5. Permeate flow with distilled water for pure PES membrane and its nanocomposites.

with DMF and Liu et al. [42] used 17% of PES and a mixture of N,N-dimethylacetamide with polyethylene glycol.

It is possible to see that the highest flow was observed in MMT 5% membrane (477 kg/h m^2) and CL Na 5% membrane (444.5 kg/h m^2). It is interesting to note that this fact occurs for sodium clays at a concentration of 5%. It is believed that this fact is related to these compositions presented the lower angles of contact when comparing with membranes that presented greater hydrophilic character.

For the other membranes, the incorporation of the clay decreased the flow and consequently the permeability of the water through the membrane. This effect can be assigned to the dispersion of clay in the polymer matrix, promoting a change in the structure of the membrane, and it may influence its permeability. Another important factor is that the membranes with this clay did not show a great increase in hydrophilicity, as observed in the contact angle with distilled water (Fig. 3a).

Mierzwa et al. [5] obtained membranes of pure PES and montmorillonite clay, in proportions of 1, 2, 3 and 5 wt%, where its largest flow was for the proportion of 2 wt% of clay with a water flow of 389.3 kg h^{-1} m^{-2} bar^{-1}. Comparing the flow results of this work with Mierzwa et al. [5], all membranes obtained larger flows. As said before, this was probably due to the concentrations used with different solvents and that favored this improvement.

3.5. Flow measurements for oil/water emulsion

The flow measurements for the oil-in-water emulsion are shown in Fig. 6. In this figure, it is possible to observe that

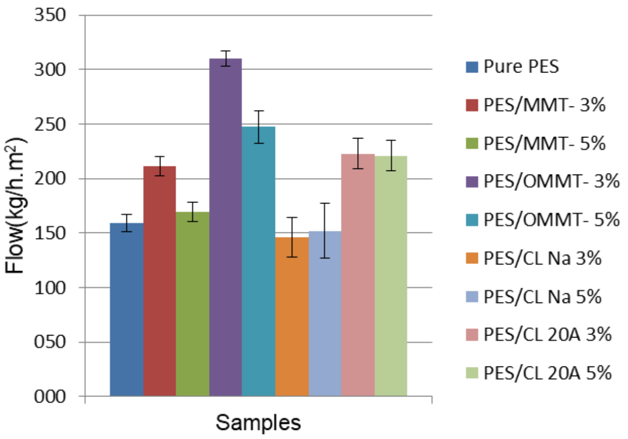

Fig. 6. Permeate flow with emulsion at 100 ppm of oil in water for pure PES membrane and its nanocomposites.

there was a reduction of the flow compared with distilled water (Fig. 5). The reduction was more significant with the membrane of pure PES, which changed from 460 kg/h m^2 (distilled water) to 159 kg/h m^2. This was probably due to the fouling of the pores, where the oil is lodged in the pores of the membrane, so that it decreases water permeation.

The inclusion of clay increased the permeated flow for the oil-in-water emulsion. The highest fluxes were obtained for the OMMT membranes, 3 and 5 wt%, with 309.66 and 247.40 kg/h m^2. The CL Na 5% membrane obtained a flow with 219.82 kg/h m^2. The membrane with CL Na 5% clay was one of those that also presented a high flow for the distilled water (Fig. 5). Probably, this effect may be related to the fact that this membrane has an increase in the hydrophilicity and decrease in lipophilicity. However, it was observed that this clay has a higher porosity, as well as a good distribution of the pore size on its surface.

In general, all the membranes presented a similar tendency observed by the flow measurements with the distilled water.

3.5.1. Yield

The permeate oil concentration (Cp) and yield (rejection coefficient) for PES and its nanocomposites membranes can be seen in Table 2. This flow measurement was performed under a pressure of 1 bar.

It is possible to verify a high yield, above 84% for all membranes tested in the process of oil/water emulsions separation, obtained concentrations below 16 ppm in the permeate. There is a significant reduction of oil in the permeate. Besides, all the membranes attended the standards and requirements defined by Resolution 430 of the National Council of the Environment in Brazil. This resolution determines that oils and greases of mineral origin can only be discarded in the environment when they have a maximum concentration of 20 ppm [24].

It was also observed that CL Na and 20A membranes presented more satisfactory results, regardless of the concentration used, since the separation efficiency was higher, where all the membranes had a concentration of oil in the permeate lower than 4.5 ppm. Therefore, the concentration of oil in the permeate was lower than PES membranes, with yield higher than 95%

Table 2
Permeated oil concentration (Cp) and yield values for PES and its nanocomposite membranes, at 1 bar pressure, using 100 ppm of synthetic oil in the feed

Membranes	Cp (ppm)	Yield (%)
Pure PES	6.0	94.01
MMT 3%	10.1	89.86
MMT 5%	15.9	84.14
OMMT 3%	8.0	92.00
OMMT 5%	10.1	89.92
CL Na 3%	2.7	97.26
CL Na 5%	1.3	98.66
CL 20A 3%	4.4	95.65
CL 20A 5%	2.3	97.70

For MMT and OMMT membranes, the result was satisfactory in relation to Environmental Legislation. However, they presented higher concentrations of permeated oil, probably due to the fact that these clays have a greater affinity with the oil. It could be verified in the contact angle test and also to the larger pores visualized in SEM images. Therefore, it favors its passage with water through membranes.

As all membranes have high yields and meet the standards required by Environmental Legislation. It is estimated that they all have great potential for application in treatment of oily emulsions.

4. Conclusions

The introduction of clays into the production of PES membranes provided considerable improvements in separation properties. The clay dispersion in membranes was efficient obtaining exfoliated and/or partially exfoliated structures. Besides, its introduction provided an increase of its hydrophilic character. Our results indicate that the higher the clay quantity, the lower its contact angle with water. The addition of Cloisite clay modified the structure of the pores, favoring a greater flow permeated with distilled water and the separation of water/oil emulsion. There was also a high yield index of water/oil separation for all membranes (all above 84%). The best results were those presented with CL Na and 20A membranes in both proportions of 3 and 5 wt%, where they presented a high yield and a good flow. All membranes are in compliance with Brazilian Environmental Legislation. Based on the obtained results, it was concluded that all membranes presented a great potential for the application in the treatment of oily emulsions.

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References

[1] K. Lee, J. Neff, Produced Water: Environmental Risks and Advances in Mitigation Technologies, Springer, New York, 2011.

[2] A. Motta, C. Borges, K. Esquerre, A. Kiperstok, Oil Produced Water treatment for oil removal by an integration of coalescer bed and microfiltration membrane processes, J. Membr. Sci., 469 (2014) 371–378.
[3] B. Chakrabarty, A.K. Ghoshal, M.K. Purkait, Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane, J. Membr. Sci., 325 (2008) 427–437.
[4] R.W. Baker, Membrane Technology and Applications, 2nd Ed., ISBN: 0-470-85445-6 (Eletrônico), John Wiley & Sons Inc., California, USA, 2004.
[5] J.C. Mierzwa, C.D. Vecitis, J. Carvalho, V. Arieta, M. Verlage, Anion dopant effects on the structure and performance of polyethersulfone membranes, J. Membr. Sci., 421–422 (2012) 91–102.
[6] M.V. Brami, Y. Oren, C. Linder, R. Bernstein, Nanofiltration properties of asymmetric membranes prepared by phase inversion of sulfonated nitro-polyphenylsulfone, Polymer, 111 (2017) 137–147.
[7] L.T. Duarte, C.C. Pereira, A.C. Habert, C.P. Borges, Polyurethane/polyethersulphone composite hollow fibers produced by simultaneous spinning of two polymer solutions, J. Membr. Sci., 311 (2008) 12–22.
[8] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, M. Adeli, M.Y. Hashemi, M.R. Moradian, Fabrication new PES-based mixed matrix nanocomposite membranes using polycaprolactone modified carbon nanotubes as the additive: Property changes and morphological studies, Desalination, 277 (2011) 171–177.
[9] J.J. Burgos-Mármol, A. Patti, Unveiling the impact of nanoparticle size dispersity on the behavior of polymer nanocomposites, Polymer, 113 (2017) 92–104.
[10] J.W. Cho, D.R. Paul, Nylon 6 nanocomposites by melt compounding, Polymer, 42 (2001) 1083–1094.
[11] E.M. Araújo, R. Barbosa, A.W.B. Rodrigues, T.J.A. Melo, E.N. Ito, Processing and characterization of polyethylene/Brazilian clay nanocomposites, Mater. Sci. Eng., A, 445–446 (2007) 141–147.
[12] C.Y. Liang, P. Uchytil, R. Petrychkovych, L.Y.C. AI, K. Friess, M. Sipek, M.M. Reddy, S.Y. Suen, A comparison on gas separation between PES (polyethersulfone)/MMT(Na-montmorillonite) and PES/TiO2 mixed matrix membranes, Sep. Purif. Technol., 92 (2012) 57–63.
[13] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li, The influence of nano-sized TiO2 fillers on the morphologies and properties of PSF UF membranes, J. Membr. Sci., 288 (2007) 231–238.
[14] T. Uragami, H. Matsugi, T. Miyata, Pervaporation characteristics of organic-inorganic hybrid membranes composed of poly(vinyl alcohol-co-acrylic acid) and tetraethoxysilane for water/ethanol separation, Macromolecules, 38 (2005) 8440–8446.
[15] R.K. Nagarale, V.K. Shahi, R. Rangarajan, Preparation of polyvinyl alcohol-silica hybrid heterogeneous anion-exchange membranes by sol-gel method and their characterization, J. Membr. Sci., 248 (2005) 37–44.
[16] Y. Ya-nan, W. Jun, Z. Qing-Zhu, C. Xue-Si, Z. Hui-Xuan, The research of rheology and thermodynamics of organic-inorganic hybrid membrane during the membrane formation, J. Membr. Sci., 311 (2008) 200–207.
[17] P.G. Ingole, W. Choi, K.H. Kim, H.D. Jo, W.K. Choi, J.S. Park, H.K. Lee, Preparation, characterization and performance evaluations of thin film composite hollow fiber membrane for energy generation, Desalination, 345 (2014) 136–145.
[18] P.G. Ingole, W. Choi, K.H. Kim, C.H. Park, W.K. Choi, H.K. Lee, Synthesis, characterization and surface modification of PES hollow fiber membrane support with polydopamine and thin film composite for energy generation, Chem. Eng. J., 243 (2014) 137–146.
[19] Z. Liu, Z. Mi, S. Jin, C. Wang, D. Wang, X. Zhao, H. Zhou, C. Chen, The influence of sulfonated hyperbranched polyethersulfone-modified halloysite nanotubes on the compatibility and water separation performance of polyethersulfone hybrid ultrafiltration membranes, J. Membr. Sci., 557 (2018) 13–23.
[20] L.B. de Paiva, A.R. Morales, F.R. Valenzuela Díaz, Organoclays: Properties, preparation and applications, Appl. Clay Sci., 42 (2008) 8–24.
[21] A.M.D. Leite, R.A. Paz, V.N. Medeiros, E.M. Araújo, H.L. LIRA, T.J.A. Melo, The use of montmorillonite clay to prepare nanocomposites and polymeric membrane, In: Justin P. Humphrey and Daniel E. Boyd. (Org.), Clay: Types, Properties and Uses, Nova York: Nova Publishres, 2011, pp. 391–406.
[22] V.N. Medeiros, T.C. Carvalho, A.M.D. Leite, E.M. Araujo, H.L. Lira, Evaluation of the effect of clay in polyethersulfone membranes, Desal. Water Treat, 56 (2015) 3554–3560.
[23] I. Cirne, J. Boaventura, Y. Guedes, E. Lucas, Methods for determination of oil and grease contents in wastewater from the petroleum industry, Chem. Chem. Technol., 10 (2016) 437–444.
[24] L.V. Amorim, C.M. Gomes, H. de L. Lira, K.B. França, H.C. Ferreira, Bentonites from Boa Vista, Brazil: physical, mineralogical and rheological properties, Mater. Res., 7 (2004) 583–593.
[25] A.P.M. Araújo, P. Agrawal, S.N. Cavalcanti, A.M. Alves, G.F. Brito, T.J.A. Mélo, Bionanocomposite obtained from poly(lactic acid)/biopolyethylene blend and clay, Macromol. Symp., 343 (2014) 59–64.
[26] S.N. Cavalcanti, A.M. Alves, P. Agrawal, M.P. da Silva, A.P.M. Araujo, E.M. Araujo, T.J.A. Melo, Effect of the content of organophilic clays and impact modifier on the mechanical properties of poly(lactic acid) PLA biocomposites, Macromol. Symp., 367 (2016) 76–81.
[27] R. Barbosa, T.S. Alves, E.M. Araújo, T.J.A. Melo, G. Camino, A. Fina, E.N. Ito, Flammability and morphology of HDPE/clay nanocomposites, J. Therm. Anal. Calorim., 115 (2014) 627–634.
[28] M. Giulio, R. Silvia, L. Nahal, P. Aldo, T.D. Nadka, P.L.M. Francesco, Intercalation effects in LDPE/o-montmorillonites nanocomposites, Eur. Polym. J., 43 (2007) 328–335.
[29] S. Hotta, R.P. Donald, Nanocomposites formed from linear low density polyethylene and organoclays, Polymer., 45 (2004) 7639–7654.
[30] T. Li, L.S. Turng, S. Gong, K. Erlacher, Polylactide, nanoclay, and core-shell rubber composites, Polym. Eng. Sci., 46 (2006) 1419–1427.
[31] K. Stoeffler, P.G. Lafleur, J. Denault, Thermal decomposition of various alkyl onium organoclays: effect on polyethylene terephtalate nanocomposites properties, Polym. Degrad. Stab., 93 (2008) 1332–1350.
[32] D.W. Litchfield, D.G. Baird, P.B. Rim, C. Chen, Improved mechanical properties of poly(ethylene terephthalate) nanocomposites fibers, Polym. Eng. Sci., 50 (2010) 2205–2215.
[33] Y. Wang, B. Zhang, J. Ye, Microstructures and toughening mechanisms of organoclay/polyethersulphone/epoxy hybrid nanocomposites, Mater. Sci. Eng., A, 528 (2011) 7999–8005.
[34] N. Ghaemi, S.S. Madaeni, A. Alizadeh, H. Rajabi, P. Daraei, Preparation, characterization and performance of polyethersulfone/organically modified montmorillonite nanocomposite membranes in removal of pesticides, J. Membr. Sci., 382 (2011) 135–147.
[35] A. Salahi, T. Mohammadi, R.M. Behbahani, M. Hemmati, Asymmetric polyethersulfone ultrafiltration membranes for oily wastewater treatment: Synthesis, characterization, ANFIS modeling, and performance, J. Environ. Chem. Eng., 3 (2015) 170–178.
[36] S. Zhzao, W. Yan, M. Shi, Z. Wang, J. Wang, S. Wang, Improving permeability and antifouling performance of polyethersulfone ultrafiltration membrane by incorporation of ZnO-DMF dispersion containing nano-ZnO and polyvinylpyrrolidone, J. Membr. Sci., 478 (2015) 105–116.
[37] G.R. Guillen, Y. Pan, M. Li, E.M.V. Hoek, Preparation and characterization of membranes formed by nonsolvent induced phase separation: a review, Ind. Eng. Chem. Res., 50 (2011) 3798–3817.
[38] H. Strathmann, K. Kock, P. Amar, R.W. Baker, Formation mechanism of asymmetric membranes, Desalination, 16 (1975) 179.

[39] R.M. Boom, I.M. Wienk, T. Vandenboomgaard, C.A. Smolders, Microstructures in phase inversion membranes. 2. The role of a polymeric additive, J. Membr. Sci., 73 (1992) 277.

[40] C.A. Smolders, A.J. Reuvers, R.M. Boom, I.M. Wienk, Microstructures in phase-inversion membranes. 1. Formation of macrovoids, J. Membr. Sci., 73 (1992) 259.

[41] D. Kim, H. Vovusha, U. Schwingenschlögl, S.P. Nunes, Polyethersulfone flat sheet and hollow fiber membranes from solutions in ionic liquids, J. Membr. Sci., 539 (2017) 161–171.

[42] M. Liu, Y.M. Wei, Z.L. Xu, R.Q. Guo, L.B. Zhao, Preparation and characterization of polyethersulfone microporous membrane via thermally induced phase separation with low critical solution temperature system, J. Membr. Sci., 437 (2013) 169–178.