



Preparation of poly (isophthalamide-graft-methacrylamide) and its utilization in the modification of cellulose acetate ultrafiltration membranes



A. Jayalakshmi^a, S. Rajesh^a, S. Senthilkumar^a, H.S. Hari Sankar^b, D. Mohan^{a,*}

^a Membrane Laboratory, Department of Chemical Engineering, Anna University Chennai, Chennai 600025, India

^b Inter University Center for Development of Marine Bio-Technology, School of Marine Sciences, CUSAT, Cochin 687016, India

ARTICLE INFO

Article history:

Received 27 November 2012

Accepted 16 April 2013

Available online 21 April 2013

Keywords:

Ultrafiltration

PIPA-g-MAA

SEM

AFM

Arsenic removal

ABSTRACT

Methacrylamide was grafted on to poly (isophthalamide) (PIPA-g-MAA) to improve its solubility and hydrophilicity. Then, PIPA-g-MAA incorporated high performance cellulose acetate ultrafiltration (CA) membranes were prepared by phase inversion technique and physical properties of the membranes were studied by various analytical methods. The efficiency of these membranes in the removal of arsenic from aqueous stream was studied and an effort has been taken to correlate the separation efficiency with morphology. Overall results suggest that membrane hydrophilicity, structure and performance were improved significantly by the addition of PIPA-g-MAA. Thus PIPA-g-MAA can be considered as an effective modification agent for CA membranes.

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1. Introduction

Polymeric membranes are of attractive alternative to many energy intensive separation processes owing to their good processability, fine-controlled structure, high separation efficiency and low operational cost [1–3]. Advanced membrane filtration techniques like ultrafiltration and nanofiltration exhibit superior performance over conventional water purification systems in the removal of chemical and biological contaminants from industrial effluents [4,5]. However, control over the membrane properties such as morphology, hydrophilicity, pore size and antifouling property is desirable to achieve desired species separation [6,7]. Most of the commercial ultrafiltration membranes are made from polymers such as cellulose acetate (CA), polysulfone (PSf), polyethersulfone (PES) and polyvinylidene fluoride (PVDF). Among

these CA has been successfully employed for the fabrication of UF membranes because of its advantages such as moderate chlorine resistance, low cost and as a raw material from sustainable resources [8]. However, much slower diffusion of the solvent and non-solvent than that of hydrophobic polymer during the diffusion induced precipitation of CA membrane, resulting in a much denser skin layer and a lower porosity in the sub-layer [9].

One of the key factors in the evaluation of the performance of membrane is the trade-off between the membrane selectivity and permeability [10]. Permeation of UF membranes is inversely proportional to the active layer thickness and thus the dense skin layer resulting from the slow diffusion in CA membranes leads to low permeability. Thus the modification of CA membranes in terms of its permeability is the endless necessity of the time and many efforts are devoted in the literature for the same [11]. Prior studies from our lab revealed that, solution blending with hydrophilic polymers is an effective method to improve the CA membranes performance in terms of permeability, simplicity, reproducibility and cost effectiveness [12].

Poly (isophthalamide) (PIPA) is one of the important aromatic polyamides because of their excellent chemical, mechanical and thermal properties [13,14]. However, there are some restrictions on selecting suitable solvents in preparing asymmetric membranes via the traditional phase inversion technique, since the PIPA materials are normally very resistant to solvent dissolution. The processability and solubility of the PIPA can be improved by

Abbreviations: CA, cellulose acetate; PIPA-g-MAA, poly (isophthalamide)-graft-methacrylamide; UF, ultrafiltration; PEG-600, polyethyleneglycol-600; NMP, N-methyl pyrrolidone; ATR-FTIR, attenuated total reflectance-Fourier transform infrared spectra; XRD, X-ray diffraction; SEM, scanning electron microscopy; AFM, atomic force microscopy; MWCO, molecular weight cut off; PEUF, polymer enhanced ultrafiltration; PEI, polyethyleneimine; AAS, atomic absorption spectroscopy.

* Corresponding author. Tel.: +91 044 22359136; fax: +91 044 22350299.

E-mail addresses: mohantarun@gmail.com, mohantarun@yahoo.com (D. Mohan).

Nomenclature

List of symbols

J_w	pure water flux ($1 \text{ m}^{-2} \text{ h}^{-1}$)
Q	quantity of pure water permeated (l)
A	membrane area (m^2)
ΔT	sampling time (h)
R	pore radius (\AA)
m	membrane weight (g)
L_d	average thickness (mm)
s	membrane area (m^2)
ρ	density of the membrane (g/cm^3)
ΔP	operational pressure (kPa)
γ_w^{TOT}	total surface tension (mJ m^{-2})
C_p	concentration of As in the permeate (mg/l)
C_f	concentration of As in the feed (mg/l)

surface graft polymerization with monomers such as 2-hydroxyethyl methacrylate, acrylic acid, methacrylic acid, and polyethylene glycol methacrylate (PEGMA). Herein, we report a new and efficient methodology to improve the solubility and hydrophilicity of PIPA by grafting methacrylamide (MAA) on to PIPA backbone by initiation through benzoyl peroxide. An extensive literature survey revealed that, this is the first attempt that explores the usage of hydrophilic poly (isophthalamide-grafted-methacrylamide) in the modification of CA membranes for UF applications.

In the current study, methacrylamide was grafted on to PIPA and grafting was confirmed by infrared spectroscopy (IR) and ^1H nuclear magnetic resonance spectra (NMR). The significant outcome of the grafting is that, it made PIPA soluble in common aprotic solvents and makes it available as a potential membrane material for the preparation of asymmetric membranes by traditional phase inversion technique. The PIPA-g-MAA incorporated CA ultrafiltration (UF) membranes were prepared by immersion cum precipitation technique. The effect of polymer blend composition on the morphology, pure water flux, porosity and hydrophilicity of CA/PIPA-g-MAA blend membranes were investigated. Further, the effect of CA/PIPA-g-MAA blend composition on the rejection of As (III) and As (V) from aqueous streams was studied by PEUF. Attempts have been made to correlate the changes in the morphology of the blend membranes with performance and separation efficiency and the results are discussed.

2. Experimental

2.1. Chemicals and reagents

Commercial grade MYCEL cellulose acetate CDA5770 ($M_w = 115 \text{ kDa}$; glass transition temperature $214 \text{ }^\circ\text{C}$ and acetyl content 39.99%) was procured from Mysore Acetate and Chemicals Company Ltd., India, and was used after recrystallization from acetone. Commercial grade poly (isophthalamide) ($M_w = 36.8 \text{ kDa}$; glass transition temperature $274 \text{ }^\circ\text{C}$) purchased from Sigma-Aldrich, India was used as supplied. Methacrylamide (MAA) and benzoyl peroxide (BPO) were purchased from Hi-media Laboratories Ltd., India. Analar grade N-methyl-2-pyrrolidone (NMP) obtained from SRL Chemicals, India Ltd., was sieved through molecular sieves (Type-5A) to remove moisture and stored in dry conditions prior to use. Methanol and acetone of analytical grade procured from SRL Chemicals Company Ltd., India, were used as received.

Sodium lauryl sulfate (SLS) of analar grade was obtained from Qualigens Fine Chemicals Ltd., India, and was used as a surfactant in the coagulation bath. Different molecular weight of polyethylene glycols (PEGs) was procured from Merck (I) Ltd. Distilled water was employed for the ultrafiltration experiments and for the preparation of gelation bath. Polyethyleneimine (molecular weight, $M_w = 600,000\text{--}1,000,000$) 50% aqueous solution was procured from Fluka Chemie AG (France) and was used for the preparation of 1 wt% aqueous solution. Analytical grade sodium arsenite and sodium arsenate procured from Sigma-Aldrich, India, were used for preparation of As (III) and As (V) solutions respectively. Hydrochloric acid and sodium hydroxide were procured from SRL Chemicals Ltd., India, and used for pH adjustment.

2.2. Synthesis of PIPA-g-MAA graft copolymers

The graft polymerization was carried out in a heterogeneous polymer–monomer reaction system using BPO as initiator. In a three-necked round bottom flask equipped with dropping funnel and mechanical stirrer, 10 g of PIPA was dissolved in 250 ml of NMP. Prior to the addition of initiator, a steady stream of nitrogen was injected into the homogeneous solution. After 30 min of initiation, 4 g of MAA was added into the reaction vessel. The polymerization was carried out for 24 h at $45 \text{ }^\circ\text{C}$ under nitrogen atmosphere. The product was washed with hot water and the grafted PIPA were collected and dried in an oven at $80 \text{ }^\circ\text{C}$ until a constant weight was reached. Scheme 1 shows the reaction steps involved in the grafting of PIPA. The percentage graft yield (G%) was calculated gravimetrically according to Eq. (1):

$$G(\%) = \left[\frac{w_g - w_0}{w_0} \right] \times 100 \quad (1)$$

where w_g is the weight of PIPA-g-MAA, while w_0 is the initial PIPA weight.

The purified form of PIPA-g-MAA was characterized for functional group determination by an FTIR spectrophotometer (Perkin-Elmer, model-Spectrum RX1), and further by ^1H NMR spectrophotometer (Bruker AM-400 spectrometer, 400 MHz).

2.3. Preparation of blend membranes

The blend solutions for the membranes preparation were formulated by dissolving CA and PIPA-g-MAA in different compositions in the absence and presence of additive PEG-600 using NMP as solvent under constant mechanical stirring for 4 h. A series of such blend solutions were prepared by varying the composition of CA and PIPA-g-MAA as shown in Table 1. The membranes were cast over a glass plate using a doctor blade. After casting, the solvent present in the cast film was allowed to evaporate for 30 s, and the cast film along with the glass plate was gently immersed in to a gelation bath consisting of 2.0% (v/v) NMP (solvent) and 0.2 wt% SLS. The preparation method involved is the same as that of the “phase inversion” method employed in our earlier works as reported by other researchers from our lab [15].

2.4. Ultrafiltration experimental set up

The ultrafiltration experiments were carried out in a batch-type, dead end cell (UF cell, Model 8400, Amicon, USA) with an internal diameter of 76 mm and fitted with a Teflon-coated magnetic paddle. The effective membrane area available for ultrafiltration was 38.5 cm^2 . The schematic representation of the ultrafiltration experimental setup has been given elsewhere [16].

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