NANOSTRUCTURED POLYSULFONE COMPOSITE MEMBRANES

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Membrane composite de polisulfona, nanostructurate, au fost obtinute printr-o tehnica noua constand in obtinerea membranelor prin inversie de faza acompaniata de reactie chimica. Membranele obtinute au fost caracterizate prin spectroscopie FT-IR, microscopie SEM, analiza termica TGA si permeatia solventilor.

Nanostructured polysulfone composite membranes were obtained by a new technique consisting in phase inversion accompanied by chemical reaction. Obtained membranes were characterized by FT-IR spectroscopy, SEM microscopy, TGA analysis, solvent permeation.

Keywords: polysulfone membrane, phase inversion, chemical reaction

1. Introduction

Polysulfone based on bisphenol A is a thermoplastic widely used as a membrane material or membrane support for liquid separation processes such as ultrafiltration or reverse osmosis [1-3].

The constant interest of the membrane scientists for polysulfone is due to its excellent characteristics [4-6]: good solubility in a wide range of aprotic polar solvents (dimethylformamide, dimethylacetamide, dimethylsulfoxide, halogen derivatives, nitrobenzenem aniline), high thermal resistance (150-170^{o}C), good chemical resistance over the entire pH range, good resistance in oxidative medium (hypochlorite 5-7 %, hydrogen peroxide 3-5 %), high mechanical resistance of the films (fracture, flexure, torsion), moderate reactivity in aromatic electrophilic substitutions reactions (sulfonation, nitration, chloromethylation, acylation, etc.). The good solubility allows all preparation methods known for polysulfone membranes, with special emphasis on phase inversion by immersion precipitation

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[7]. The chemical resistance allows sterilization (both thermal and chemical), while biocompatibility and the moderate reactivity allows functionalisation by aromatic electrophilic substitution or other reactions [8-11].

In order to combine the advantages of polysulfone as a membrane material and the requirements for enhanced selectivity, this paper reports the results obtained for the synthesis of polysulfone-polyaniline (PSf–PANI) composite membranes using a new technique. This consists of phase inversion by immersion precipitation accompanied by chemical reaction, leading to a composite different from that obtained by electro–polymerization [12, 13].

2. Experimental

The polymer (polysulfone-PSf) was supplied by BASF (Ultrason S3010). It was further purified from a chloroformic solution by re-precipitation with methanol, and dried in vacuum at 60^{o}C. N,N'–dimethylformamide (DMF), aniline (Merck), and chloroform (Fluka) were used as solvents for polysulfone. Cyclohexanol, acetone, propanol, methanol, ethanol, ethylic ether, ethyl acetate, and octanol were used as non–solvents for membrane phase inversion. Ammonium peroxodisulfate (Fluka) and hydrochloric acid (HCl) (Merck) were used for aniline polymerization.

Preparation of polysulfone solution. The required amount of solvent (aniline) was introduced into an Erlenmeyer glass and small portions of polymer were added under magnetic stirring until the desired concentration was achieved. The air was then removed from solution into a vacuum dessicator for 30 minutes.

The membranes formation.

Method 1: 5 mL of polymer solution was deposited onto a spectral glass and the blade was fixed at a standard thickness of 250 μm. The polymer film formed was immersed into the coagulation bath (I), containing 200 mL cyclohexanol.

Method 2: A polysulfone solution was prepared by combining a DMF polymer solution, 80 %, and an aniline polymer solution, 20 %. 5 mL of this polymer solution was deposited onto a spectral glass and the blade was fixed at a standard thickness of 250 μm. The polymer film formed was immersed into the coagulation bath (II), containing 200 mL methanol aqueous solution (50 %).

PSf/aniline membrane functionalisation. The crude membranes (obtained either by method 1 or 2) were transferred from the coagulation bath into a tank (III) containing hydrochloric acid, 1 M and were stored in this solution for 30 minutes. Afterwards, the membrane was introduced into the tank (IV) containing the polymerization initiator (ammonium peroxodisulfate in HCl) for 4 hours. In order to finish the functionalisation (aniline oxidation at polyaniline), the

composite membrane was kept into a persulfate acid solution for 24 hours. The obtained membranes were stored in water : methanol mixture (1:1).

Membranes characterization. Membrane samples (4.8, 5.2, and 9.0 cm diameter disks) were characterized by Fourrier transformed infrared spectroscopy (FT-IR) using a Bruker Tensor 37 instrument, scanning electron microscopy (SEM) using a FESEM Hitachi S 4500 instrument, and thermo–gravimetric analysis using a Shimadzu DTA-TG-51H instrument. Membranes were dried in vacuum at 60^{o}C for 4 hours before characterization.

Any membrane was washed and kept in distilled water for 24 hours before running the hydrodynamic tests. Perm-porometry (Porometer®), solvent permeation, and solvent flux determination were perfomed (Sartorius installation). 500 mL of pure solvent (water, methanol, propanol, buthanol) were introduced in the tank, and then a pressure between 2 and 6 atm was applied. The permeate specific flux was then calculated by means of relation (1):

$$J_v = V_p / S_m * \tau \qquad cm^3/cm^2 \cdot min \qquad (1)$$

where J_v = flux, V_p = permeate volume, S_m=membrane surface, τ = time.

3. Results and discussion

A relatively small number of papers and researchers reported phase inversion with chemical reaction so far. The regenerated cellulose films were made by spinning cellulose xantogenate (Cell-O-CS S^-Na^+) into a coagulation bath containing sulfuric acid as main reagent and sodium sulfate, or zinc sulfate and surfactant [14, 15]. Mulder et al. [13] tried to promote reactive systems in phase inversion by immersion precipitation using poly benzimidazole / sulfuric acid, in alkaline solution; this technique didn't develop too much and it was beaten by other phase inversion methods.

One of the arguments in favour of this technique is the fact that from a polymer/solvent/non–solvent system, even if there is a chemical reaction between solvent and non–solvent, the membrane is formed from the initial polymer dissolved in solution: polysulfone, polyamide or polybenzimidazole.

A previous tentative [16] related to *in situ* polymer functionalisation by phase inversion using PSf/DMF and $POCl_3$ (Vilsmeyer-Haak reaction) yielding formylated polysulfone membrane did not have the expected impact. This is the reason why results related to polysulfone and polysulfone/polyaniline (PANI) membranes synthesis using a relatively new system, PSf/aniline [17-19], are presented in this paper.

Aniline is miscible with alcohols, halogen derivatives, ethers, esters, and this fact allows the approach of phase inversion in many ways for the polysulfone/aniline/non solvent system. As an alkaline species ($pK_a \approx 9$), aniline allows phase inversion with chemical neutralization reaction, as well as different organic reactions such as oxidation and condensation.

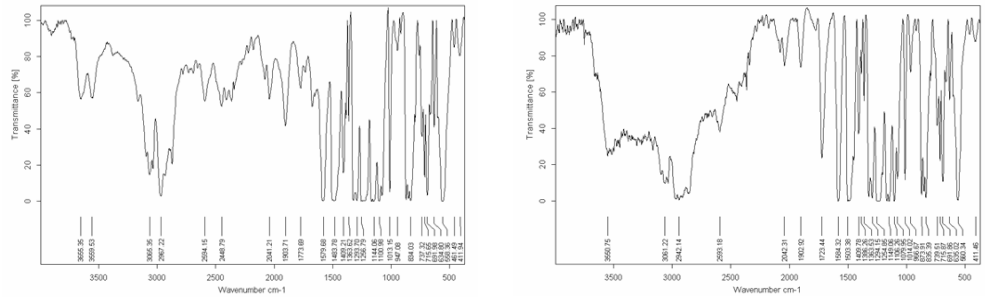
Polysulfone membranes preparation from polysulfone/solvent/non–solvent systems is well known. One should find the adequate non solvent so that starting from a known polymer concentration in solvent to be able to obtain a membrane for micro-, ultra-, nano-filtration or pervaporation [20-24].

The study has followed two steps: a) the synthesis of polysulfone membranes by classical immersion-precipitation from a polysulfone/aniline/non–solvent system and from a polysulfone/aniline–DMF/non–solvent system, b) the synthesis of polysulfone-polyaniline composite membranes from polysulfone/aniline/non–solvent (oxidant) system and a polysulfone/aniline–DMF/non–solvent (oxidant) system by phase inversion with chemical reaction. The characterization and testing of the membranes for an adequate membrane process are additional goals of the study.

For the polysulfone/aniline-dimethylformamide/non–solvent system only three coagulants were tested: iso-propanol in water (50 %), ethanol in water (50 %) and methanol in water (50 %). The membranes obtained from polysulfone/aniline-dimethylformamide/propanol system and polysulfone/aniline-dimethylformamide/ethanol system have small pores diameter and are not suitable for the polymerization of aniline to polyaniline. The best results were obtained for the polysulfone/aniline-dimethylformamide/methanol system.

A study related to membrane formation through phase inversion was performed. Additionally, polysulfone solutions in aniline at three concentrations (7 %, 11 % and 15 %) were used. For polysulfone/aniline/non solvent system several coagulants were tried (cyclohexanol, acetone, propanol, ethylether, ethylacetate and octanol, and some mixtures of these solvents). A small number of obtained membranes may be used in a membrane process, most of them presenting surface damages and non-homogeneity. This may be explained only by formation of solvent-non–solvent synergic mixtures which interact with polymer and cause resolubilization, swelling, and local agglomeration of the polymer film. The best results were obtained for polysulfone/aniline/cyclohexanol system.

The obtained membranes were characterised by FT-IR (Fig. 1).



a b

Fig. 1 FT-IR spectra of obtained membranes: a – PSf in aniline, b – PSf-PANI from PSf/aniline/cyclohexanol system

There are obvious differences between polysulfone membranes synthesised from aniline and polysulfone-polyaniline composite membranes. The specific band for amino group (2967 cm^{-1}) is shifted and specific vibrations for new iminic groups appear at 3601 cm^{-1}. The entire spectrum area between 2500–3500 cm^{-1} indicates the formation of polyaniline inside the polysulfone membrane. At the same time, the characteristic polysulfone bands are not modified in the 400-1600 cm^{-1} range.

Before using a membrane type for a specific membrane process, this should be characterized by SEM, perm-porometry and solvents permeation (water, methanol, ethanol, *i*-propanol, buthanol). The data from perm-porometry were correlated with the results obtained from the gravimetric method.

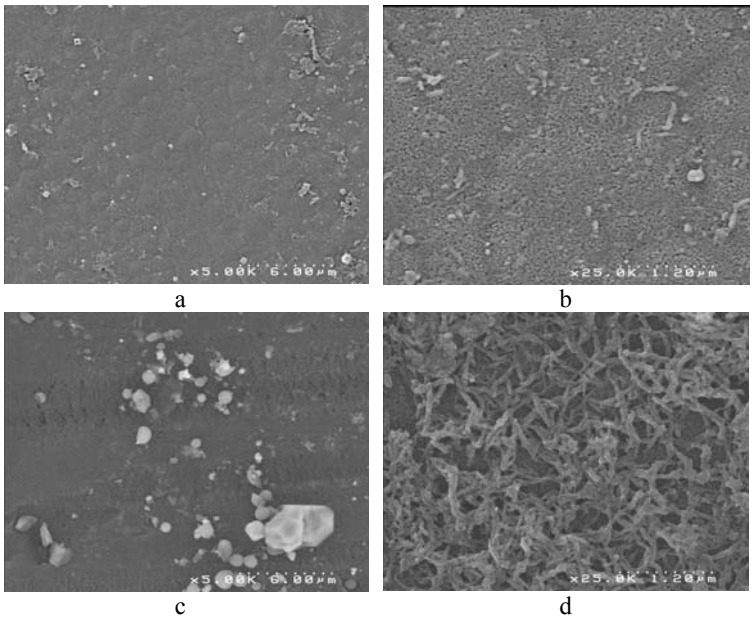
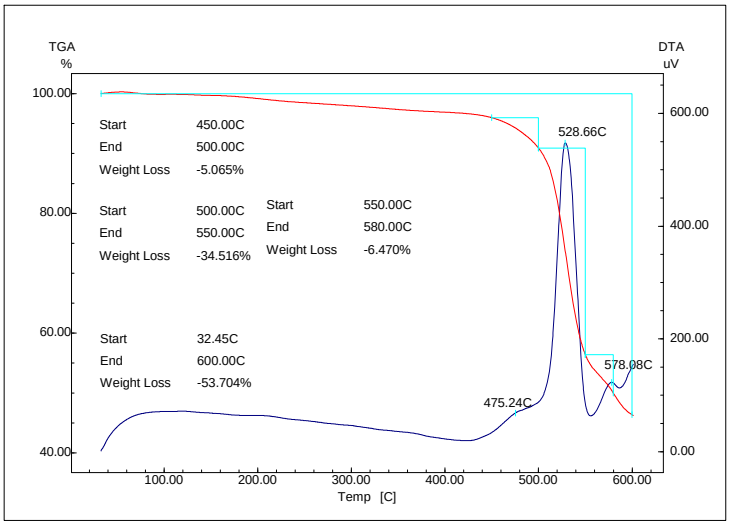


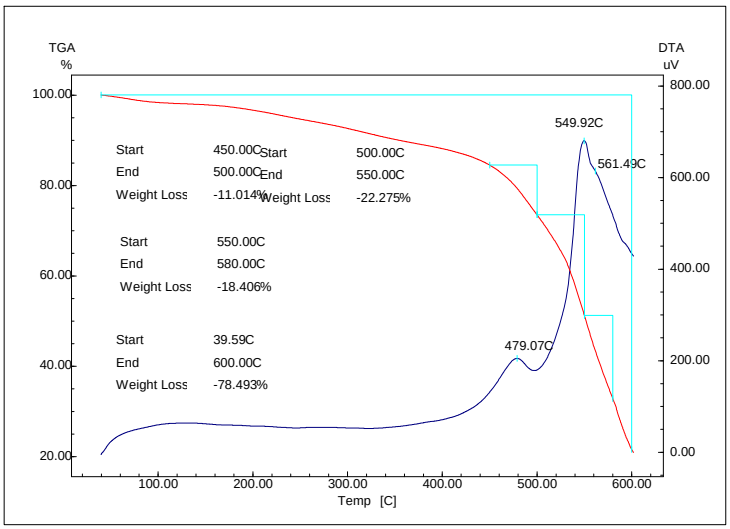
Fig. 2 Scanning electron microscopy of obtained membranes: 1 – PSf-PANI from PSf/aniline/cyclhexanone system and 2 – PSf-PANI from PSf/aniline-DMF/methanol at a – X5000 and b – X25000

The SEM images of the obtained membranes (Fig. 2) give important information related to the material synthesis and characteristics. The membranes obtained from PSf/aniline/cyclohexanol system are more compact than the membranes obtained using the classical PSf/DMF/methanol system. The polyaniline obtained in polysulfone membranes from PSf/aniline-dimethylformamide/methanol system presents a homogeneous surface, with long (aprox. 1-1.5 μm, fig. 2d) and constant diameter (aprox. 100 nm) polyaniline

fibres. This is not observed for the PSf/aniline/cyclohexanol system (fig. 2b). This is explained by the constant structure and the big dimension of pores in membranes obtained from system PSf/aniline-dimethylformamide/methanol.



a



b

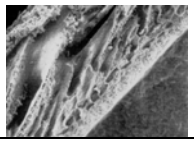
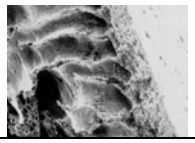
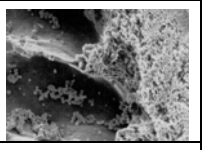
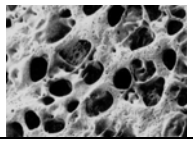
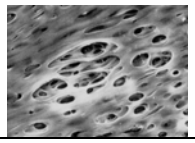
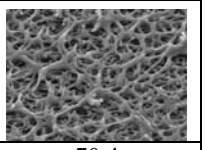
Fig. 3 TGA spectra for polysulfone membrane (a) and polysulfone-polyaniline composite membrane (b).

The formation of polysulfone-polyaniline composite membrane is also supported by thermal analysis, where a maximum loss point at 561.49°C for polyaniline is observed (Fig. 3). Further comments related to TGA results will be presented elsewhere.

Pervaporation tests were performed into a multisystem CELFA installation at room temperature and results are presented in Table 1.

Table 1

Main characteristics of membranes synthesized from polysulfone-aniline and polysulfone aniline-dimethylformamide solutions (ε-total porosity, d_p-medium pore diameter, n_p-density of pores on membrane surface, J_v-solvent flux at 4 atm, W-water, M-methanol, E-ethanol, P-propanol, B-buthanol and representative SEM images of obtained membranes-realised at X1000 magnification for cross section and X5000 for top surface)

Pseudo-Ternary System		PSf/A/CH	PSf-PANI/A/CH	PSf-PANI/A-DMF/CH
SEM cross section				
SEM top surface				
ε (%)		47.3	56.9	70.4
d_p (μm)		0.80	0.25	0.15
n_p (cm^{-1})		$1.3x10^6$	$3.0x10^7$	$8.2x10^9$
J_v (cm^3/cm^2s)	W	$0.9x10^{-3}$	$0.1x10^{-3}$	$0.2x10^{-4}$
	M	$1.0x10^{-3}$	$0.1x10^{-3}$	$0.9x10^{-4}$
	E	$1.1x10^{-3}$	$0.2x10^{-3}$	$1.1x10^{-4}$
	P	$1.3x10^{-3}$	$0.2x10^{-3}$	$1.2x10^{-4}$
	B	$1.7x10^{-3}$	$0.4x10^{-3}$	$1.6x10^{-4}$

The experimental hydrodynamic data demonstrate that if the initial polymer solution contains 7 % or 11 % PSf in aniline, the membranes are suitable for micro- and ultrafiltration, while an initial 15 % PSf in aniline leads to efficient pervaporation membranes.

4. Conclusions

PSf-aniline system leads to membrane formation through: a) phase inversion by immersion precipitation into a coagulation bath containing cyclohexanol; b) phase inversion by immersion precipitation with oxidation

chemical reaction of aniline yielding a polysulfone-polyaniline composite membranes (in situ modification). Cyclohexanol gave the best results in comparison to other oxygenated organic solvents such as inferior alcohols, esthers, ethers, ketones. The obtained membranes exhibited pore dimension suitable for micro- and ultrafiltration (if initial polymer solution is 7 % or 11 % PSf in aniline) and pervaporation (if initial polymer solution is 15 % PSf in aniline).

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