

ELABORATION AND CHARACTERIZATION OF ORGANIC MEMBRANES: EFFECT OF POLYMER BLENDING ON COMPETITIVE TRANSPORT OF METAL IONS

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Polymeric membranes used for selective transport and separation of metallic ions have emerged in recent times. Their expansion depends on the method of preparation and their suitable structure and physico-chemical characteristics. In this paper, a novel category of membranes for ions separation is reported. The membranes were synthesized by the solvent evaporation method, using a mixture of polysulfone (PSL) and cellulose triacetate (CTA) or poly(methyl methacrylate) (PMMA). The synthesized membrane exhibited hydrophobicity and thermal stability at more than 120 °C, as well as a more or less porous structure. The competitive transport of Ni(II), Zn(II) and Pb(II) from aqueous solutions through the polymeric membranes was studied. Competitive transport experiments through the synthesized membranes showed that Ni(II) was selectively and efficiently transported by the three types of membranes, a transport efficiency exceeding well over 45% being achieved by using the PSL based membrane at an optimal concentration of 25 ppm.

Keywords: membrane, blend polymers, characterization, heavy metals

INTRODUCTION

Polymeric materials are increasingly related to our daily life and hydrophilic/hydrophobic polymer blend systems have gained significant attention in the last few years, particularly in applications related to environmental issues. Polymer blending is a way of producing novel materials with improved physicochemical properties, that is why it has been considered an important research field for several decades.¹ Most of the polymers are immiscible with each other.²⁻⁵ Therefore, extensive research has been carried out in the area of polymer/polymer miscibility by analyzing the specific intermolecular interactions.⁶⁻¹⁰ Further, the use of membrane technologies is limited to systems with suitable chemical and mechanical stabilities and useful lifetimes.¹¹ Thus, efforts have been devoted to the development of such membranes and, in this sense, some promising approaches have been described. Depending on the electrostatic interaction, a significant number of polymers show varied degrees of swelling and even

complete solubility in solvents. In this sense, membranes based on organophilic polymers, such as polypropylene, low density polyethylene, polyvinylidene fluoride (PVDF) are known.^{12,13} Cellulose based polymers, *i.e.* cellulose acetate,^{14,15} several copolymers, such as copolymers of polyacrylonitrile–polymethyl acrylate block polymer, acrylate, styrene, have been investigated,¹⁶ similarly to those from PVDF.¹⁷⁻¹⁹

Polymer membrane technology has become a viable and interesting alternative to conventional solvent extraction methods for selective separation of compounds, such as acids and metals from aqueous solutions, since it combines extraction and stripping operations into a single stage. In the last 30 years, several membrane separation techniques have been explored with the aim to reduce the needed energy and reactants for solvent extraction, and hence, the economic and environmental impact of the process. Among these, polymer inclusion membranes (PIM) and

supported liquid membranes (SLM) stand out due to their high transport rates, good selectivity and long-term stability. Polymeric membranes have been successfully used in the extraction of metals using solvating-type extractants, such as crown ethers, trioctylphosphine oxide (TOPO), calix[4]-crown-6, cyanex 471X, tributyl phosphate (TBP) and di-(2-ethylhexyl) phosphoric acid (D2EHPA).²⁰⁻³⁰ The superior stability of PIM membranes over other systems and the suitable permeability and selectivity for industrial applications have led the scientific community to increasing the fundamental research in PIM based technologies, considering these membranes an effective alternative to traditional approaches in some niche areas, such as separations in biotechnology, food processing, precious metal recovering, radioactive waste treatment and environmental clean-up of waters, among others.³¹ This paper reports on the synthesis of a novel class of polymeric membranes prepared by the solvent evaporation method using a mixture of two polymers: polysulfone (PSL) and cellulose triacetate (CTA), or PSL and poly(methyl methacrylate) (PMMA). The morphological, structural, thermal and mechanical properties of the membranes were determined, as well as their transport efficiency.

EXPERIMENTAL

Chemicals

Polysulfone (PSL beads Mw = 22000), poly(methyl methacrylate) (PMMA powder Mw = 15000) and tetrahydrofuran (THF) were obtained from Sigma Aldrich; cellulose triacetate (CTA pellets Mw = 72000-74000) from Fluka, Chloroform (CHCl₃) and copper sulfate (CuSO₄.5H₂O) from Carlo-Erba, zinc sulfate (Zn SO₄.7H₂) from Analytica and nickel sulfate (NiSO₄.5H₂O) from Riedel-de Haen. All reagents were used as received, without any supplementary purification. Aqueous solutions were prepared by dissolving the different reagents in 18 MΩ.cm water from a Milli-Q water purification system.

Membrane preparation

PSL, PSL+CTA and PSL+PMMA membranes were prepared by a previously described procedure.³² Specifically, 0.5 g of PSL was dissolved in 20 mL of THF, 0.75 g PSL+0.25 g PMMA were dissolved in 20 mL of THF, and 0.75 g PSL+0.25 g CTA were dissolved in 20 mL of CHCl₃. The solutions were prepared at room temperature with the help of a magnetic stirrer until complete polymer dissolution, *i.e.*, until a homogeneous and transparent solution was obtained. The solution was transferred into a glass plate and the solvent was allowed to evaporate slowly during 24 hours to obtain a polymer film. The resulting membrane was extracted by addition of water.

Analysis methodology

The metal concentrations were determined by sampling at the end of transport (6 hours) aliquots of 0.5 mL each from the feed and strip solutions, and analyzed by flame atomic absorption spectrometry (AAS, Perkin Elmer A Analyst 700). The FTIR spectra were recorded with a Jasco FT/IR-4100 and collected in the ATR mode from 4000 to 500 cm⁻¹ after 32 scans with a resolution of 4 cm⁻¹. Scanning electron microscopy (SEM) images of the PIMs were obtained using a Quanta 650 FEG (FEI) Scanning Microscope with an acceleration voltage of 10 kV. The membranes were previously coated with a thin gold layer using sputter coating (Polaron, model SC502 sputter coater). The thermo-gravimetric analyses were achieved using a TGA/SDTA 851 Mettler Toledo apparatus under a high purity nitrogen atmosphere (99.99% minimum purity) and a flow rate of 50 mL.min⁻¹. Samples of approximately 4 mg were placed in an aluminum oxide crucible and heated from 25 to 850 °C at 10 °C.min⁻¹.

Transport experiments

The cell used for transport experiments consisted of two Teflon compartments with a maximum filling volume of 100 mL, separated by the membrane (Fig. 1). The active membrane area was 9.61 cm². The feed compartment contains various concentrations of ions mixture, the other compartment contains distilled water. Each compartment was provided with a mechanical stirrer.

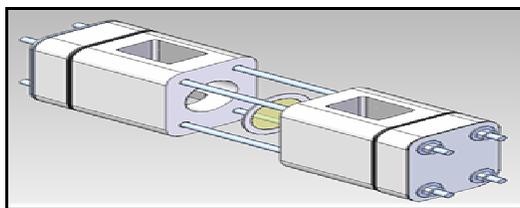


Figure 1: Scheme of transport cell

The stirring speed of 800 rpm was used, since it was previously verified that such a speed is suitable to minimize the thickness of the boundary layer.²⁹ The experiments began when starting the stirring motors in the two compartments of the cell. All experiments were performed at 25 °C.

RESULTS AND DISCUSSION

Membrane characterization

Physical characteristics of synthesized membranes

The densities, thicknesses, the water content and the contact angles (θ) of the various membranes are presented in Table 1 and Figure 2. The density was measured by weighing the same area of samples in the dry state, expressed as the mass ratio (mg)/area (cm²). The thickness was calculated using a Fischer coating thickness measuring instrument. The water content, *i.e.* the quantity of water contained in the membrane, was expressed as a ratio ranging from 0 (completely dry) to the value of the material porosity at saturation. The contact angle measurements

(sessile drop in dynamic mode) were performed at room temperature in a Data Physics OCA20 device, using ultrapure water (3 μ L droplets) as test liquid. At least 3 measurements were performed on each sample, in different sample locations and the average contact angle was calculated.

The results in Table 1 show that all the developed membranes are strongly hydrophobic. The values obtained for the thickness and density are quite comparable to those of the commercial supports used for the preparation of membranes used in dialysis and in electro dialysis.

The blend of two polymers should modify the contact angle of the membranes, as illustrated by the sequence of contact angle images in Figure 2. The membrane consisting only of polysulfone has a relatively high contact angle, which confirms the hydrophobicity of this polymer. However, the addition of PMMA and especially CTA resulted in a very pronounced decrease in contact angles.

Table 1
Chemical and physical characteristics of membranes

Membrane	Thickness (μ m)	Density (mg/cm ²)	Water content (%)
PSL	28	6.25	0.79
PSL+TAC	34	5.90	3.04
PSL+PMMA	71	14.50	0.86

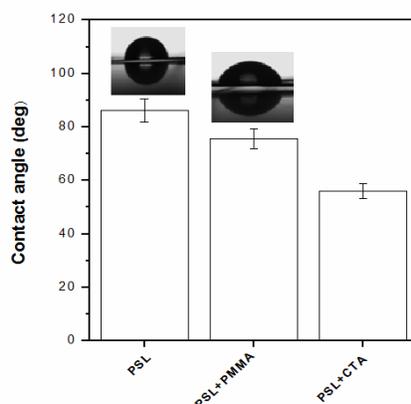


Figure 2: Water contact angle of different membranes, with the corresponding representative contact angle image for each membrane

Characterization by FTIR

In order to further evaluate the characteristics of the membranes, the FTIR spectra of PSL, PSL+CTA and PSL+PMMA membranes are shown in Figure 3. The FTIR spectrum of PSL

mainly reveals several absorption bands characteristic of the functional groups of this polymer. Table 2 lists the values of the peaks obtained from the FTIR spectra of the different membranes prepared with one or two basic

polymers, as well as their corresponding assignments. The disappearance of the bands

around 830 cm^{-1} and 554 cm^{-1} has been noted.

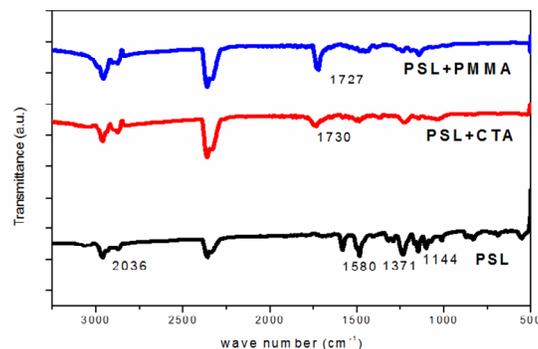


Figure 3: FTIR spectra of the different membranes

Table 2
FTIR peaks and their corresponding assignments of the PSL based membranes

Membrane	Wavenumber (cm^{-1})	Functional group
PSL	3036	C-H sym
	2855	C-H asym
	1580	C=C
	1485	-CH ₃
	1371	SO ₂
	1231	(C-O-C) asym
	1040	(C-O-C) sym
	1144	S=O
	554	C-S
PSL + CTA	The same bands as for PSL and 1730	C=O (CTA)
	Disappearance of bands around 830 and 554	
PSL + PMMA	The same bands as for PSL and 1727	C=O (PMMA)
	Disappearance of bands around 830; 554 and 1580	

Characterization by SEM

SEM micrographs provide important qualitative (dense or porous structure) and quantitative (porosity and layer thickness) information.¹³ Figure 4 presents the SEM micrograph images of the surface and cross section of the membranes. The morphology of the PSL membrane shows the presence of some pores that can reach a diameter of up to 10 microns. This partial porosity decreases sharply with the addition of the second polymer (CTA or PMMA). This decrease could be caused by possible specific interactions that develop between the two polymers.

Characterization by TGA

The thermal properties of the membranes were studied by TGA. Figure 5 shows the thermograms of PSL based membranes. Firstly, the PSL membrane decomposes in two steps, the first one at $155\text{ }^{\circ}\text{C}$, where the membrane loses only 15% of its initial mass. This mass loss corresponds to the release of the residual solvent. During the second degradation step, which is around $474\text{ }^{\circ}\text{C}$, the membrane loses 85% of its mass, and this corresponds to the degradation of the polymer chains. Meanwhile, the PSL + CTA and PSL +

PMMA blend membranes decompose in a three steps process.

For both, the first step is attributed to the release of the residual solvent, the second step

represents the thermal degradation of CTA and PMMA, respectively, and the third one is ascribed to the degradation of the PSL polymer.

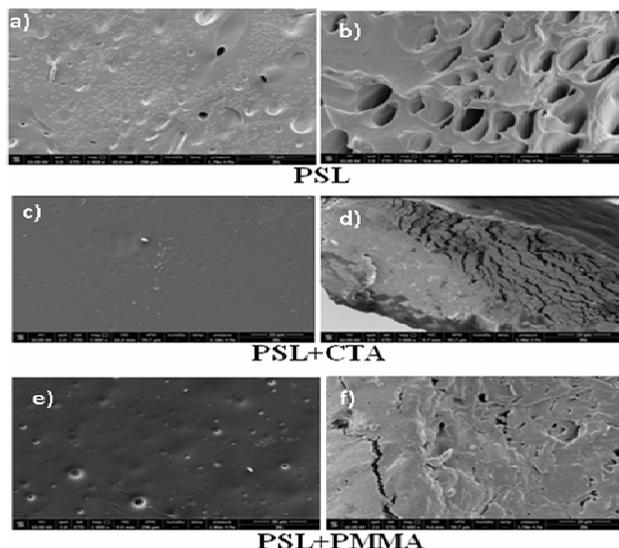


Figure 4: Surface (a, c and e) and cross section (b, d and f) SEM micrographs of the different membranes

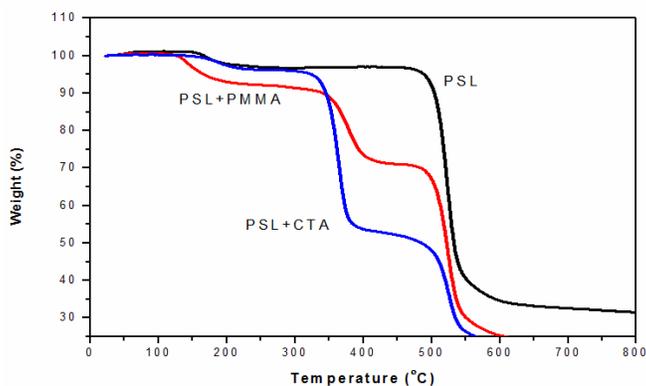


Figure 5: TGA thermograms of the processed membranes

Determination of mechanical strength of the membranes

Adequate mechanical properties are essential for the use of polymeric membranes in various filtration systems, in which good resistance to deformation is necessary. As a result, stress–strain measurements of the developed membranes were made at the Physics Center of Minho University (Portugal). The molecular weight, the degree of crystallinity and the microstructure of the polymeric films are the main factors influencing the mechanical properties. The tensile stress is

measured as a function of the elongation, the test ending at the rupture of the sample.

Figures 6 and 7 illustrate that the PSL membrane is the least elastic because it has the weakest elongation at break. On the other hand, the membrane consisting of the polymer mixture (PSL + PMMA) is the most elastic one, as it has the highest value of elongation at break. However, the membrane (PSL + TAC) is the most resistant one, as it recorded the highest tensile strength and the highest Young modulus. From these results, we can conclude that adding PMMA to

polysulfone makes the membrane more elastic, while when adding TAC to PSL, the membrane becomes more resistant.

Transport properties of the membranes

The prepared membranes were used to study the effect of the polymer mixture on the selective transport of three metal ions: Zn²⁺, Cu²⁺ and Ni²⁺. Figure 8 presents the variation of the transfer percentage of Zn²⁺, Cu²⁺ and Ni²⁺, as a function of the nature of the membrane and of the initial

concentration of the three metal ions in the feed phase, respectively. The transfer of Zn²⁺ and Cu²⁺ is very low throughout the concentration range of 25-100 ppm. On the other hand, the nickel ion is efficiently transported from the feed phase to the receiving phase, especially with the membrane consisting solely of polysulfone (PSL), where the optimum concentration of 25 ppm is the one that gave a better yield (47%), which could be explained by the presence of pores, comparing with the other two membranes.

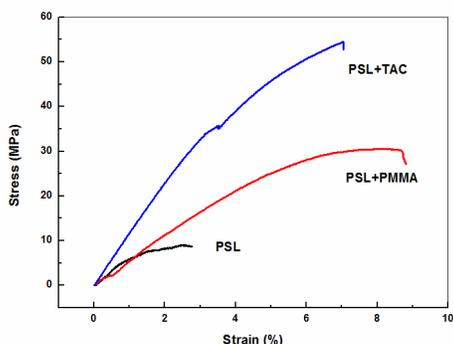


Figure 6: Stress–strain curves of PSL-based membranes

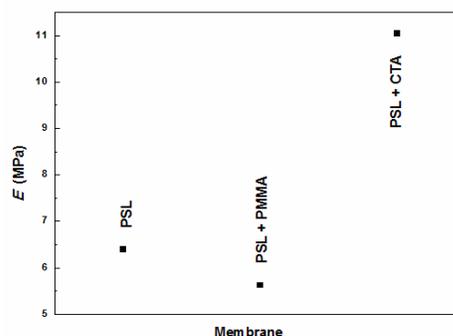


Figure 7: Young's modulus for the different PSL-based membranes

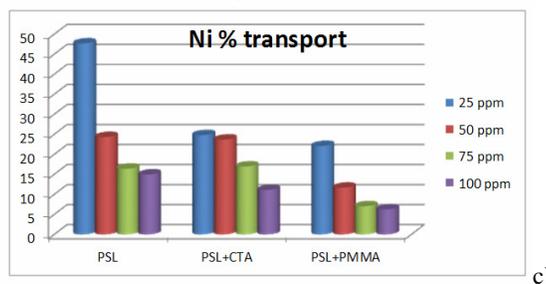
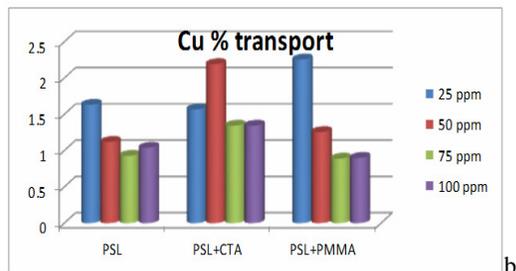
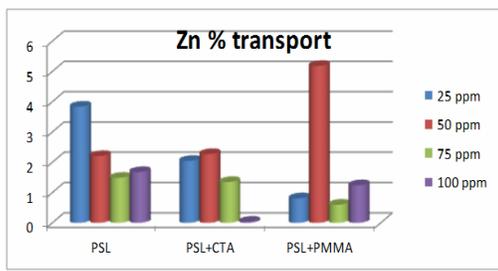


Figure 8: Transport percentages for (a) Zn²⁺, (b) Cu²⁺ and (c) Ni²⁺

CONCLUSION

PSL, PSL + CTA and PSL + PMMA membranes have been prepared by the solvent evaporation method. The functional groups of all the constituents of each membrane are present. The PSL membrane presents a homogenous porous structure, but this porosity decreases after

adding the second polymer (CTA or PMMA). All the membranes have good thermal stability. The addition of the second polymer to the PSL reduces the hydrophobicity of the membranes, which is due to the presence of hydrophilic groups within the CTA and PMMA polymers. The comparative study of the transport across the

polymeric membranes yielded very encouraging results, recommending the use of the PSL based membrane for the selective separation of Ni²⁺.

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