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Comparative study of selected materials for the preparation of ultrafiltration membranes: PAN-based copolymers vs. polysulfone-based polymer blends

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ABSTRACT

In membrane processes, the membrane quality is at the core of the process. In this context, taking an interest in membrane materials is important. This paper focuses on polymer materials used in the preparation of ultrafiltration membranes. Two polymers were chosen for their recognized quality as membrane materials, poly(acrylonitrile) and polysulfone. Poly(acrylonitrile) homopolymer, PAN, poly(acrylonitrile-co-hydroxyethyl methacrylate) copolymers, AH1 and AH3, poly(acrylonitrile-co-sodium styrene sulfonate) copolymers, AS1 and AS3, and poly(acrylonitrile-co-hydroxyethyl methacrylate-co-sodium styrene sulfonate) terpolymers, AH1S2, AH1.5S1.5, and AH2S1 were synthesized and materials of various compositions were obtained and used to prepare ultrafiltration membranes by classical phase-inversion method. The PAN-based membranes were used in a laboratory-scale study to ultrafilter aqueous solutions of carboxymethylcellulose, CMC. Before use, the membranes were characterized employing Fourier Transform Infrared Spectroscopy (FTIR), to verify the occurrence of copolymerization, and thermogravimetric analysis (TGA), to examine the thermal properties of the polymers. The paper gives a comparison between PAN-based co and terpolymers and polysulfone-based polymer bends formed by polysulfone (PS) and poly(sodium 4-styrene sulfonate) (PSSNa), PS-S1 and PS-S3. The membranes AH3, AS1, and AH2S1 were the most efficient with regard to the separation ability. Besides, their solvent flux regeneration after use was the best, indicating promising durability for practical usage.

KEYWORDS: ultrafiltration, polymer-based membranes, poly(acrylonitrile), polysulfone, copolymerization, polymer blends.

1. INTRODUCTION

Ultrafiltration is a pressure-driven membrane process used for the separation, by molecular sieving, of small species and macromolecules dissolved in solution. The membrane retains macromolecular species, concentrated in the concentrate or retentate, while small molecules and solvents pass freely through it and constitute the ultrafiltrate or permeate. Compared to alternative separation processes, ultrafiltration does not involve a phase change allowing it to consume much less energy. Besides, it is exclusively physical, and either permeate or retentate can be reused, allowing its classification in the range of soft processes, and explaining its numerous industrial and water treatment applications [1-7]. The quality of an ultrafiltration membrane can be quantified by its good filtration performances, good mechanical properties, and good chemical and thermal stability. However, all these qualities are useless if the membrane material isn’t resistant to irreversible fouling. The phenomenon of ultrafiltration membrane fouling could be summarized by surface

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fouling and internal fouling. Surface fouling is the deposition of macro-solute materials on the membrane. It is formed during the running process, and it consolidates over time. The formed fouling layer can be controlled by high turbulence, regular cleaning, and using hydrophilic or charged membranes to minimize adhesion to the membrane surface. These procedures could make the surface fouling reversible. Internal fouling is caused by the penetration of macro-solute materials into the membrane. The result is the plugging of the pores. Thus, internal membrane fouling is generally irreversible [3]. These phenomena in, on, and near the membrane cause flux decline and can also cause a loss in selectivity or an additional undesired selectivity. Thus, while preparing materials, the focus must be on limiting the causes of their occurrence to ensure membrane performance. That is, good operating ability, extended lifetime, and constant performance without the need for aggressive cleaning procedures. For this purpose, the first step is the judicious choice of membrane materials as reported in richly documented literature which reveals that the work began very early and is still not finished [8-20]. It is known that hydrophilic membranes are more fouling-resistant, but less robust than hydrophobic ones. For this reason, water-soluble polymers such as poly(vinyl pyrrolidone) or poly(ethylene glycol) are often added to the membrane-casting solutions of hydrophobic polymers [21-23]. However, during the membrane precipitation step, most of the water-soluble polymer is leached from the membrane, and one mainly relies on enough remains to make the membrane surface hydrophilic [18]. Thus, the choice of strong chemical and/or physical links seems more judicious to ensure that the hydrophilic species stay in the membrane materials, and this choice of membrane materials made of copolymers of hydrophobic-hydrophilic comonomers and/or polymer blends of miscible hydrophobic-hydrophilic polymers was made by numerous researchers.

This paper aims to highlight the copolymerization and the blending methods, illustrated by our experimental works, and to discuss the pertinence of choosing one or the other method to prepare ultrafiltration membrane materials. For this purpose, two polymers were chosen for their recognized quality as membrane materials, poly(acrylonitrile) and polysulfone. The paper gives a comparison between PAN-based co and terpolymers and polysulfone-based polymer bends namely, poly(acrylonitrile) homopolymer, PAN, poly (acrylonitrile-co-hydroxyethyl methacrylate) copolymers, AH1 and AH3, and poly (acrylonitrile-co-hydroxyethyl methacrylate-co-sodium styrene sulfonate) terpolymers, AH1S2, AH1.5S1.5, and AH2S1, poly(acrylonitrile-co-sodium styrene sulfonate) copolymers, AS1 and AS3, and polymer blends of polysulfone (PS) and poly(sodium 4-styrenesulfonate) (PSSNa), PS-S1 and PS-S3. Co and terpolymers were labeled according to each polymer's HEMA (2-Hydroxyethyl methacrylate) and SSNa (Sodium 4-styrene sulfonate) comonomer composition, and polysulfone-based materials were labeled according to PSSNa composition in the polymer blend.

HEMA and SSNa comonomers were chosen for the high hydrophilicity of the two species and to make it possible to observe the difference in behaviour between PAN-based materials containing hydrophilic species of neutral nature (HEMA) or charged nature (SSNa). The choice of blending PSSNa with PS was then obvious to make the comparison coherent between the PAN-based membranes and the PS-based membranes, since PSSNa is the homopolymer of the SSNa monomer. In this study, the synthesis conditions and the characterization, using FTIR and TGA, of the co and terpolymers containing HEMA comonomers are given, while those of copolymers containing SSNa comonomers and PS/PSSNa blends are given in previous papers [24, 25]. Without detailing, the results of these studies are used here as tools of comparison. Ultrafiltration membranes were prepared, with these polymer materials, by the classical phase-inversion method and were employed to treat aqueous solutions of carboxymethylcellulose, CMC. Before the application of the membranes in the ultrafiltration of CMC aqueous solutions, the thermal analyses of the co and terpolymer-based membranes and the blend-based membranes was done to compare their thermal properties.

2. DERIVATIVES OF POLY(ACRYLONITRILE) AND POLYSULFONE AS POLYMER MATERIALS FOR ULTRAFILTRATION MEMBRANES

Poly(acrylonitrile), PAN, is a widely used polymer for the preparation of ultrafiltration membranes.

Hardness, high resistance to common chemicals, and withstanding temperatures up to 200 °C place the PAN among the more robust membrane polymeric materials. Furthermore, polymers and copolymers of acrylonitrile are generally risk-free, thanks to the low amount of residual acrylonitrile monomer in finished products, approaching approximately 1 ppm in the acrylic backbone [26]. However, these advantages are counterbalanced by the hydrophobicity of PAN membranes which constitutes their main limitation because of making them sensitive to fouling that induces flux decline during membrane use, increases the cleansing frequency, and leads to high operating costs and short membrane lifespan. Numerous methods are described in the literature to improve the hydrophilicity of PAN membranes [18]. The most cited ones are related to surface modification by adsorption [27] or grafting [28, 29] of species of high hydrophilicity, blending by the addition of hydrophilic polymeric additives to PAN-based copolymers in the membrane cast solution [19, 30], and copolymerization without surface modification, nor blending [11, 12, 31, 32]. Despite their uncontestable role in enhancing the membrane hydrophilicity and the ultrafiltration process performance, the membrane surface modification and the polymer blending sometimes fall in terms of simplicity and whole pertinence. Indeed, there are many drawbacks inherent to the membrane surface modification methods such as the wastage of expensive starting materials because of parasite homopolymerizations in the case of the polymer grafting method, and the fact that the modifying polymers may not remain on the surface permanently due to the weak forces between them and the substrate, in the case of the polymer adsorption method [14]. The main issues related to the blending method are the poor compatibility that might occur between two polymers, principally in the case where a high concentration of blended polymer is used, and the leaching of the additives, especially when the hydrophilic blended polymers have small molecular weights [13, 33]. For these reasons, simple copolymerization of acrylonitrile with co-monomers of high hydrophilicity seems to be easier and safer. In the present study, heteropolymers of acrylonitrile and hydroxyethyl methacrylate and/or sodium styrene sulfonate are used as polymer-based material and the hydrophilic nature of the chosen co-monomers undoubtedly helps to improve the hydrophilicity of the PAN-based ultrafiltration membranes. Before use, the membranes were characterized using FTIR, to verify the occurrence of the copolymerization, and TGA to examine and compare the thermal properties of the polymer materials.

Polysulfone, PS, and derivatives are also widely used polymers for the preparation of ultrafiltration membranes and are recognized as robust membrane polymeric materials thanks to their hardness, high resistance to common chemicals, and excellent resistance to thermal and irradiation degradation [34]. These qualities are unfortunately counterbalanced in PS-based membranes, such as PAN-based membranes, by their important hydrophobicity making them sensitive to fouling. Thus, to improve the hydrophilicity of PS-based membranes, the most cited methods in the literature are those related to surface modification of preformed PS-based membranes and blending PS or PS-based polymers with hydrophilic polymers [35-40]. The second way was chosen for this study with the poly(sodium 4-styrene sulfonate) (PSSNa) as a hydrophilic polymer to improve the hydrophilicity of PS-based ultrafiltration membranes. Polymer blending is a versatile process, relatively simple, and cheaper than polymer synthesis. Polymer blends are mixtures of two or more polymers intimately mixed allowing the creation of new materials that combine and enhance their properties [41-46]. The principal difference between copolymerization and blending is that no covalent bonds connect the individual component polymers in the blends, and the blended materials' cohesion is ensured by physical links exclusively. If classifying them in terms of their method of preparation, it is possible to enumerate the mechanical blends, the chemical blends, the solution-cast polymer blends, and so on [47]. The solution-cast polymer blending process consists of dissolving the constituent polymers in a common solvent such that the solutions have about the same viscosity and mixing the solutions thoroughly. The PS-based blends presented in this study were prepared using a slightly modified version of this method which is described in the Materials and Methods section of this paper. The occurrence of strong physical links between the blended polymers (PS and PSSNa) was verified using FTIR analysis, and differential scanning calorimetry (DSC) was used to confirm their miscibility. TGA analysis was used to complete the thermal characterization of the polymer blends.

3. MATERIALS AND METHODS

3.1. Chemicals

Polymer, copolymer, and terpolymer synthesis: acrylonitrile (AN) (Merck; GC 99%), sodium styrene sulfonate (SSNa) (Aldrich; T ≥ 90%), 2-hydroxyethyl methacrylate (HEMA), sodium persulfate ($Na_2S_2O_8$) (Fluka; T ≥ 98%) and dimethyl sulfoxide (DMSO) (Biochem; min 99%). Polymer blends: polysulfone (PS) (Aldrich; MW: 35 000), and poly(sodium 4-styrene sulfonate) (PSSNa) (Aldrich; MW: 70 000). Solvents for membrane preparation: N-methyl pyrrolidone (NMP) (Merck; GC 99%) and DMSO. Membrane cut-off determination: Dextran (Fluka AG; MW: 15 000; 40 000; 70 000; 100 000; 500 000; 10^6). Macromolecular solute for ultrafiltration trials: carboxymethylcellulose (CMC) (Aldrich; MW: 90 000; DS = 0.7). All chemicals were used without further purification.

Figure 1 gives the structures and acronyms of the polymers employed as membrane materials and Figure 2 gives the structure of CMC which is a cellulose derivative with carboxymethyl groups ($CH_2COO^-Na^+$) substituting H of some hydroxyl groups of the glucopyranose units of the cellulose backbone. Different preparations may have different degrees of substitution (DS), generally in the range of 0.6 to 0.95 derivatives per monomer unit.

3.2. Polymerization, copolymerization, and polymer blends preparation

Poly(acrylonitrile) homopolymer, PAN, poly(acrylonitrile- co-hydroxyethyl methacrylate) copolymers, AH1 and AH3, and poly(acrylonitrile-co-hydroxyethyl methacrylate-co-sodium styrene sulfonate) terpolymers, AH1S2, AH1.5S1.5, and AH2S1 were synthesized by solution radical polymerization. The copolymers were synthesized according to the procedures mentioned in the literature [9, 10]. The reactions were performed at 65 °C in DMSO, using sodium persulfate as initiator and the polymers were precipitated in hot salted water and then washed several times using distilled water to remove salt and residual solvent. The conversion was calculated after reaching constant weight. The copolymers were labeled according to the theoretical composition of 2-hydroxyethyl methacrylate units in the polymer, 1% and 3%. The terpolymers were labeled according to the theoretical

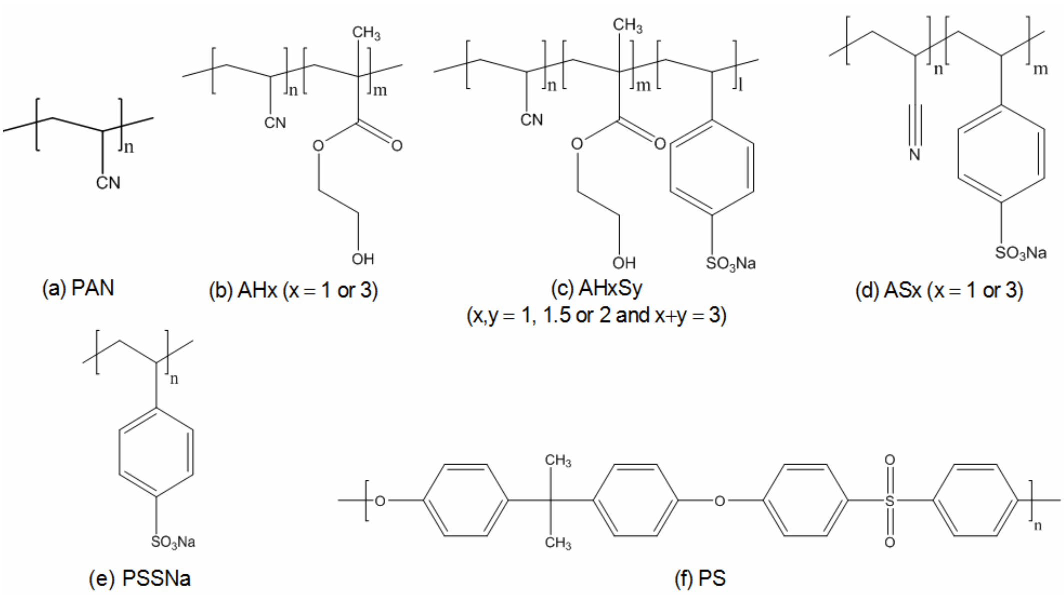

Figure 1. Structures and acronyms of (a) poly(acrylonitrile), (b), poly(acrylonitrile-co-hydroxyethyl methacrylate), (c) poly(acrylonitrile-co-hydroxyethyl methacrylate-co-sodium styrene sulfonate), (d) poly(acrylonitrile-co-sodium styrene sulfonate), (e) poly(sodium 4-styrene sulfonate), and (f) polysulfone.

composition of 2-hydroxyethyl methacrylate and sodium styrene sulfonate units in the polymer, namely 1%, 1.5%, and 2%. These compositions were calculated based on the Mayo–Lewis copolymerization equation [48, 49]. Poly(acrylonitrile-co-sodium styrene sulfonate) copolymers, AS1 and AS3 synthesis procedures were similar and given in a previous paper [24]. Table 1 summarizes the synthesis conditions.

PS-S1 and PS-S3 blends were prepared as follows: the needed amount of PSSNa was dissolved in 0.5 mL of water. As soon as the dissolution was reached, 7.5 g of NMP was added, and then 2 g of polysulfone was gently incorporated under continuous stirring until a homogenous solution was obtained. Before use as a cast solution for the membrane preparation, the mixture was left under stirring for almost 24 hours in a covered beaker to prevent it from being affected by ambient moisture.

3.3. Characterization

The characterization of all the polymers was done using FTIR and TGA. The FTIR spectra were recorded using a Jasco FT/IR-4200 under 64 scans and 2 cm^{-1} resolution conditions. The thermogravimetric analysis was done using a METTLER TOLEDO TGA 2 between 25 and 700 °C with a heating rate of 20 °C/min under a nitrogen flow of 50 mL/min. The DSC analysis of the PS-based blends was done using a Perkin Elmer Jade DSC between 25 and 350 °C with a heating rate of 20 K/min under nitrogen flow of 20 mL/min. The ultrafiltrates were analyzed using the Dubois phenol-sulfuric acid spectroscopic method [50-52]. The UV-vis spectra were obtained using a Jasco V-630 double-beam Spectrometer.

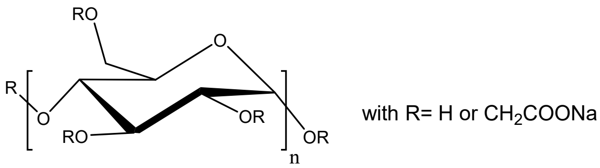

Figure 2. Structure of CMC.

3.4. Membrane preparation, apparatus, and experimental procedures

The ultrafilters were obtained by the classical Loeb and Sourirajan phase-inversion method [7, 53]. The solvents used were DMSO or NMP, and the polymer solutions were cast on a glass plate using a film applicator (Bird 284, Erichsen) that allowed to obtain casted films of 200 µm thickness. The cast polymer solutions were, then, immersed in a 45 °C water bath to ensure the coagulation of the cast films. The membranes were labeled according to the names of the employed polymer materials depicted in Figure 1. Table 2 summarizes the nature and composition of the membrane materials.

The membranes were employed in a Millipore magnetic stirred cell (Cat. No. XFUF 076 01) and the device was operated in a batch mode. The effective membrane area was 45.3 cm^2, the feed volume was 300 mL and the rotational speed was set to 500 rpm during all the trial runs. The ultrafiltration cell was pressurized with nitrogen, and pressure was controlled by a manometer placed at the top of the cell. Thanks to its very

Table 1. Polymerization conditions.

Polymer	AN (mol)	HEMA (mmol)	SSNa (mmol)	DMSO (mL)	Initiator (mg)	Time (h)	Conversion (%)
PAN	1.15	0	0	220	23	1.5	19.74
AH1	1.00	2.68	0	200	25	4.5	26.02
AH3	1.00	8.49	0	200	25	5.0	25.85
AS1	1.00	0	16.07	200	20	4.0	23.32
AS3	1.00	0	38.59	200	25	3.0	19.84
AH1S2	1.00	2.81	23.91	200	25	4.0	29.6
AH1.5S1.5	1.00	4.29	19.29	200	25	6.0	23.64
AH2S1	1.00	5.84	14.12	200	25	4.5	25.97

Table 2. Composition of the membranes.

Membrane	**Materials' nature**		**Amount of polymer and solvent in the cast solution (g)**										
		PAN	**AH1**	**AH3**	**AH1S2**	**AH1.5S1.5**	**AH2S1**	**AS1**	**AS3**	**PS**	**PSSNa***	**DMSO**	**NMP**
PAN	Homopolymer	1.00	–	–	–	–	–	–	–	–	–	9.00	–
AH1	Copolymer	–	1.00	–	–	–	–	–	–	–	–	9.00	–
AH3	Copolymer	–	–	1.00	–	–	–	–	–	–	–	9.00	–
AH1S2	Terpolymer	–	–	–	1.00	–	–	–	–	–	–	9.00	–
AH1.5S1.5	Terpolymer	–	–	–	–	1.00	–	–	–	–	–	9.00	–
AH2S1	Terpolymer	–	–	–	–	–	1.00	–	–	–	–	9.00	–
AS1	Copolymer	–	–	–	–	–	–	1.00	–	–	–	9.00	–
AS3	Copolymer	–	–	–	–	–	–	–	1.00	–	–	9.00	–
PS	Homopolymer	–	–	–	–	–	–	–	–	2.00	–	–	8.00
PS-S1	Blend	–	–	–	–	–	–	–	–	1.98	0.02	–	7.50
PS-S3	Blend	–	–	–	–	–	–	–	–	1.94	0.06	–	7.50

*As mentioned above, PSSNa was incorporated in the cast solution dissolved in 0.5 mL of water.

small dead-end volume, this cell permits flux measurements immediately after applying pressure. However, the first 10 mL of permeate was discarded in all trial runs before registering fluxes and rejections.

The fluxes were calculated from the flow rates after the elution of 1 to 5 mL of solution and were expressed by volume flux per unit time and unit area (L/h.m^2). The measurements were done at least five times until achieving constant flow. To highlight the resistance to irreversible fouling of the membranes after ultrafiltration of CMC aqueous solutions, the ratio of the solvent flux after use to the solvent flux before use was calculated. This ratio, expressed in %, illustrates the solvent flux recovery [15], and it is a good indicator of the antifouling capability of ultrafilters. The solvent flux and the flux recovery ratio (FRR) were calculated as follows:

$$J = \frac{V}{A \times \Delta t} \qquad (1)$$

where V is the volume of permeated solvent (L), A is the membrane area (m^2), and Δt is the operation time (h).

$$\mathrm{FRR}(\%) = \frac{J_{\mathrm{After}}}{J_{\mathrm{Before}}} \times 100 \qquad (2)$$

where J_{Before} and J_{After} (L.m^{-2}.h^{-1}) are the pure solvent flux through the membrane before and after use, respectively.

Rejection rate R (%) was calculated using the expression below:

$$R(\%) = \left(1 - \frac{c_P}{c_0}\right) \times 100 \qquad (3)$$

where:

c_0: the concentration of solute upstream of the membrane

c_p: the concentration of solute downstream from the membrane

4. RESULTS AND DISCUSSION

4.1. Characterisation

4.1.1. FTIR analysis

FTIR analysis of PAN homopolymer, AH1 and AH3 copolymers, and AH1S2, AH1.5S1.5, and AH2S1 terpolymers was used to confirm that the copolymerization has occurred (Figure 3). All the FTIR spectra present a sharp absorption band in the region 2300-2200 cm^{-1} characteristic of the nitrile group. The spectra of AH1, AH3, AH1S2, AH1.5S1.5, and AH2S1 indicate the appearance of a new band situated between 1760–1700 cm^{-1} attributed to the C=O stretching vibration of ester groups contrarily to the spectrum of PAN which doesn't exhibit any absorption band in this area. In addition, the intensity of this band increases with the increase of hydroxyethyl methacrylate comonomer units either in the spectra of copolymers or in those of the terpolymers. The spectra of AH1S2, AH1.5S1.5, and AH2S1 indicate the appearance of bands situated between 3100–3000 cm^{-1} attributed to symmetric stretching of aromatic C–H, present in the comonomer units of SSNa, contrarily to the comonomer units of acrylonitrile and comonomer units of hydroxyethyl methacrylate. Additionally, the range 1330–800 cm^{-1} gives characteristic absorption peaks of SSNa comonomer. These results allowed the confirmation of the formation of copolymers and terpolymers.

The results of FTIR analysis of the copolymers AS1 and AS3, and the blends PS-S1 and PS-S3, were given in previous work [24] and confirm the copolymerization for the first systems and the occurrence of strong physical links for the second ones.

4.1.2. DSC analysis of the polymer blends

To confirm the miscibility of the blended polymers, DSC analysis was used. The thermograms of PS, PSSNa, PS-S1, and PS-S3, revealed the appearance of a single glass transition temperature, T_g, for each of the two blends PS-S1 and PS-S3, intermediate between T_g's of PS and PSSNa. These results were in agreement with those obtained by FTIR analysis. This was expected since there are great similarities between the PS and PSSNa back-bone structures allowing the prediction of good miscibility of the two polymers. Indeed, even if no specific interactions exist between the two polymers, the aromatic rings contained in both PS and PSSNa chains are conducive to the establishment of strong van der Waals interactions explaining the miscibility of the two polymers [54-56]. Table 3 summarises the obtained results and Figure 4 gives the DSC thermograms.

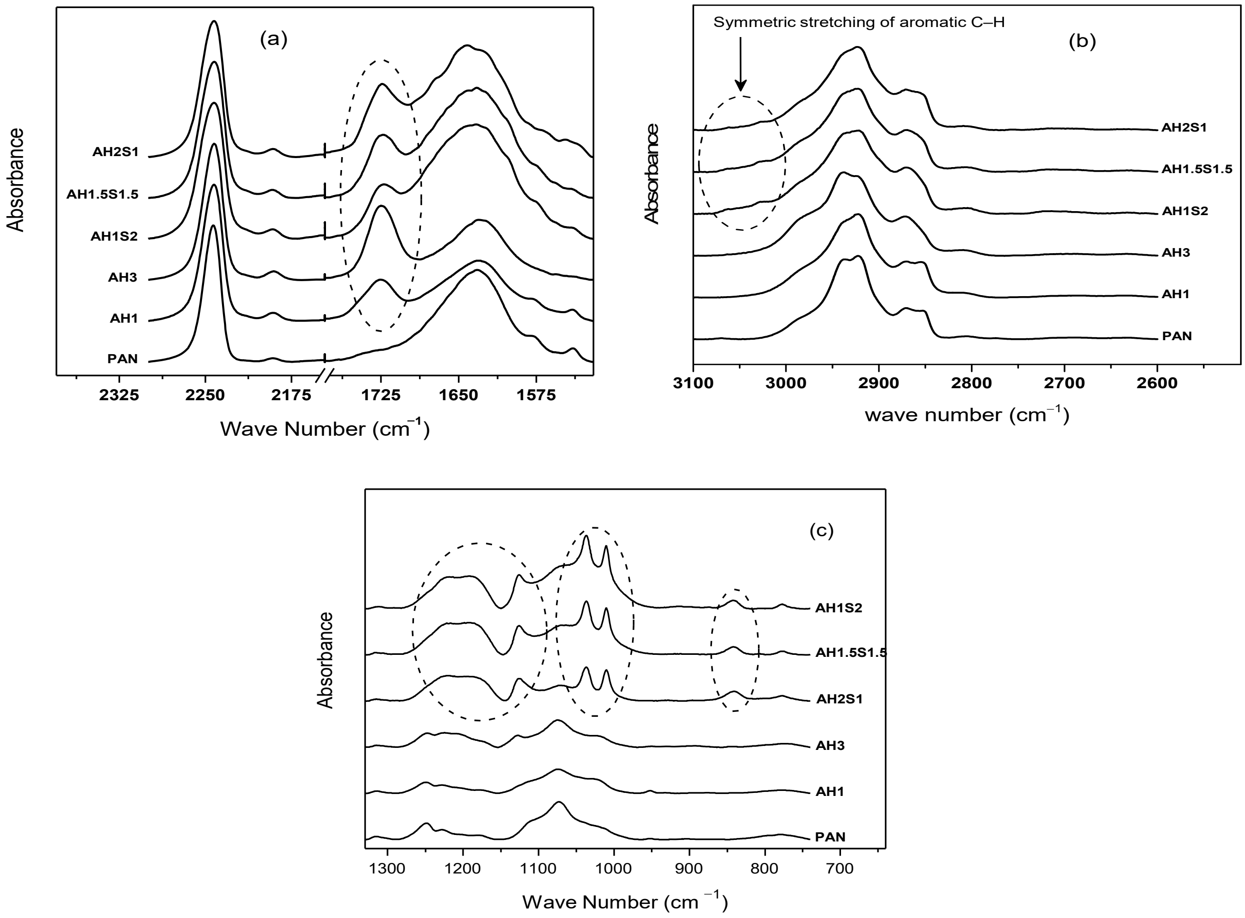

Figure 3. FTIR spectra of PAN, AHx, and AHxSy (a) in the range 2325–1575 cm^{-1}, (b) in the range 3100–2600 cm^{-1}, and (c) in the range 1330–800 cm^{-1}.

Table 3. The glass transition temperature of PS, PSSNa, and PS-based membranes.

Materials	PS	PSSNa	PS-S1	PS-S3
T_g (°C)	185.17	223.94	186.08	187.93

4.1.3. Thermogravimetric analysis

Thermogravimetry is used to measure a material's change in mass as a function of temperature. The mass losses observed throughout the analysis occur during the sample's physical or chemical transformations or decomposition [57]. In this study, TGA was used to investigate the effect of copolymerization and blending on resistance to thermal degradation of the membrane materials. Indeed, the membranes used in this study were directed to the ultrafiltration of aqueous solutions of carboxymethylcellulose acting as textile sizing agents. For this specific application, it is important to choose membrane materials that are resistant to long thermal exposure since the de-sizing step produces hot wastewater [58]. One of the advantages of the ultrafiltration process here is, in fact, the recovery of hot water, in addition to the decreasing of wastewater volume by recycling and the recovery of the sizing agents from the recycling system. It is therefore important not to lose this advantage because of the handicap that would constitute a low thermal resistance of the membrane materials.

Table 4 summarizes the results extracted from the thermograms obtained for all the studied systems. The detail of the study for PAN, AS1, AS3, PS, PSSNa, PS-S1, and PS-S3 was given in a previous paper [24]. Figure 5 gives the thermograms of AH1 and AH3 copolymers, and AH1S2, AH1.5S1.5, and

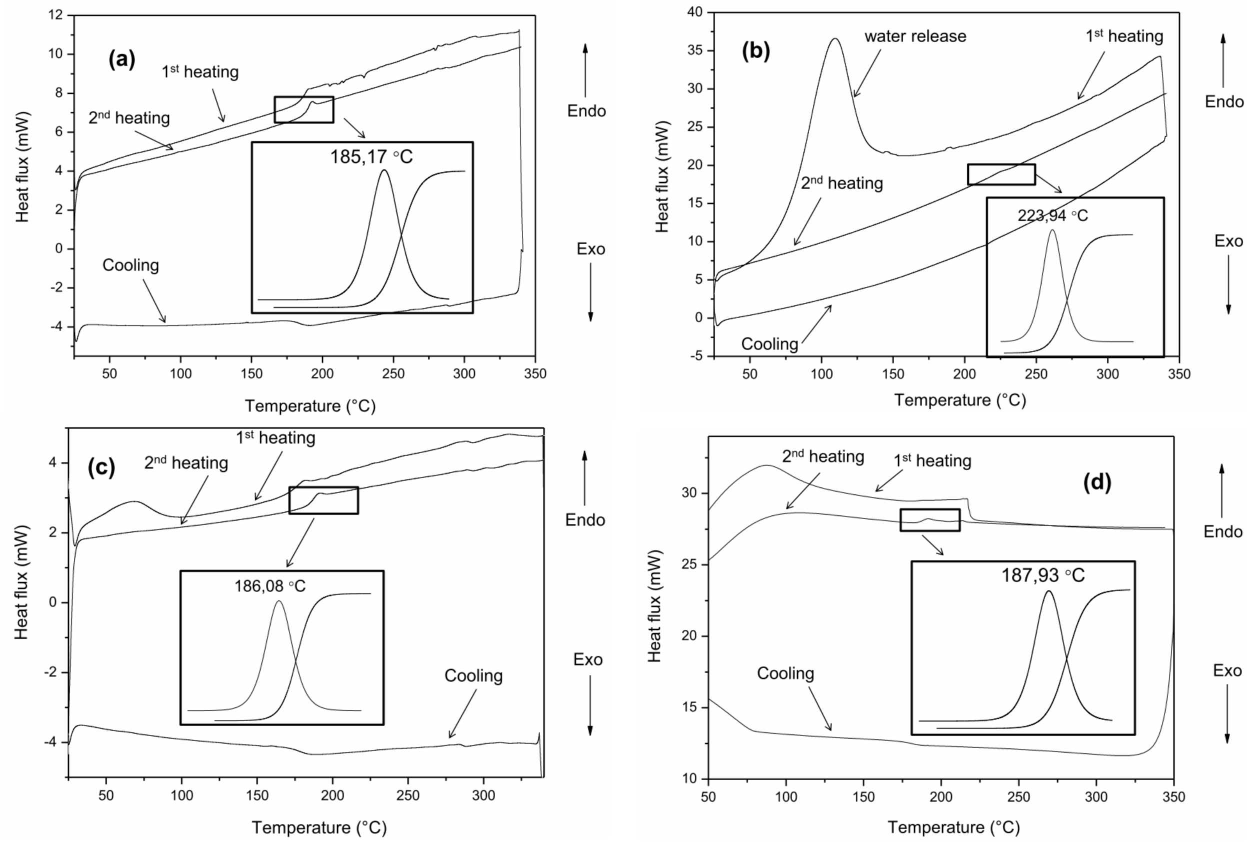

Figure 4. DSC thermograms of (a) PS, (b) PSSNa, (c) PS-S1, and (d) PS-S3.

Table 4. The number of degradation steps and the initial temperature of degradation* of the studied membrane materials (extracted from TGA thermograms of each one).

Materials	The number of degradation steps	The initial temperature of degradation (°C)
PAN	2	257.67
AH1	3	211.01
AH3	3	187.01
AH1S2	4	285.33
AH1.5S1.5	4	278.63
AH2S1	4	247.74
AS1	4	261.93
AS3	3	287.67
PS	1	442.62
PSSNa	2	311.26
PS-S1	2	433.62
PS-S3	2	375.66

*The initial temperature of degradation was determined according to [59].

AH2S1 terpolymers. The particular temperatures involved and the changes of mass occurring during the loss of mass were determined by the standards DIN 51 006 [59] and ISO 11358-1 [60]. Table 5 gives the nomenclature of the important parameters of the degradation steps. Table 6 gives the summary of the thermal degradation characteristics of PAN, AHx, and AHxSy polymers.

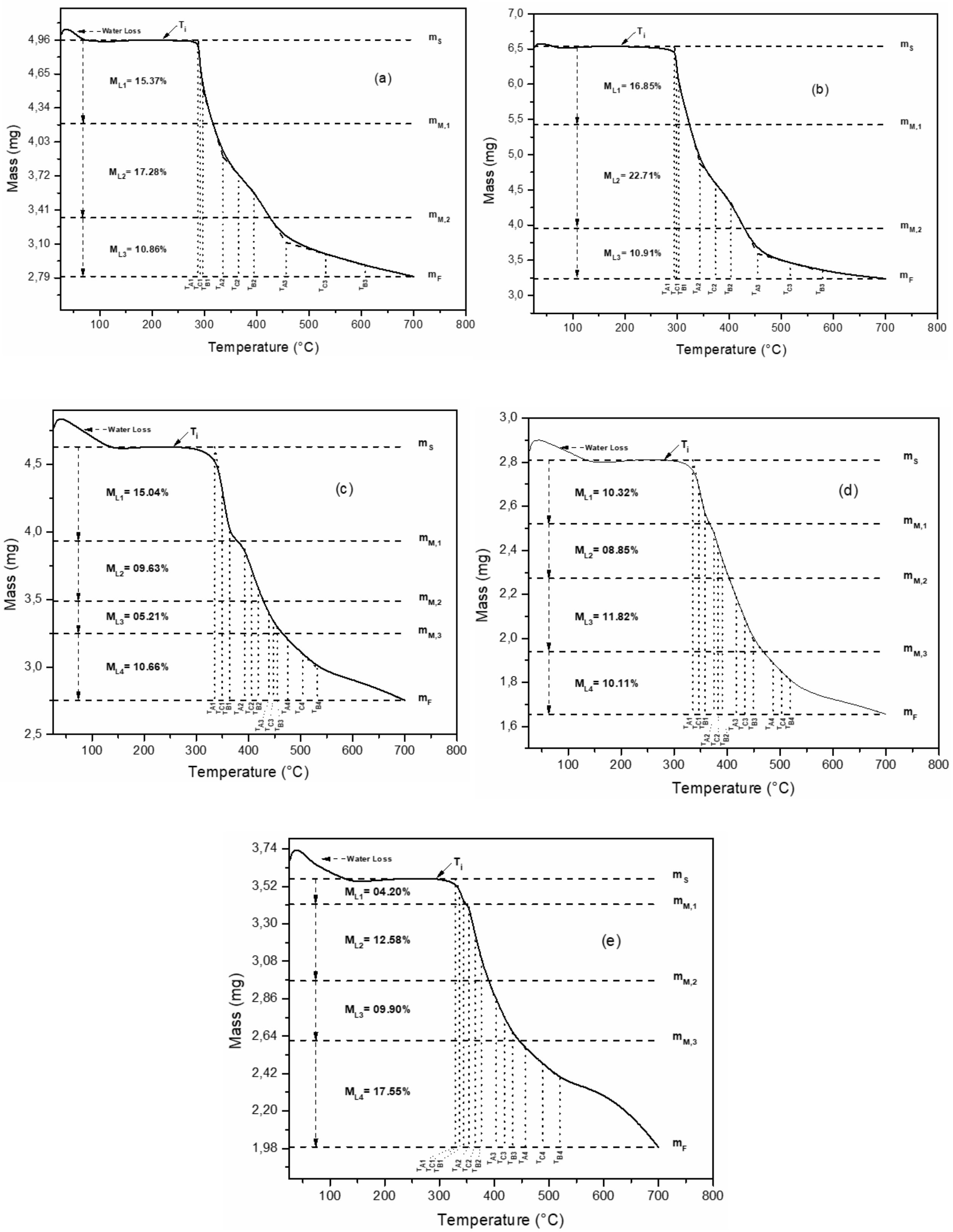

Figure 5. TGA thermograms of (a) AH1, (b) AH3, (c) AH2S1, (d) AH1.5S1.5, and (e) AH1S2.

Table 5. The terms describing the characteristics of the TGA curves.

Term	Designation	Calculation
A	The starting point.	The intersection of extrapolated starting mass with the tangent applied to the maximum slope of the TG curve.
B	The endpoint.	The intersection of extrapolated end mass, after reaction, with the tangent applied to the maximum slope of the TG curve.
C	The midpoint.	The intersection of the TG curve with the line parallel to the abscissa that is midway between A and B.
T_{Ai}	The onset temperature of the i^{th} degradation step.	–
T_{Bi}	End temperature of the i^{th} degradation step.	–
T_{Ci}	Midpoint temperature of the i^{th} degradation step.	$T_{Ci} = \frac{T_{Ai}+T_{Bi}}{2}$
m_S	Starting mass.	–
m_F	Final mass.	–
$m_{M,i}$	Midpoint mass of the i^{th} degradation step between $m_{A(i+1)}$ and m_{Bi}.	$m_{M,i} = \frac{m_{A(i+1)} + m_{Bi}}{2}$
M_{Li}	Loss of mass of the i^{th} degradation step.	$M_{Li}\ (\%) = \frac{m_S - m_{M,i}}{m_S} \times 100$ or $M_{Li}\ (\%) = \frac{m_{M,i} - m_{M,i+1}}{m_S} \times 100$ or $M_{Li}\ (\%) = \frac{m_{M,i} - m_F}{m_S} \times 100$
T_i	Initial temperature (of degradation) according to [59].	–

Table 6. The thermal degradation characteristics of PAN-based homo, co, and terpolymers.

Polymer	The number of degradation steps	The initial temperature of degradation (°C)	The onset temperature of each step (°C)			
			T_{A1}	T_{A2}	T_{A3}	T_{A4}
PAN	2	257.67	300.54	605.35	–	–
AH1	3	211.01	287.68	335.63	455.92	–
AH3	3	187.01	294.68	343.94	454.57	–
AH1S2	4	285.33	328.71	353.52	403.64	457.28
AH1.5S1.5	4	278.63	335.20	374.98	417.16	486.69
AH2S1	4	247.74	335.24	392.44	439.34	475.72

The initial temperature of degradation and the onset temperature of each step were determined according to [59] and [60] respectively.

4.1.3.1. Effect of copolymerization on the thermal properties of PAN-based materials

The results of the TGA analysis of the PAN-based materials revealed that the PAN homopolymer was degraded in a two-step process. The copolymers, except AS1, have three degradation steps and the terpolymers have four degradation steps.

The initial temperatures of degradation of PAN, homo, co, and terpolymers, determined according to DIN 51006 [59], revealed that a slight improvement in the resistance to thermal degradation was induced by the introduction of SSNa comonomer units in the PAN backbone, contrarily to HEMA comonomer which has the opposite effect. Indeed, the comparison of the initial temperature of degradation of PAN to those of the copolymers and the terpolymers revealed a gain of 4.3 to 30.0 °C thanks to the introduction of SSNa comonomer units and a loss of 47.7 to 70.7 °C when the HEMA unit quantities increase. The evolution was well correlated between the co and the terpolymers. Indeed, for AH1S2, AH1.5S1.5, and AH2S1 terpolymers, the materials gain up to 27.7 °C in initial temperature of degradation by increasing SSNa units in the PAN backbone and lose up to 10.0 °C in initial temperature of degradation by increasing the amount of HEMA units. Thus, although HEMA units decrease the thermal performance of PAN-based materials, SSNa units effectively counteract this negative effect.

4.1.3.2. Effect of blending on the thermal properties of PS-based materials

The results of the TGA analysis of the PS-based materials revealed that PS was degraded in a one-step process, while the blends PS-S1 and PS-S3 have two degradation steps. Besides, contrary to the case of the PAN-based copolymers, the addition of SSNa species in the PS-based blends alters the resistance to thermal degradation of PS-based materials. This is easily explained by the fact that the initial temperature of degradation of PSSNa polymer is lower by more than 130 °C compared to that of the PS. The blends PS/PSSNa are therefore increasingly affected as the amount of PSSNa increases in the mixture. This could suggest that the introduction of the SSNa hydrophile species by copolymerization, instead of introducing it by blending, would be more efficient to obtain membrane materials of more thermal resistance, but, in fact, it isn't the case since the polysulfone has a great thermal resistance, even more important than that of PAN, and since the T_g of the PS-blends was reinforced by the addition of PSSNa polymer.

4.2. Ultrafiltration of CMC aqueous solutions

In previous papers [24, 25], the variation of the permeate flux with the applied pressure for pure distilled water and macromolecular aqueous solutions of CMC was studied by ultrafiltration of the solutions through the AS1, AS3, PS-S1, and PS-S3 membranes. The results obtained for the PAN-based membranes and the PS-based membranes were almost similar and revealed a linear evolution of flux of solvent with pressure and a low discrepancy from the linear proportionality of flux for the macromolecular solutions. The notable remarks were, on one hand, the mediocre comportment of the AS3 membrane which permitted the conclusion that the augmentation of the amount of the sodium styrene sulfonate co-monomer in the poly(acrylonitrile-co-

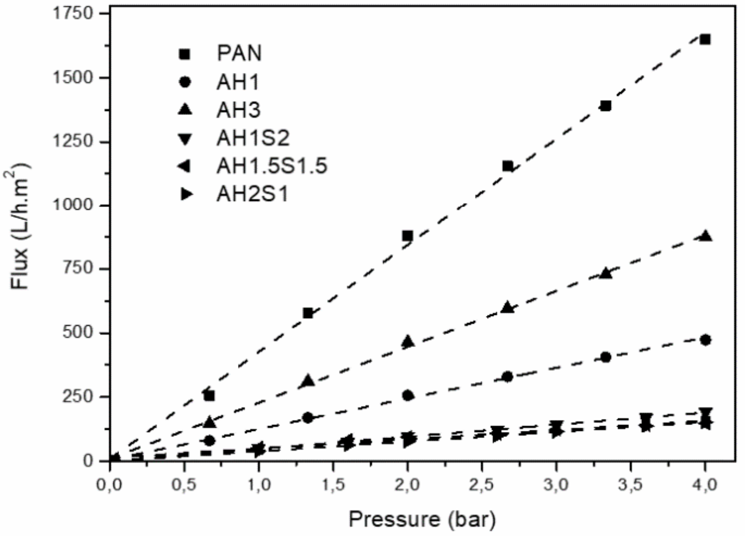

Figure 6. Solvent flux before use for PAN, AH1, AH3, AH1S2, AH1.5S1.5, and AH2S1 membranes.

sodium styrene sulfonate) was inefficient for this specific use and on the other hand, the fact that even if fluxes were better for PS-S1 and PS-S3 membranes, fluxes recovered after use remained better for the AS1 membrane. In the next paragraphs, the results of the hydrodynamic characterization and the selectivity of PAN, AHx, and AHxSy membranes are first given, and then the performances of the studied membranes are compared.

4.2.1. Solvent flux before use for PAN, AHx, and AHxSy membranes

The study of the variation of the permeate flux with the applied pressure for pure distilled water ultrafiltered through the PAN, AHx, and AHxSy membranes permitted the observation of a linear evolution of flux with pressure for all the membranes (Figure 6). These results were in accord with the Darcy law, which describes the flux of solvent through a porous medium. The solvent fluxes through the copolymer and terpolymer-based membranes were lower than those of the PAN homopolymer-based membrane and the effect was more pronounced as the amount of SSNa increased. The very small fluxes observed for terpolymer-based membranes permitted a first partial conclusion regarding the confirmation of the inefficiency of the augmentation of the amount of the sodium styrene sulfonate co-monomer in the PAN-based membranes. Besides, these results permitted a preliminary selection of the AH1, the AH3, and the AH2S1 membranes for the continuation of the work.

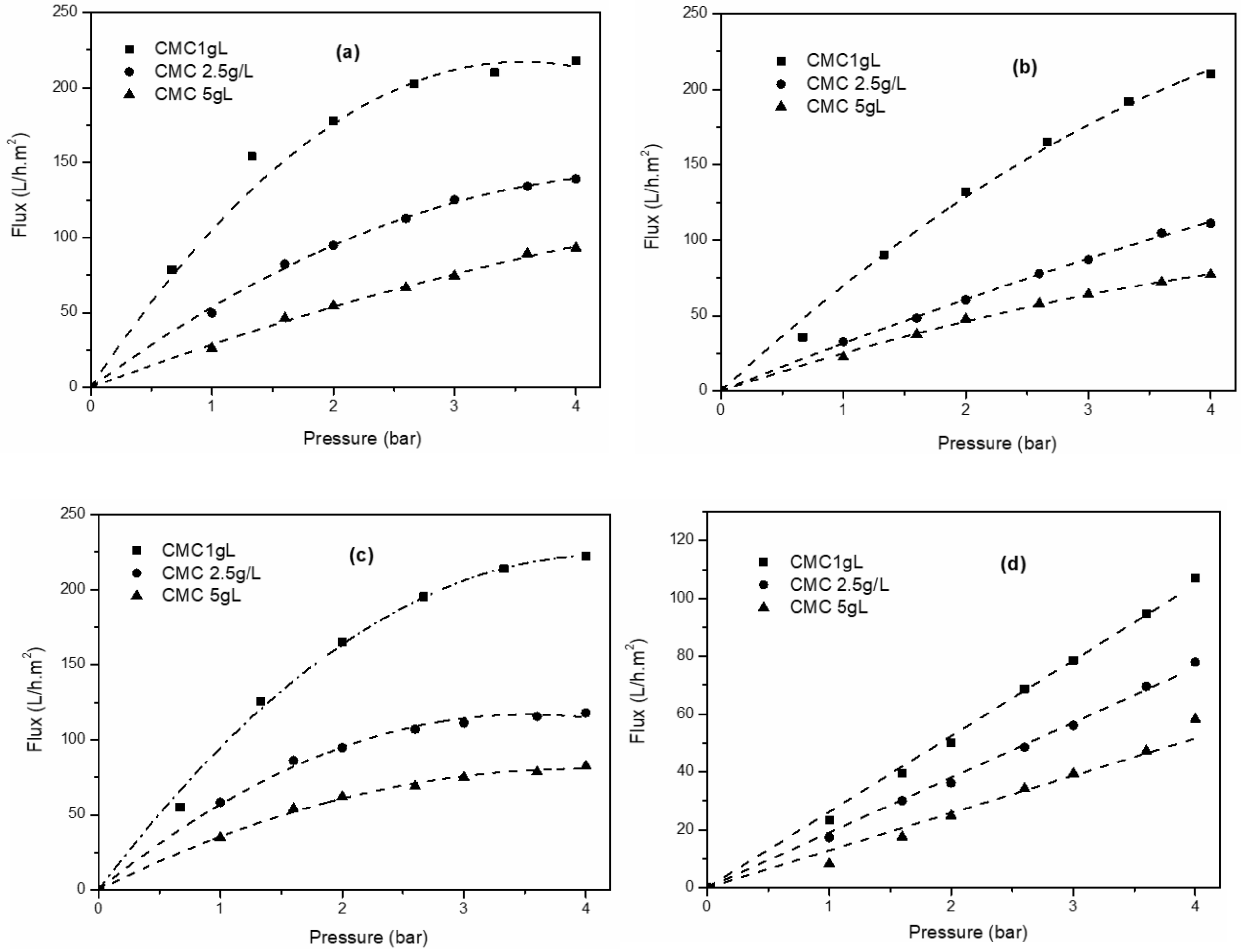

Figure 7. Ultrafiltration of aqueous solutions of CMC through (a) PAN membrane, (b) AH1 membrane, (c) AH3 membrane, and (d) AH2S1 membrane.

4.2.2. Ultrafiltration of CMC through the PAN, AH1, AH3, and AH2S1 membranes

The variation of permeate flux with the applied pressure was studied for CMC aqueous solutions of different concentrations ultrafiltered through the PAN, AH1, AH3, and AH2S1 membranes (Figure 7). More or less discrepancy from the linear proportionality of flux to applied pressure was observed from membrane to membrane. This phenomenon reveals the establishment of a concentration polarization layer near the membrane, and it is more pronounced for the PAN homopolymer-based membrane and the membranes containing the HEMA co-monomer. The PAN-based membrane with SSNa co-monomer was less affected. However, as expected, this membrane has an important drop in permeate fluxes comparatively to those of the PAN homopolymer-based membrane. Indeed, the comportment of the AH2S1 membrane correlates with the negative effect of the SSNa co-monomer on membrane permeability as indicated below. However, despite this concern which has to be solved, its efficiency to avoid or even cancel the establishment of a concentration polarization layer near the membrane pleads in favor of keeping it among the chosen membranes for further studies since this property is a serious indicator of its resistance to fouling.

4.2.3. Solvent flux recovery

Figure 8 gives the solvent flux recovery after the ultrafiltration of 1 g/L CMC aqueous solutions through all the studied membranes. Important solvent flux recovery was observed for the PAN-based membranes AS1, AH3, and AH2S1 comparatively to the PS-based membranes for which the solvent flux recovery was also relatively important, but less than that of the PAN-based ones.

The AS1, AH3, and AH2S1 membranes were then selected and used with more concentrated solutions to confirm this good comportment for each of the membranes (Figure 9).

The antifouling capability is confirmed for the three membranes with a particularly good solvent flux recovery of 75% in the case of AH2S1 membrane, even after multiple uses to ultrafiltrate concentrated solutions, contrarily to PAN membrane which exhibits mediocre comportment after the ultrafiltration of the more concentrated CMC solution. These results allowed the confirmation of the pertinence of using the PAN-based copolymers and terpolymers to obtain membrane materials of enhanced antifouling capabilities.

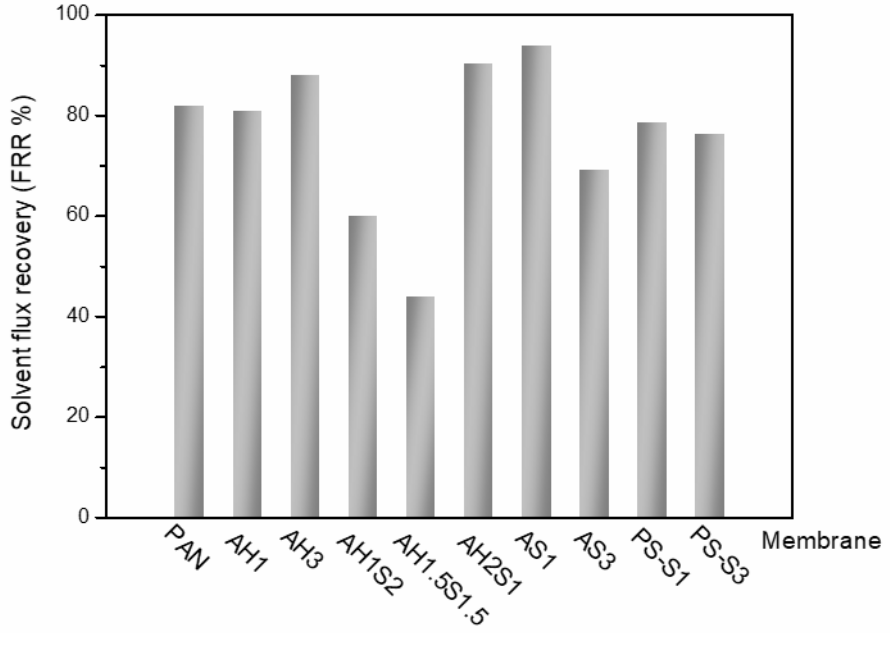

Figure 8. Solvent flux recovery after ultrafiltration of 1 g/L CMC aqueous solutions.

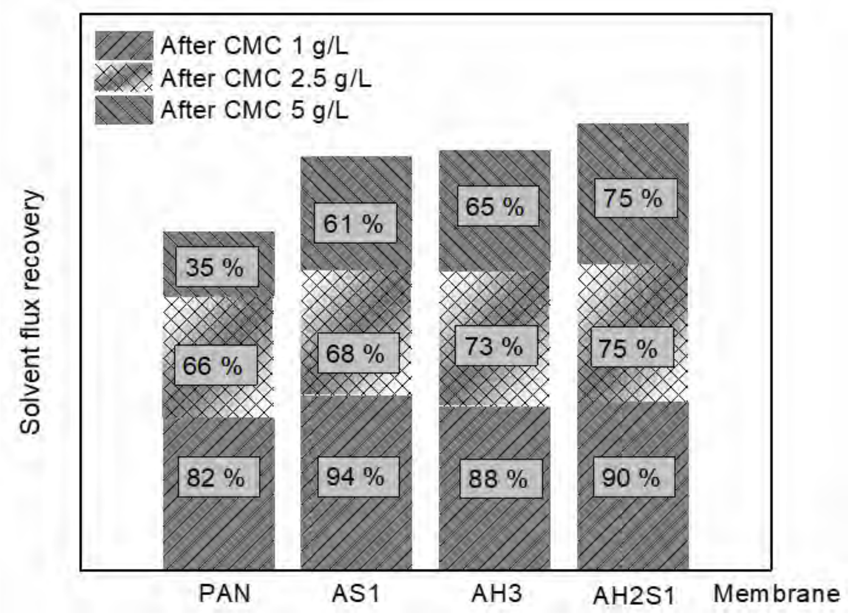

Figure 9. Solvent flux recovery after ultrafiltration of CMC aqueous solutions of different concentrations through the membranes PAN, AS1, AH3, and AH2S1.

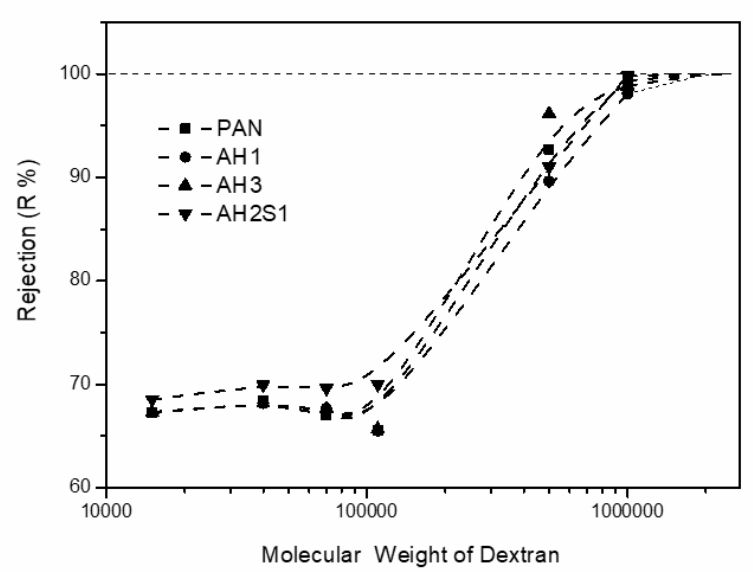

Figure 10. The molecular cut-off curve of the membranes PAN, AH1, AH3, and AH2S1.

4.2.4. Selectivity

4.2.4.1. Cut-off determination

The molecular cut-off curves of ultrafiltration membranes are determined according to the usual experimental determination of the membrane selectivity from plots of the variation of the retention rate of tracer molecules, like Dextran, with their molecular mass [61]. This method was used to determine the cut-off of selected PAN-based membranes and PS-based membranes among the most efficient ones. The curves of PAN, AH1, AH3, and AH2S1 membranes are gathered in Figure 10 and permitted to estimate their cut-off at 500 kDa.

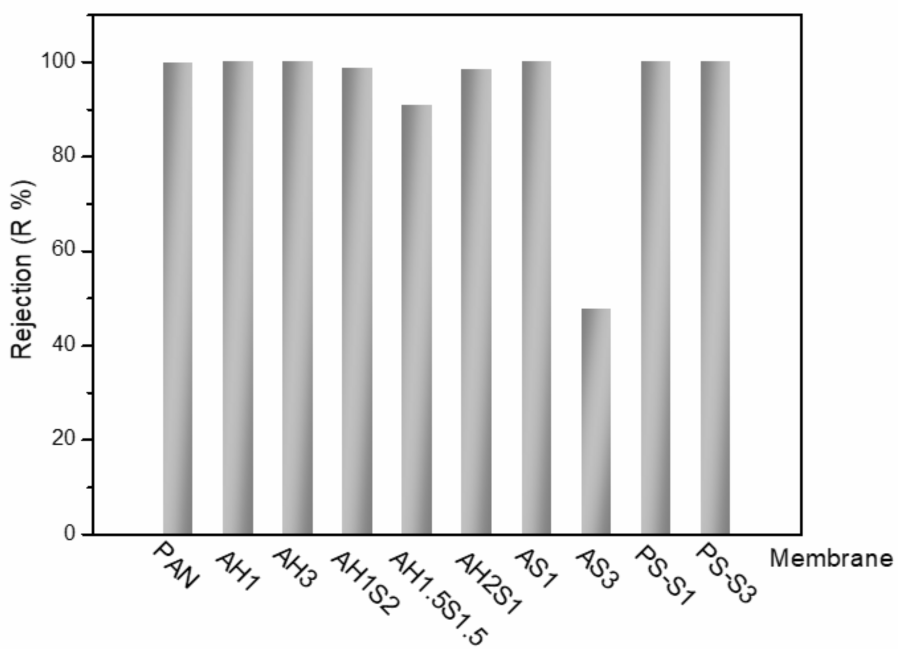

Figure 11. Membrane rejection (R%) of CMC 1 g/L.

The cut-off curves of the membranes AS1 and PS-S1 were given in previous papers [24, 52] and the cut-off was estimated to be 100 kDa and 50 kDa, respectively.

4.2.4.2. Efficiency of the membranes in the rejection of CMC

The efficiency of the PAN-based membranes and the PS-based membranes for the rejection of CMC and its removal from aqueous solutions is summarized in Figure 11 which reveals the almost complete rejection of CMC by all the membranes except the AS3 one. Indeed, as was predictable, the AS3 membrane was not efficient because of the mediocre properties observed during the permeability characterization.

Therefore, when the AS3 membrane is removed from the comparison, the differences between the other membranes appear, as shown above, in the antifouling capability of each one, without affecting the rejection efficiency. And from this point of view, the membranes that stand out remain AS1, AH3, and AH2S1.

5. CONCLUSION

PAN-based copolymers and terpolymers were synthesized and characterized using FTIR analysis and TGA analysis. FTIR spectra confirmed the occurrence of the copolymerization thanks to the appearance of bands characteristic of HEMA and SSNa units in the co and terpolymers spectra. TGA revealed the increase of thermal stability with the addition of SSNa units in the ASx copolymers and the AHxSy terpolymers and its decrease with the addition of HEMA units, in both the AHx copolymers and the AHxSy terpolymers. Next, the PAN-based polymers were used to prepare membranes that were employed to ultrafiltrate aqueous solutions of CMC. Solvent flux measurements, before and after the ultrafiltration of the macromolecular solutions revealed an important solvent flux regeneration for all the membranes after CMC ultrafiltration without any special cleaning, except for the AH1S2, AH1.5S1.5, and AS3 membranes. The partial recovery of initial solvent flux revealed good anti-fouling capabilities for AS1, AH1, AH3, and AH2S1 membranes. The introduction of HEMA and SSNa units in the polymer materials was efficient to improve the resistance to fouling of the membranes which also revealed a great selectivity against CMC. The results of this study allowed saying that HEMA comonomers improved the anti-fouling capabilities of the PAN-based membranes, even after multiple uses in ultrafiltration of concentrated solutions, while SSNa comonomers improve their thermal stability and their anti-fouling capabilities when introduced in small amounts, and the two comonomers preserved the good selectivity of the membranes.

To investigate if blending is better than copolymerizing to render ultrafiltration membranes more resistant to fouling, or, on the contrary, it is the opposite, PS-based blends were used to prepare membranes employed to ultrafiltrate the aqueous solutions of CMC that were treated by the PAN-based membranes. Before use, the polymer blends were characterized using FTIR, DSC, and TGA analysis. FTIR analysis revealed the occurrence of physical links between PS and PSSNa. DSC analysis confirmed the miscibility of the blended polymers thanks to the appearance of a single T_g for each of the PS-S1 and PS-S3 blends, intermediate between T_g's of PS and PSSNa. TGA revealed the decrease of thermal stability of the blend polymers with the addition of PSSNa contrary to the effect of the SSNa comonomers in the PAN-based polymers which improved their thermal stability. The ultrafiltration of CMC solutions through the PS-S1 and PS-S3 membranes revealed a great selectivity, shared with the PAN-based membranes, making it impossible to settle based on this criterion. However, solvent flux recovery after ultrafiltration of CMC aqueous solutions was more important for the PAN-based membranes than for the PS-based ones indicating a difference regarding antifouling properties of the ones and the others.

Thus, for the specific application reported in this study, copolymerization seems to be slightly more appropriate than blending, but it is not a law, since copolymerization and blending have the same raison d'etre which is developing materials having enhanced performances. The two methods are efficient to improve antifouling properties of polymer-based membranes and the choice of copolymerization or blending could, in fact, be motivated only by the intended application and the constraints linked to the available financial means and the stability of the membrane materials under the imposed operating conditions.

CONFLICT OF INTEREST STATEMENT

The authors certify that the present paper is an original work with no conflict of interest of any kind.

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