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SPC/PVDF membranes for emulsified oily wastewater treatment

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1. Introduction

Membrane processes constitute an efficient technology that is applied to achieve water recovery from emulsified oily effluents. Fouling is a phenomenon that limits the economy of the said process as it manifests as a diminution in permeate flux as operating time increases. In a cross-flow system, this phenomenon can be diminished by both augmenting tangential filtration velocity and diminishing transmembrane pressure. Another way to minimize fouling is by obtaining membranes that are capable of lowering the solutes' tendency to deposit on the membrane surface [1]. To achieve this goal, membrane material can be modified or functionalized by: (1) synthesis of new polymers with defined characteristics [2]; (2) functionalization of polymeric membranes; (3) preparation of homogeneous or heterogeneous blends starting from different polymeric materials or particles from organic or inorganic origin [3].

Kim and Paul [4] have exhaustively studied the blend of PC with polystyrene (PS), polymethylmetacrylate (PMMA), bisphenol A PC (BPA-PC), and tetramethylbisphenol A PC (TMPC). Results indicated that polar groups in PC achieved enhanced miscibility in blends containing PMMA, and methyl groups in PC did the same with PS. Moussaif and Jerome [5–7] studied a PVDF/PC blend using PMMA as compatibilizer and demonstrated that 40% of PMMA generates an increase in miscibility and a beneficial effect on the mechanical properties of the resulting membrane. Lee et al. [8] have analyzed composite membranes of polyaniline/sulfonated poly-

ABSTRACT

New membranes based on sulfonated polycarbonate (SPC) and polyvinylidene fluoride (PVDF) were prepared. SPC was obtained by treating polycarbonate (PC) with acetyl sulfate. The ion exchange capacity (IEC) of the sulfonated polymer was 0.6753 meq/g. Scanning electron microscopy revealed that the SPC/PVDF membranes constituted heterogeneous blends. Porosimetric measurements by liquid-liquid displacement indicated that there is no substantial change in pore-size distribution due to growing SPC content. Membrane performance was assessed using an oil-water emulsion. Results indicated that the membranes present lower fouling as SPC content increases. When using the resistances-in-series model to quantify fouling, membranes containing 20% of SPC did not present irreversible fouling.

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carbonate (SPC). In these membranes, ion exchange capacity is increased by a rise in SPC content, thus allowing increased electric conductivity but simultaneously lowering mechanical stability.

Bowen et al. [9] have obtained membranes using blends of polyetherimide (PEI) and sulfonated polyether–ether–ketone (SPEEK). They found that hydraulic permeability (L_h) increases from 24×10^{-11} to 36×10^{-11} m³ s⁻¹ N⁻¹, and that the PEG rejection coefficient increases from 60 to 93.1% indicating that the addition of SPEEK contributes to high surface porosity but low pore size. In a different report, the same research group [10] informed a blend of PSf and SPEEK that achieved high permeability membranes capable of rejection retentions of almost 100% against 4 kDa dextrans.

Ochoa et al. [3] carried out the preparation of a blend of PVDF and PMMA, dissolved in *N*,*N*-dimethylacetamide. The good blending of both polymers is due to the presence of basic oxygens in PMMA and acidic hydrogens in PVDF, thus enabling H-bond interactions. Results indicated that an increase in membrane hydrophilicity was obtained by increasing PMMA, thus lowering the contact angle. Results indicated that membranes containing higher PMMA levels achieved lower fouling and enhanced permeate quality with lower COD as compared to a PVDF membrane.

Blanco et al. [11] obtained nanofiltration membranes by sulfonation of polysulfone (PSf), polyethersulfone (PES) and PES-CardoTM at different coagulation conditions. This sulfonation promoted high levels of macrovoid vitrification, as observed in SEM photomicrographs. The sulfonated-polymers/PSf blend generated membranes presenting irregular macropores and a finger-like structure.

Wang et al. [12] have obtained ultrafiltration membranes from a blend of a block copolymer of pluronic-b-polyethylenglycol (P123-b-PEG) and polyethersulfone. The results of ultrafiltration experiments revealed that the reversible fouling resistance



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composed the dominated part of total fouling resistance, which endowed the blend membranes containing P123-b-PEG copolymers with higher flux recovery ratio. In order to prepare ultrafiltration membranes, Malaisamy et al. [13] have studied the blend of polyurethane (PU) and sulfonated polysulfone (SPSf) at different compositions. Thus, they obtained mean pore sizes that varied from 30 to 100 Å when increasing SPSf.

Lang et al. [14] have prepared polyvinylidene fluoride (PVDF)-perfluorosulfonic acid (PFSA) blend hollow fiber ultrafiltration (UF) membranes. The anti-fouling property of the PVDF-PFSA-H blend UF membrane was superior to that of the PVDF-PFSA-Na blend membrane. Mahendran et al. [15] have studied the effect of annealing on cellulose acetate/sulfonated polysulfone and cellulose acetate/epoxy resin blend UF membranes. Annealing in membranes reduces the flux of pure water, and the presence of SPSf considerably reduces membrane fouling when using BSA. Arthanareeswaran et al. [16] have studied cellulose acetate/sulfonated polyethersulfone (SPES) blend UF membranes. This group achieved membranes presenting a 29-69 kDa molecular weight cut-off and an increase in hydraulic permeability accordingly to SPES content. SEM images show an increase in pore size according to the increase in SPES content. The same authors [17] performed Cr (VI) removal at pH 6 and at different concentrations of polyvinylalcohol as macroligand; the percentage rejection improved at a macroligand concentration of 2 wt.%.

Sajitha et al. [18] obtained cellulose acetate/carboxilated polysulfone (PSf-COOH) blend UF membranes achieving an increase in hydraulic permeability when rising PSf-COOH content. Wang et al. [19] performed a blend of an acrylonitrile copolymer containing ionic groups and phenolftalein-PES. These membranes showed low BSA adsorption at high pH values. In another report [20], the same authors analyzed the same membrane using SEM, water flux and polyethylenglycol rejection. These membranes showed images of rough surfaces, reduction of water flux 230–40 L m⁻² h⁻¹ (as measured at 100 kPa), and rejection of PEG20000 and PEG35000 was increased from 12.9 to 73.89% and from 55.28 to 91.00%, respectively.

Shen et al. [21] have obtained sulfonated polyetherimide (SPEI)/polyetherimide (PEI) blend hollow fiber UF membranes. These SPEI–PEI membranes showed anti-fouling properties regarding BSA flux at pH 8, achieving 32% reduction as compared to 75% in PEI.

In summary, the blend of two different polymers confers important characteristics – such as structure alteration and anti-fouling properties – to ultrafiltration membranes. Our interest is to generate membranes that – in addition to separating an emulsion by size exclusion – show low flux declinations – low fouling – due to electric exclusion by means of having surface and pore charge of the same sign as the emulsion charge.

In order to reach this goal, we have prepared SPC/PVDF membranes that have not been reported up to date. These were characterized by FT-IR, SEM and by the liquid–liquid displacement technique in order to reveal structure. The material's electrical charge was expressed by determining its ion exchange capacity (IEC). Finally, the membranes were assessed through fouling tests using an oily emulsion, observing permeate quality, and applying the resistance-in-series model.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) high viscosity was provided by Solef[®] 1015 supplied by Solvay Belgium, Polyvinylpyrrolidone (PVP) K30 from Fluka, polycarbonate (Lexan, General Electric). Isobuthanol, methanol, methylene chloride, *N*,*N*-dimethylacetamide (DMAc), NaOH, HCl were provided by Merck. Commercial emulsify oil (Insignia[®] oil) was purchased from JyM S.A. Lubricantes (Argentina). Viledon 2431 non-woven support was kindly provided by Carl Freudenberg, Germany.

2.2. Polycarbonate sulfonation

The used sulfonation technique was similar to that informed by Smitha et al. [22] and Elabd and Napadensky [23]. Ten (10) grams of PC were dissolved in 100 mL of methylene chloride. After polymer dissolution, the reactive mix (7.5 mL of acetic anhydride and 7 mL of concentrated H_2SO_4 in 40 mL of methylene chloride) was added and set to reflux at 50 °C during 1 h. Following, the sulfonated polymer was precipitated in methanol, filtered and dried at 60 °C during 24 h.

2.3. Preparation of blend charged membranes

The general preparation procedure is as follows: PVDF and PVP are dissolved in DMAc at 50 °C in a concentration of the 15 and 5 wt.% respectively until a clear solution is obtained, then the SPC is added to the solution. The mixture was stirred during 5 h at the same temperature. At this time, a heterogeneous dispersion was observed. The final mixture was cast onto the non-woven support using a film extensor. The solution is then coagulated with bidistilled water at 25 °C. Afterwards membranes are stored in a water bath until being used. Table 1 shows the different SPC/PVDF ratio used in each membrane.

2.4. Microscopy

Scanning electron microscopy images were obtained using an EVO40 Carl Zeiss microscope (Cambridge, London). Membrane samples were freeze-fractured and then coated by sputtering a thin gold layer. They were observed under high vacuum.

2.5. FT-IR spectra

FT-IR analyses of Polymer and sulfonated PC were carried out by Nicolet PROTEGE 460 Spectrometer to characterize the films. FT-IR spectra were measured in the wavenumber range 400–4000 cm⁻¹.

2.6. Pore-size measurement by liquid-liquid displacement

Three liquids (mixture of isobutanol/methanol/water; 15/7/25, v/v/v) (surface tension, $\gamma = 0.35$ mN/m) are used to analyze pores applying relatively low pressures [24]. The procedure consists on filling the membrane with a liquid (the wetting liquid, aqueous phase) and then displacing it from the pores with the organic phase (isobutanol saturated with water and methanol). Flux through the membrane is obtained by using a syringe pump (ISCO 500D) to gradually increment the flux on the organic-phase side. Simultaneously, equilibrium pressure is measured in each incremental stage using a pressure transducer (OMEGA DP200).

Table 1Weight percent relation SPC/PVDF.

Membrane	%PVDF	%SPC
PVDF	100	-
5SPC	95	5
10SPC	90	10
20SPC	80	20

When the applied pressure and flux through the membrane are monitored, then the radii of the pores opened at each applied pressure can be calculated using Cantor's equation, which is valid when it can be assumed that the used liquid effectively wets the membrane (i.e. with a null contact angle).

$$r_p = \frac{2\gamma}{\Delta p} \tag{1}$$

where Δp = applied pressure, γ = interfacial tension and r_p = pore equivalent radium. Assuming that pores are cylindrical, the Hagen–Poiseuille relationship can be used to correlate volumetric flux density J_{vi} to a given pore radium r_p . In each stage of incremental volumetric flux density, the corresponding pressure (Δp_i) is measured and, therefore, distribution Q_i can be written as:

$$Q_i = \frac{dJ_{vi}}{d\,\Delta p_i} = \sum_{k=1}^{i} \frac{n_k \pi r_k^4 \,\Delta p_i}{8\eta l} \tag{2}$$

In order to obtain the distribution of pore numbers in function of pore radium, the equation can be written as follows:

$$\frac{dn_i}{dr_{pi}} = -\frac{\eta\tau l\,\Delta p_i^6}{16\pi\gamma^6}\frac{d^2 J_{\nu i}}{d\,\Delta p_i^2}\tag{3}$$

where η = dynamic viscosity, τ = tortuosity, and l = pore longitude which corresponds to membrane thickness.

2.7. Ion exchange capacity

The ion exchange capacity (IEC) – with units meq/g of dry polymer – of the sulfonated membranes was measured using the standard experimental method that consists in the following: the membrane is immersed in 1N HCl for 24 h, followed by soaking in distilled water to remove excess acid; subsequently, the membrane samples are soaked for 1 day in 2 M NaCl solution (exchange of H⁺ by Na⁺ within the film) and then the solution is titrated with 0.01N NaOH to determine the concentration of the exchanged protons [25].

Data on ion exchange capacity offer information regarding ionizable groups available on the membrane. The IEC expression is as follows:

$$IEC(meq/g) = \frac{(VN)_{memb} - (VN)_{blank}}{m}$$
(4)

where *V* and *N* are the volume and normality of the NaOH spent on the membrane and blank; and m is the mass of the membrane sample.

2.8. Filtration experiments

All experiments of filtration were carried out in a Minitan-S ultrafiltration device from Millipore Corp. The experimental protocol was as follows: first, the membrane was compacted at 100 kPa pressure of transmembrane during 30 min [26]. Then, different pressures from 100 to 20 kPa were applied measuring the corresponding pure-water fluxes.

Once measurements were carried out, the membrane was mechanical cleaned with pure water for 1 h at 67 kPa with a feed flow of 1 L/min. After that, no fouling was observed. Then, fouling test experiments with oil emulsion were performed for 2 h at the same pressure and feed flow. After that, the membrane was cleaned with pure water at high feed rate. Finally, pure-water flow was measured under the same emulsion conditions. Emulsion was obtained adding Insignia[®] oil to distillated water at 8.333 Hz (500 rpm). The emulsion with 0.1 wt.% of oil concentration has the following characteristics [1]: pH 7, average oil droplet diameter of 2.5 µm and COD 1700 ppm.

2.9. Oil content

Oil content was evaluated by UV–vis spectroscopy based on wavelength of 220 nm.

2.10. Chemical oxygen demand (COD)

Samples were refluxed in strongly acid solution with a predetermined excess of potassium dichromate. Consumed oxygen was measured against standards at 600 nm by U-2001 UV–Visible Hitachi spectrophotometer according to the 5220D Standard Method for the Examination of Water and Wastewater.

3. Results and discussion

Qualitatively, PC sulfonation was verified by IR spectroscopy. Fig. 1 shows the results of FT-IR spectra for PC and SPC. The detection of a broad peak at approximately 3400 cm^{-1} has been ascribed to stretching modes of hydroxyl groups of $-SO_3H$ groups and water molecules retained by the sample. The typical peaks of SO_3H are absorption at 1250-1150 and $1060-1030 \text{ cm}^{-1}$ [27]. The strong band of the frequency, $1250-1150 \text{ cm}^{-1}$, can be ascribed to stretch vibration for S=O, and the absorption band at the $1060-1030 \text{ cm}^{-1}$ is assigned to the symmetric stretching band. However, the stretching band of C=O is $1765-1720 \text{ cm}^{-1}$ in the ester group for PC, while



Fig. 1. FT-IR spectrums of polycarbonate and sulfonated polycarbonate.

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(a) -PVDF. Magnification 658 X

(b)- 5SPC. Magnification 658 X



Fig. 2. Membrane SEM microphotographs.

the C–O–C for asymmetric stretching band is $1290-1180 \text{ cm}^{-1}$, and the O–C–O peak is $645-575 \text{ cm}^{-1}$.

Micrographs (Fig. 2) show that there is a small effect of SPC on the membrane's structure: porous substructure densifies in presence of SPC (see the hydraulic permeability section for further discussion).

Images obtained by backscattered electrons allow observation of phase changes in a given material. By using this technique (see Fig. 3), small SPC spheres appear in the PVDF matrix. The polymeric blend of polycarbonate and PVDF is heterogeneous [5,6]. Therefore, sulfonation does not generate a higher compatibility between these polymers and small spheres can be observed as inserted in the PVDF structure of approximately 1 μ m in all the transversal section and surface image (Fig. 4).

Table 2 shows the ion exchange capacity determined for sulfonated polycarbonate and for SPC/PVDF membranes. Results indicate that an increase in the SPC content of the membrane increment the IEC. However, PVDF exerts a shielding effect that results



Fig. 3. Backscattered-electron SEM micrograph, of 20SPC membrane. Magnification $678\times$.



Fig. 4. Backscattered-electron SEM micrograph of 20SPC membrane surface. Magnification $600 \times$.



Fig. 5. Membrane r_p distributions.

in lower ion exchange capacities, as compared to IEC theoretical values. The IEC theoretical values are 0.0337 meq/g for 5SPC, 0.06753 meq/g for 10SPC, and 0.135 meq/g for 20SPC.

Fig. 5 shows pore-size distributions obtained from liquid–liquid displacement technique. Slight diminutions in mean pore size (r_{pDLL}) due to the presence of SPC can be explained by the increase in viscosity that SPC generates in the polymeric solution (see Table 2). The viscosity of the PVDF-casting solution is 6945×10^{-3} Pa s (6945 cP). This values increases upon a SPC content rise, reaching 7855×10^{-3} Pa s (7855 cP) at 20 wt.% SPC/PVDF. This increase in the viscosity of the casting solution leads to a diminution of pore size as is commonly pointed out in literature [1].

The hydraulic permeability test was performed by comparing hydraulic permeability after fouling and water washing (L_{hla}) in function of initial hydraulic permeability (L_{hi}). Table 3 lists data on hydraulic permeability of the blend membranes.

Data in Table 3 clearly indicate a decrease in hydraulic permeability paralleling an increase in sulfonated polycarbonate content. This phenomenon could be justified by considering that a viscosity increase in the casting polymeric solution due to the presence of SPC would provoke an increase in porous substructure densification that in turn generates a diminution of $L_{\rm hi}$. This decrease in hydraulic permeability can be recorded from 11.81×10^{-10} to 7.61×10^{-10} m Pa⁻¹ s⁻¹ and can be analyzed by

Table 2

Membrane ion exchange capacities and pore radii.

Membrane	IEC (meq/g)	r _{pDLL} (nm
SPC	0.6753	-
PVDF	0.0009	46.06
5SPC	0.0191	41.32
10SPC	0.0272	37.57
20SPC	0.0362	35.89

Table 3

Membrane hydraulic permeabilities ($m s^{-1} Pa^{-1}$).

Membrane	$L_{\rm hi} imes 10^{10}$	$L_{\rm hla} imes 10^{10}$
PVDF	11.81	4.74
5SPC	11.33	4.40
10SPC	10.60	5.03
20SPC	7.61	4.95



Fig. 6. Normalized flux (J_v/J_{vo}) vs. time.

observing macrovoid diminutions in the transversal sections of the different membranes showed in the micrographs in Fig. 1.

Fig. 6 shows the normalized flow decline of the oily effluent with prepared membranes. There is a more marked flow decline in the non-charged membrane, and therefore a higher fouling. As the SPC content in the membrane increases, this decline becomes less and less sharp, until the fouling phenomenon disappears in 20SPC membrane. In a previous work [1] can be seen that, at pH 7 emulsion particles are negatively charged. As sulfonic groups content in the membrane increase the electrostatic exclusion phenomena become an important factor in the filtration of this emulsion.

Mass permeation flux during filtration can be expressed in terms of a resistance model as

$$J_{\nu} = \frac{dV}{A\,dt} = \frac{\Delta p}{\eta(R_{\rm M} + R_{\rm F})} \tag{5}$$

where J_{ν} is the permeate flux (m³/m² s), Δp the applied pressure (Pa), $R_{\rm T}$ the total resistance of permeation (m⁻¹), and η (Pa s) is the permeate viscosity. $R_{\rm T}$ involves the intrinsic resistance of membrane, $R_{\rm M}$, and the fouling resistance, $R_{\rm F}$. The osmotic effect, the effect of polarization by concentration, and the effect of fouling are all included in $R_{\rm F}$, which is subdivided into reversible fouling ($R_{\rm RevF}$) and irreversible fouling ($R_{\rm IrrevF}$).

$$R_{\rm F} = R_{\rm RevF} + R_{\rm IrrevF} \tag{6}$$

The model's data are informed in Table 4. Charged membranes present lower fouling compared to non-charged membranes. PVDF membranes present reversible and irreversible fouling, while 5% SPC content (IEC 0.0191 meq/g) can markedly reduce irreversible fouling. When the IEC reaches a value of 0.0272 meq/g or higher (10SPC or 20SPC membranes), then fouling resistance is lowered and irreversible fouling is eliminated (Fig. 7). Only a small diminution of permeate flux occurs in these membranes. This diminution is reverted by washing with a flux of pure water thus removing particles that are weakly adhered to pores and membrane surface. Table 5 shows both the oil rejection coefficient *R* and COD data for blend membranes. *R* was calculated as a percentage according to the following expression:

$$R = \left(1 - \frac{C_{\rm P}}{C_{\rm Feed}}\right) 100\tag{7}$$

where C_{Feed} is the oil concentration in the feed, and C_{P} is the oil concentration in the permeate.

Table 4		
Membrane	resistance	data.

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Membrane	$R_{\rm M} \times 10^{-12} \ (m^{-1})$	$R_{\rm T} \times 10^{-12} \ (m^{-1})$	$R_{\rm F} \times 10^{-12} \ (m^{-1})$	$R_{\rm RevF} \times 10^{-12} \ (m^{-1})$	$R_{\rm IrrevF} \times 10^{-12} \ (m^{-1})$
PVDF	0.8470	2.3500	1.5000	0.1100	1.3900
5SPC	0.8830	1.1400	0.2530	0.2526	0.0004
10SPC	0.9430	1.1700	0.2230	0.2230	0.0000
20SPC	1.3100	1.4100	0.0985	0.0985	0.0000



Fig. 7. Fouling resistance (R_F), R_{RevF} and R_{IrrevF} vs. membrane ion exchange capacity.

Table 5

Permeate quality obtained from membranes.

Membrane	R (%)	COD (ppm)
PVDF	95.46	80.30
5SPC	96.66	69.48
10SPC	96.71	69.51
20SPC	96.63	69.69

Regarding oil content rejection, values reach 95.46% in PVDF membranes, while other membranes containing SPC present similar values ranging from 96.63 to 96.71%. COD in all membranes is below 100 ppm (water quality according to Law 5420, the Province of San Luis, Argentina).

4. Conclusions

Preparation of charged blend membranes is achieved according to the process of wet phase inversion, by adding growing amounts of SPC to PVDF casting solution. The increase in SPC content generates an increase in the ion exchange capacity of these membranes and a slight diminution in pore mean radium. Hydraulic permeability data clearly indicate that a decrease in hydraulic permeability data clearly indicate that a decrease in hydraulic permeability occurs when there is an increase in the sulfonated polycarbonate content because there is an increase in porous substructure densification, as is shown in the SEM images. These micrographs also reveal that the PVDF/SPC blend is heterogeneous. When the IEC reaches a value of 0.0272 meq/g or higher (10SPC or 20SPC membranes), then fouling resistance is lowered and irreversible fouling is eliminated. The permeate COD is lower than the value established by law, that is lower than 100 ppm; and rejection to oily content in membranes containing SPC was always higher than 96.63%.

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