

Preparation of polymer blend membranes based on cellulose acetate and quaternized polyethersulfone for ultrafiltration

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Abstract

Aim: The present study was aimed to develop the ultrafiltration (UF) membranes were prepared from blends based on cellulose acetate (CA) and quaternary ammonium salt of polyethersulfone (QASPES) at various compositions. **Materials and Methods:** All membranes were prepared by the diffusion-induced phase separation method, namely casting a thin film of the polymeric solution on a glass plate and, after allowing the solvent to evaporate for a predetermined period at the desired humidity and temperature conditions, immersing it into a bath of non-solvent (water, solvent, and surfactant) for final precipitation. Before membrane casting, a gelation bath of 2 L of distilled water (non-solvent), containing 2% N,N-dimethyl formamide (DMF) (solvent) and 0.2% sodium lauryl sulfate (surfactant) was prepared and cooled to 10°C. **Results and Discussion:** QASPES conformed by Fourier transform infrared and nuclear magnetic resonance. The blend membranes prepared are characterized in terms of compaction time, pure water flux, water content, and scanning electron microscopy. It is observed that the surface hydrophilicity of the CA-QASPES blend membranes has enhanced remarkably with increase of QASPES content. During compaction study, the steady-state flux is reached within 3–4 h at 414 kPa pressure. Pure water flux and water content of the membranes are found to increase, especially when QASPES content in CA membrane is simultaneously increased. Cross-section morphology of the membranes is analyzed using scanning electron microscope. **Conclusion:** We conclude that the incorporation of the hydrophilic moiety (QASPES) in blend membranes plays a major role in improving the flux and performance characteristics of membranes. The proposed techniques would be economical, convenient, and safe.

Key words: Pure water flux, quaternized polyethersulfone scanning electron microscopy, ultrafiltration

INTRODUCTION

The world is facing enormous challenges in meeting rising demands of clean water as the available supplies of freshwater are decreasing due to the rapid population growth of global population, urbanization, rapid industrialization, global climate change, and more stringent health-based water quality standards.^[1] Nowadays, industrial growth, especially in developing countries, has led to increasing industrial waste discharge into the environment. These wastewaters contain dangerous toxins such as heavy metals and their discharge into the environment can cause air, soil, and water

pollution.^[2] The pollution with heavy metals is a problem of great concern nowadays associated with the industrial production of high amounts of wastewaters containing heavy metals. Heavy metals are extremely dangerous for the human health and for the environment because of their toxicity, non-biodegradability, and tendency to be accumulated in living organisms.^[3] Once they enter the food chain, large concentrations of heavy metals may

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accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders.^[4] Efficient separation processes are needed in the food and pharmaceutical industries to obtain high-grade products to supply communities and industries with high-quality water and to remove and recover toxic or valuable components from industrial effluents.^[5] There are many significant advantages of using membranes for industrial processes which make membranes as a popular technology in various fields such as water treatment. Membrane technology is modular which is easy to scale up, simple in operation, relatively low-energy consumption, and no chemical additives.^[6-9] Ultrafiltration (UF) process, which is employed to separate microsolute from macromolecules and to treat wastewater, has been applied to different industries such as metallurgical, pharmaceuticals, beverages, potable water, dairy, and electrocoating paint mixtures.^[10] Cellulose acetate (CA) was one of the first membrane polymers that has been used for aqueous-based separation and used as both a reverse osmosis and a UF membrane material.^[11,12] However, similar to the great majority of polymeric filtration membranes, CA membranes are biologically inert and can undergo bacterial attachment and biofouling formation.^[13] CA membrane has been often modified by blending with other polymers to obtain an excellent separation performance, such as higher flux and better selectivity. Blending CA with an appropriate polymer maybe improves the performance of CA membrane owing to the fact that polymer blends have provided a desirable way to fulfill new requirements for practical applications.^[14,15]

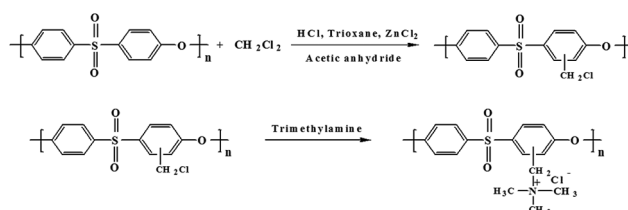
Polyethersulfone (PES) is a versatile high performance polymer and gained particular interest in the fabrication of both UF membranes prepared integrally skinned uncharged PES symmetric membranes by dry-wet phase inversion method.^[16] The aromatic sulfone units provide high performance properties such as considerable mechanical strength, thermal stability, and chemical resistance, while the flexible ether linkages provide good processability. PES has been successfully used in the preparation of asymmetric membranes for gas separation and oil-water separation. PES has certain drawbacks such as strict membrane casting conditions, relative low rejection, and low gas permeability. The use of PES for aqueous phase is restricted due to its hydrophobicity. Hence, it is desirable to make the PES membrane hydrophilic when PES is used in aqueous-based UF applications. The hydrophilicity and permeability of PES may be increased by quarternization. Many researchers have focused on the hydrophilization of hydrophobic UF membrane materials.^[17] Objectives of the present study deal with the preparation of a derivative of PES containing quaternary ammonium salt (QASPES) and CA-QASPES blend UF membranes. The CA-QASPES blend membranes have been characterized in terms of compaction, pure water flux, membrane hydraulic resistance, percentage water content, and surface morphology.

MATERIALS AND METHODS

Commercial grade MYCEL CA CDA 5770 with acetyl content of 39.99 wt. % (Mysore Acetate and Chemicals Company Ltd., India) was used as such without purification. Commercial grade PES (Gafone 3300) obtained as a gift sample from Gharda Chemicals Pvt., Ltd., India, was used as supplied. Trimethylamine (Merk, India) was purified by distilling under reduced pressure. Dichloromethane (DCM) (Glaxo India Limited) and trioxane (SRL, Mumbai), and zinc chloride (SRL, Mumbai) were used without any purification. Absolute ethanol was prepared by refluxing dilute alcohol with CaO and then distilled. Analar grade N,N-dimethyl formamide (DMF) (Qualigens Fine Chemicals) was sieved through molecular sieves (Type-4A^o) to remove moisture and stored in dry conditions before use. Other analar grade solvents such as acetone and methanol (Qualigens Fine Chemicals Ltd., India) were used as supplied. Analar grade sodium lauryl sulfate (SLS) (Qualigens Fine Chemicals Ltd., India) was used as surfactant. Polyethylene glycol 600 (PEG 600) (Merck (I) Ltd.) was used as supplied, as a non-solvent additive for the whole study. Deionized and double distilled water was used for the preparation of the gelation bath.

Preparation of QASPES

At first, chloromethylation of PESs is carried out as follows. In a 500 ml three-necked flask, 100 ml of 2,2- DCM was taken and 30 g of PES was dissolved in it. A mixture of trioxane, hydrochloric acid, and zinc chloride was added.^[14] The reaction mixture was stirred for 6 h and precipitated using ethanol. The resultant product is chloromethylated PES. The viscous white product was dissolved in DMF. Trimethylamine was added and the reaction mixture was constantly stirred for 12 h and poured into ethanol and washed repeatedly with hot ethanol followed by deionized water until inorganic salt and solvent were removed thoroughly. The purified polymer was then dried in a vacuum oven at 100°C for 48 h. The yield of the product was 85% it is shown in Scheme 1. The authenticity of chloromethylation and quarternization of polymer (QASPES) backbone was confirmed by Fourier transform-infrared (FT-IR) and nuclear magnetic resonance (¹H-NMR) spectroscopic techniques.



Scheme 1: Preparation of quaternary ammonium salt of polyethersulfone

Preparation of Membranes

Solution blending of polymers

The blend solutions based on CA and quaternized PES polymers (total polymer concentration = 17.5 wt. %) were prepared by dissolving in DMF the two polymers with different compositions as shown in Table 1 under constant mechanical stirring at 30 rpm in a round-bottomed flask for 4 h at 40°C. The homogeneous solution that was obtained was allowed to stand at room temperature for 1 day in an airtight condition to get rid of air bubbles.

Casting of polymer membranes

The method of preparation of the membranes involved is the same as that of the “phase inversion”^[18] method employed in earlier works as reported by other researchers.^[19] The total polymer concentration was optimized and was maintained at 17.5 wt. % to have a balanced casting solution viscosity to yield membranes between pure spongy type and high macrovoidal type. Before membrane casting, a gelation bath consisting of 2 L of distilled water (non-solvent), 2% DMF (Solvent), and 0.2% of the surfactant, SLS was prepared and cooled to 10°C. The thickness of the membranes was maintained at 0.22 ± 0.02 mm and measured with a micrometer having a precision of 0.01mm.

RESULTS AND DISCUSSION

Characterization of QASPES

FT-IR spectrum

The IR spectrum of QASPES is shown in Figure 1, the C-H stretching frequency of the methyl and methylene groups is observed at 2925/cm and 2855/cm, respectively. The S=O stretching of sulfone group is observed 1744/cm. The ring breathing vibrations of aromatic ring due to C=C stretching are observed at 1590, 1463, and 1409/cm. The C-N stretching vibrations of the quaternary ammonium moiety are observed at 1231/cm. The C-O stretching due to ether group is observed at 1107/cm. The C-H out of plane bending vibration of aromatic ring is observed at 831/cm and 793/cm.S

¹H NMR spectrum

¹H NMR spectrum of QASPES is shown in Figure 2, the aromatic protons which are nearer to the sulfone group show signals at 7.97 and 7.94 ppm. The aromatic protons away from sulfone group are observed at 7.28 and 7.26 ppm. The N-methyl group gave a singlet at 3.31 ppm. The peak at 2.56 ppm is attributed to the methylene protons adjacent to the nitrogen atom.

Table 1: Composition and casting conditions of cellulose acetate-QASPES blend membranes

Blend composition (%) polymer		Wt. %	
CA %	QASPES %	Additive, PEG 600	Solvent, DMF
100	0	0	82.5
90	10	0	82.5
80	20	0	82.5
70	30	0	82.5
100	0	2.5	80.0
90	10	2.5	80.0
80	20	2.5	80.0
70	30	2.5	80.0

QASPES: Quaternary ammonium salt of polyethersulfone, PEG 600: Polyethylene glycol 600, DMF: N, N-dimethyl formamide, CA: Cellulose acetate

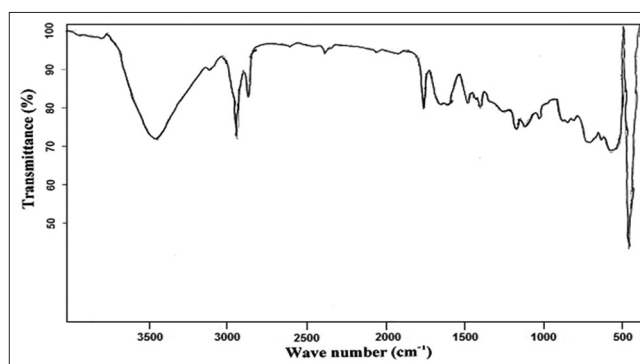


Figure 1: Fourier transform-infrared spectrum of quaternary ammonium salt of polyethersulfone

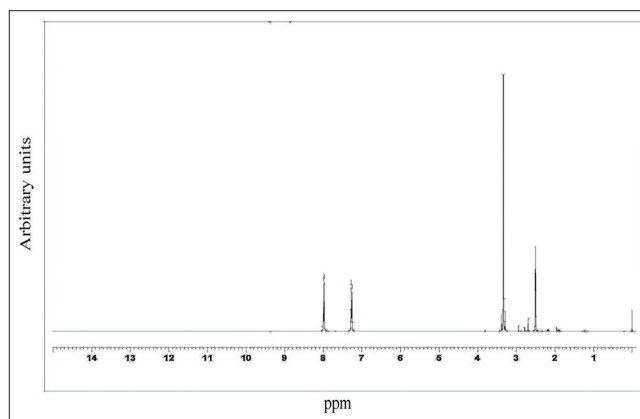


Figure 2: ¹H nuclear magnetic resonance spectrum of quaternary ammonium salt of polyethersulfone

Membrane characterization

Compaction

The aim of compaction study was to make the pores of the membranes uniform and rigid to get steady-state flux. The effect of various ternary blends, CA/QASPES, on pure

water flux of prepared membranes at various compaction times is shown in Figure 3. In general, the pure water flux decreases as compaction time increases for all the prepared membranes. During compaction under hydraulic pressure, the polymeric chains reorganize and this leads to change in the structure with a lowered volume of porosity. This leads to an increase in the hydraulic resistance offered by the membrane, and consequently lowers the flux. It is seen that the pure water flux of 100 wt. % CA membrane at steady state after 6 h of compaction is comparable to the values obtained in previous studies.^[20] Blending of 20 wt. % QASPES with 80 wt. % CA resulted in membrane with an initial flux of 124.8 L m⁻² h⁻¹ and a steady-state flux of 77.5 L m⁻² h⁻¹, which is higher than that of membrane prepared in the absence of QASPES (35.6 L m⁻² h⁻¹). Similar observations have been reported.^[21] After 6 h of compaction, the water flux decreased. This increase in flux

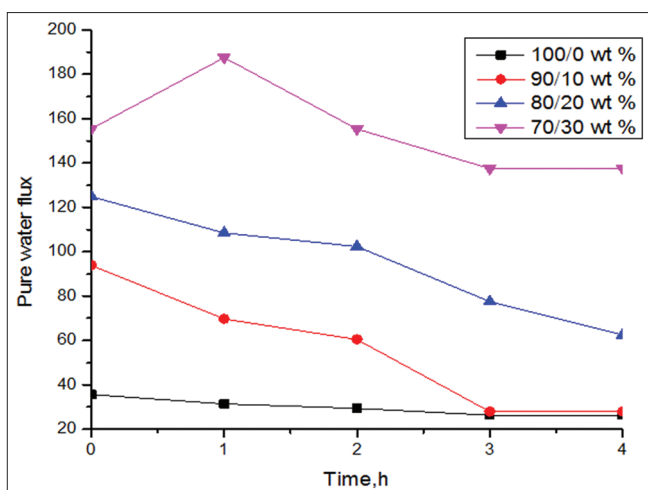


Figure 3: Effect of compaction time on pure water flux of CA/QASPES blend membranes with different QASPES contents

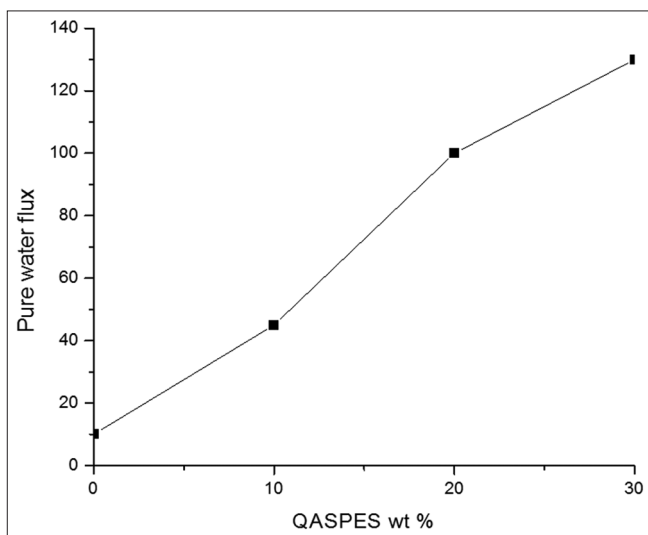


Figure 4: Pure water flux of cellulose acetate/quaternary ammonium salt of polyethersulfone (QASPES) blend membranes with different QASPES contents

on increase in QASPES component due to the increase in the hydrophilic nature as well as the porosity of the blend membranes.^[22]

Pure water flux (PWF) and water content

The pure water flux of CA is 10 L m⁻² h⁻¹ and water content is 64% in the absence of QASPES. Further, the PWF increases from 45 to 130 L m⁻² h⁻¹ and the water content increases from 67.8 to 81% with increase in the concentration of QASPES from 10 to 30 wt. %. It is shown in Figures 4 and 5. This enhancement in flux due to the increase in hydrophilic nature of blend membranes due to incorporation of QASPES in blend composition and also increasing nature of immiscible phase behavior of blend due to low molecular attractive forces between the blend components. During gelation, this, in turn, enhances the diffusion rate of water from the gelation bath into the pores of the membranes, leading to larger pores on the membrane surface and hence the observed higher flux. It is evident in Figure 6.

Similar observation had also been reported by other researchers.^[23] Further, the incorporation of QASPES into the

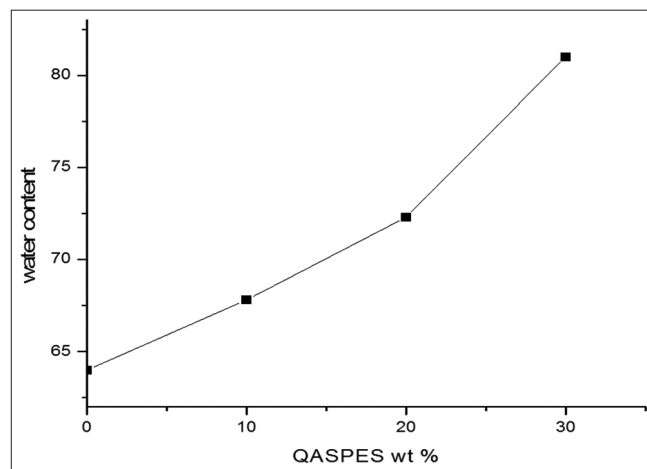


Figure 5: Water content for cellulose acetate/quaternary ammonium salt of polyethersulfone (QASPES) blend membranes with different QASPES contents

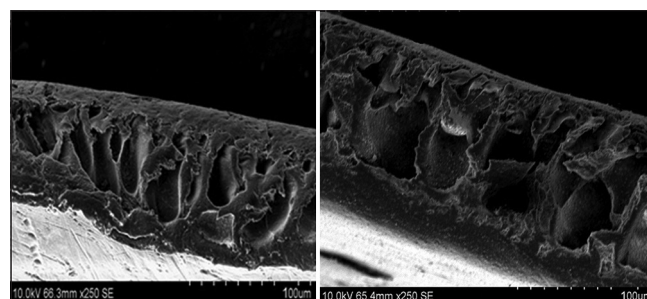


Figure 6: Scanning electron microscope cellulose acetate (CA)/quaternary ammonium salt of polyethersulfone (QASPES) blend membranes with different QASPES contents. Cross section: (a) 90/10% of CA/QASPES. (b) 80/20% of CA/QASPES

CA up to 30 wt. %, as expected, increases the flux to 130 L m⁻² h⁻¹ due to the macrophase separation of blend membrane which, in turn, enhances the pore size of membranes.^[24]

Water content is the important character of the membrane. As QASPES composition increased from 10 to 30 wt. %, the hydrophilic nature of prepared membranes improved it leads to increase the water absorbing capacity. It is evident from the higher pore size as illustrated in the morphological studies. It is shown in Figure 6.

Similarly, the higher percent water content increases with increase the blend composition. When the concentrations of QASPES and PEG 600 are increased simultaneously, the repulsive forces between polymer segments along with leachability of PEG 600 are enhanced. It favors the formation of macrovoids due to the occurrence of more number of large size pores^[25] resulting in higher PWF and percent water content at higher QASPES in CA membrane.

CONCLUSION

Quaternized PES is found to be compatible with CA. The extent of compatibility of CA with aminated PES under room conditions is 70/30 of CA/QASPES wt. %. Further, blending of CA with quaternized PES results in blend membranes with enhanced UF performance such as high water content, lower hydraulic resistance coupled with higher water flux. The addition of QASPES altered the molecular membrane structure and the mechanical properties of the membranes. The improved surface hydrophilicity, due to surface enrichment of quaternary ammonium salt content, endowed the CA/QASPES blend membranes. We conclude that the incorporation of the hydrophilic moiety (QASPES) in blend membranes plays a major role in improving the flux and performance characteristics of membranes.

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