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Preparation, characterization and performance study of cellulose acetate membranes modified by aliphatic hyperbranched polyester

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ABSTRACT

Two generations of aliphatic hyperbranched polyester (HBPE) were synthesized from 2,2-bis(methylol) propionic acid and 1,1,1-trihydroxymethyl propane (TMP) as the core moiety by melt condensation method and were blended with cellulose acetate to prepare asymmetric membrane using a phase inversion process. Characterization of the prepared membranes for thermal behavior and morphological studies also has been made using TGA, DSC and SEM techniques. Water contact angle, pure water flux, water content, hydraulic resistance and molecular weight cut-off determinations were applied in order to study of filtration properties and surface and bulk hydrophilicity of the membranes. FTIR/ATR and contact angle results proved existence of (HBPE) on the surface of modified membranes and (FE-SEM) images have good correlation with flux and MWCOs. The result shows that, the surface hydrophilicity of membranes incorporating HBPE is much higher than pure CA or even (PEG-600) modified CA membranes. Furthermore, results show CA-HBPE membranes have lower flux and MWCOs, higher hydraulic resistance and better thermal and mechanical properties in comparison to the membranes modified by linear pore-forming agent.

1. Introduction

Cellulose acetate (CA) membranes have several advantages over other membranes due to their moderate flux, high salt rejection properties, renewable source of raw material, etc. [1]. CA as a polymeric material for membranes preparation for mainly pressure-driven processes had been widely studied and used previously. It is well-known that the first RO membranes applied in sea water desalination used to be casted from CA. But the well-known disadvantages of this polymeric material against others prevented the widespread application of this material for further commercial membrane preparation. Therefore CA membranes are currently commercially used in very limited number of applications while other polymers have found their way for commercially available membranes of different structure (PA, PVDF, PES, PS, PAN etc.). Many studies have been done to improve the thermal or ultrafiltration properties of the CA membranes with the addition of organic or inorganic substances [1–6]. Performance of CA can be improved by mixing it with appropriate hydrophilic polymers to fulfill new requirements and associated membrane properties [7,8]. Recently branched polymers have been investigated as additive in blend membrane compositions [9]. Because of their highly branched structure, these polymers can hardly crystallize, and possess larger free volume than the linear polymer with a similar structure of unit [10]. So far, few attempts have been made to use hyperbranched polymers as additives in porous membrane preparation. Since dendritic polymers are totally different from the additives currently used in terms of the molecular structures, it is possible to get some interesting results when hyperbranched polymers used as additive [11]. These studies have been shown that the increasing content of hyperbranched polymer in the casting solution led to an increase in surface pore size and porosity of the membranes, which in return increased the pure water flux of the blend membranes. However, these reports were mainly focused on the pervaporation and ultrafiltration [12–14]. Aliphatic hyperbranched polyesters based on 2,2-bis(methylol)propionic acid are most important and widely studied hyperbranched polyester in the last decade with wide application because of easy synthesis and commercial availability [15–17]. Since the additives structure and their content are key parameters that determining the CA overall properties, we emphasized on effect of these parameters on surface and bulk morphologies, filtration properties, wettability, thermal behavior and hydrophilicity. So after synthesis of HBPEs with two molecular weights, blend membranes of CA and HBPEs with different compositions were prepared through a typical phase inversion method, comparison with PEG

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modified CA was made and effect of the generation number of HBPEs on properties of CA membranes were investigated.

2. Experimental

2.1. Materials

Cellulose acetate (average Mn ~30,000 and 39.8 wt% acetyl) and BSA were purchased from Sigma-Aldrich. Acetone (>99%), formamide, phenol, sulfuric acid and PEG (different molecular weights), were supplied from Merck. 2,2-Bis(methylol)propionic acid (Bis-MPA), TMP and p-TSA for synthesis of various generations of HBPE were purchased from Merck. Dextran (M_r ~40,000) was supplied from Fluka.

2.2. Synthesis of hyperbranched polyester

Bis-MPA, TMP, and p-TSA in stoichiometric correspondence to a perfect generation of each generation were mixed in a three-necked flask equipped with an argon inlet, a drying tube, and a stirrer. The flask was placed in an oil bath previously heated to 140 °C. The mixture was left to react under a stream of argon, removing the water formed during the reaction. After 2 h, the argon stream was turned off the flask sealed and vacuum was applied for 1 h before the reaction mixture was removed from the flask. FTIR showed no remaining carboxylic acid (1682.47 cm^{-1}, carbonyl) but only ester (1724.28 cm^{-1}, carbonyl). 3 and 4th generations of poly(Bis-MPA) were synthesized with this methodology with M_n=3370, 6620 g mol^{-1} for HBPEG3 and HBPEG4 respectively [18].

2.3. Preparation of membranes

Different blend compositions prepared (as shown in Table 1) and stirred under medium speed for 4 h at 35 °C. Because of great effect on morphology and performance of membranes [19], polymer percent in solution was kept at 20% and thermodynamic conditions were fixed on constant values. Mixture of acetone/formamide with a ratio of 3:2 was used as the solvent which was optimized for best results. Solutions were kept under air tight conditions for 24 h to remove air bubbles. Then solutions were cast on smooth glass using a Dr. blade with 220 ± 10 μm in thickness. After 30 s for solvent evaporating, films were immersed in 2 l of distilled water with 2 wt% of additional solvent, which previously cooled to 0 °C. After 30 min membranes washed and kept in distilled water until tests were done.

Table 1
Blend solution compositions.

Sample	Blend composition				Solvent (wt%)
	CA (wt%)	HBPEG3 (wt%)	HBPEG4 (wt%)	PEG (wt%)	
M0	100	0	0	0	80
M1	97.5	2.5	0	0	80
M2	95	5	0	0	80
M3	92.5	7.5	0	0	80
M4	90	10	0	0	80
M5	97.5	0	2.5	0	80
M6	95	0	5	0	80
M7	92.5	0	7.5	0	80
M8	90	0	10	0	80
M9	100	0	0	2.5	77.5
M10	100	0	0	5	75
M11	100	0	0	7.5	72.5
M12	100	0	0	10	70

2.4. Membrane characterization

The surface and cross-section (fractured in liquid nitrogen) morphologies of membranes were imaged on a field emission scanning electron microscopy (S-4160, Hitachi, Japan). Samples were coated with gold before images were taken. The surface compositions of membranes were characterized using attenuated total reflectance Fourier transform infrared spectroscopy (FTIR/ATR) (Equinox 55, Bruker Optics, Switzerland). DSC measurement of the prepared membranes were carried out using a differential scanning calorimeter (Q100, TA instruments, USA) at a heating rate of 10 °C/min under argon atmosphere. Thermogravimetry studies were carried out using a (Q50, TA instruments, USA) instrument at heating rate of (20 °C/min) under argon atmosphere and flux of 60 ml min^{-1}. Surface contact angles were measured with water droplet (4 μL) using (OCA15plus, Dataphysics, Germany) equipped with a CCD camera for picture and video capture. Average contact angles were obtained from four values measured for each sample. For mechanical tests, 15 mm in width strips prepared from each sample and tensile strength and Young's module measured with (F81502, FRANK, Germany) instrument.

2.4.1. Flux and fouling resistance determinations

Flux measurements were carried out by loading the membranes in a batch type, dead-end cell at a pressure of 500 kPa for 30 min, and then the membranes were subjected to pure water flux estimation at a hydraulic trans-membrane pressure of 400 kPa (J_{w1}). After that, feed was switched to 1.0 mg/ml BSA in phosphate buffer solution (pH=7.0). Finally membranes and cell were rinsed several times with distillated water and then retained flux (J_{w2}) was determined, too. BSA solution or pure water flux determined as follows [20]:

$$J_{w,p} = Q/A\Delta t \quad (1)$$

where Q is the quantity of permeate collected (in L), J_w is water flux (in l m^{-2} h^{-1}), Δt is the sampling time (in h), and A is the effective membrane area (in m^2). Flux recovery ratio (FRR) used as a parameter, in order to evaluate the fouling resistance and hydraulic cleaning properties of membranes, which calculated as follows:

$$FRR = [J_{w2}/J_{w1}] \times 100 \quad (2)$$

To evaluate the antifouling property of pure CA and blend membranes, the degree of irreversible flux loss caused by irreversible fouling (R_{ir}) and reversible flux loss caused by reversible fouling (R_r) is calculated using the following equations respectively:

$$R_{ir} = [(J_{w1} - J_{w2})/J_{w1}] \times 100 \quad (3)$$

$$R_r = [(J_{w2} - J_p)/J_{w1}] \times 100 \quad (4)$$

The specific flux, J_s, allows for the normalization of the water flux with the trans-membrane pressure and membrane class determination [21]

$$J_s = J_w/P_{tm} \quad (5)$$

where J_w is water flux (in l m^{-2} h^{-1}) and P_{tm} is the trans-membrane pressure (in kPa).

2.4.2. Hydraulic resistance (R_m)

The membrane hydraulic resistance (R_m) was calculated by measuring the pure water flux at different trans-membrane pressures (Δp) at 300, 400 and 500 kPa and slope of water flux versus trans-membrane pressure (Δp) obtained using the following equation [20]:

$$R_m = \Delta p/J_w \quad (6)$$