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Influence of surface modifying macromolecules on the surface properties of poly(ether sulfone) ultra-filtration membranes

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ABSTRACT

The separation performances and physico-chemical characteristics of poly(ether sulfone) membranes were evaluated by blending of surface modifying macromolecules (SMMs). Hydrophobic SMMs (bSMM) and charged SMMs (cSMM) were synthesized and characterized. By addition of SMMs, glass transition temperature decreased and membrane pore size increased. The membrane became more hydrophobic by blending of bSMM, and became more hydrophilic after addition of cSMM. It was also demonstrated by the result of surface free energy study that the bSMM blended membrane showed the lowest solid–liquid (water) interaction by low Lifshitz–van der Waals interaction and Lewis acid (liquid)–base (solid) interaction. In contrast, cSMM blended membrane showed the highest Lewis acid–base interaction, which resulted in the highest interaction energy between membrane surface and liquid (water). It was also found from the result of differential scanning calorimeteric measurement that bound water was formed in the cSMM blended membrane.

1. Introduction

Nowadays, membrane technologies are playing an important role in water treatment processes due to the reliability of contaminant removal without producing any harmful by-products. However, the most common problem associated with the application of the membrane process in water treatment is fouling, i.e., the flux declines with operation time. There are various techniques to solve the problem; e.g. pretreatment process installation, membrane cleaning (physical and chemical), membrane surface modifications (by blending, grafting, nanoparticle incorporation, surface chemical reaction, etc.), ultrasonic entrenchment, etc. In particular, membrane surface modification has become one of the most important fields in the research [1].

Blending polymers with hydrophilic functional groups is one of the methods of surface modification [2–11]. Very recently, commercial track-etched membranes made of polycarbonate–poly(vinyl pyrrolidone) (PC–PVP) were modified by coating polymer nanotubules to incorporate Sn^{2+} ions [2]. Liu et al. modified poly(ether sulfone) (PES) membranes through the grafting of poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), and chitosan after UV/ozone treatment [3]. All the membranes with additives showed more hydrophilic surface property and lower protein adsorption, but the PEG grafted membrane showed the most favorable results in terms of hydrophilicity and protein adsorption. The modified membranes functioned as a separation barrier based on size, charge and hydrophobicity of the small molecules in the feed. Poly(methyl methacrylate) (PMMA)–single-walled carbon nanotubes (SWNTs)–subtilisin Calsberg (SC) composite membranes having excellent anti-biofouling activity were fabricated [4]. The SC enzymes break down the bio-film and disperse in the PMMA matrix. In the presence of SWNT, the SC could be loaded 30 times more than without SWNT, resulting in tremendous enhancement of the biocatalyst activity. Idris et al. studied the performance of membranes made by the addition of low molecular weights (200, 400, and 600 Da) of PEGs in PES solution [5]. De Bartolo et al. modified the polymer solution using plasma treated acrylic acid (AA), followed by immobilization of the amino acid sequence [6]. The immobilized membranes showed better performance in terms of protein secretion and biotransformation of human hepatocytes. Reddy et al. coated PES membranes through *in situ* polymerization of various acrylates and made nanofiltration membranes [7]. Ochoa et al. reported that addition of PVP with various molecular weights in the casting solution of PES resulted in increased permeability without significant change in selectivity [8]. The membranes with PVP of higher molecular weights had larger pores and exhibited higher pure water permeation (PWP). The membrane surface became rougher with increased molecular weight of PVP. Wang et al. found that the addition of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), PEO–PPO–PEO, triblock copolymers in the casting solution of PES exhibited less fouling in bovine serum

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albumin (BSA) filtration [9]. Cho et al. modified PES membranes by using low-temperature plasmas of oxygen, AA, acetylene (AC), diaminocyclohaxane (DACH), hexamethyldisiloxane (HMDSO) [10]. The oxygen, AA, and DACH plasma treated membranes were more hydrophilic whereas AC and HMDSO treated membranes were more hydrophobic compared to the original membrane. The hydrophilic membranes showed higher initial fluxes as well as improved fouling resistance. On the other hand, the hydrophobic membranes displayed both lower fluxes and lower fouling resistance. The PEO/PPO substituted ethylene diamine was added to the casting solutions of PES. The modified membranes provided low fouling in milk filtration and could be easily cleaned by water compared to the control membrane [11]. Blending PEG, PEO, PVA, PVP, etc., into the casting solution increases the surface hydrophilicity of membranes and thus may reduce the fouling. However, they will eventually leach out from the surface due to their high solubility in water [12]. Wang et al. reported that blending of an amphiphilic sulfobetaine copolymer in PES casting solution decreased the flux reduction in BSA filtration [13]. These additives may also be leached out after a long period of operation.

In some of the above approaches, not only the surface but the whole bulk of the membrane is modified by blending the second component to the host polymer. Membrane surface modification by blending surface modifying macromolecules (SMMs) is, on the other hand, clearly targeting the modification of the membrane surface based on the principle of surface migration of SMMs, which renders the membrane surface either hydrophilic, hydrophobic or charged, while leaving the bulk of the membrane intact. Moreover, SMMs remained at the membrane surface for a much longer period due to the affinity between their central polyurethane (PU) segment and the host base polymer [14–22].

The objective of this work is to study the surface properties of the SMM blended poly(ether sulfone) (PES) membranes and also to investigate the relationship between the surface properties and the membrane performance.

Tailor-made hydrophobic SMM and charged SMM were synthesized by end-capping the PU prepolymer with oligomeric fluoro-alcohol, OFA, and with hydroxybenzene sulfonate, sodium salt (HBS). The surfaces of SMMs blended and control membranes were investigated by the cross-flow ultra-filtration (UF), differential scanning calorimeter (DSC), and static contact angle (SCA).

2. Experimental

2.1. Materials

All chemicals used in this work and their chemical abstract service (CAS) number are enlisted in Table 1.

2.2. SMMs synthesis and characterization

2.2.1. SMMs synthesis

The SMMs were synthesized using a two-step polymerization process described in detail elsewhere [12–14,20–22]. The first step was conducted in a solution with a predetermined composition to form polyurethane for the reaction of methylene bis(*p*-phenyl isocyanate) (MDI) with poly(propylene glycol) (PPG) or PEG as a prepolymer. The prepolymer was then, in the second step, end-capped. Addition of oligomeric fluoro-alcohol (OFA) as the end-capping agent resulted in hydrophobic SMM (bSMM) solution in the organic solvent. On the other hand, addition of hydroxybenzyl sulfonate (HBS) resulted in charged SMM (cSMM) solution. The ratio of the monomers used in the SMM synthesis was MDI:PPG425:OFA = 3:2:2 and MDI:PEG200:HBS = 3:2:2, respectively, for bSMM and cSMM. Here PPG425 represents the PPG of typical number average molecular weight (M_n) 425 Da and PEG200 represents the PEG of typical M_n 200 Da. All the SMMs were precipitated in water and dried in an oven over 3 days before use.

The chemical structures of the SMMs are shown in Fig. 1. The names of the bSMM and cSMM are poly(4,4′-diphenylenemethylene propylene-urethane) with both ends capped by OFA and poly(4,4′-diphenylenemethylene ethylene-urethane) with both ends capped by HBS, respectively.

2.2.2. SMMs characterization

The elemental analysis of fluorine content in the prepared bSMM was carried out using standard method in ASTM D3761. A certain amount (about 10–50 mg) of sample was placed into the oxygen flask bomb combustion (Oxygen Bomb Calorimeter, Gallenkamp).

Table 1
The materials used in this work.

Material description	CAS number	Source
Polyethersulfone[a] (PES) (Victrex 4100P, powder)	25667-42-9	ICI Advanced Materials, Billingham, Cleveland, England
Poly(ethylene oxide) (PEO), typical M_w of 100,000 and 200,000 Da	25322-68-3	Aldrich Chemical Company, Inc., Milwaukee, WI, USA
Poly(ethylene glycol) (PEG), typical M_w of 35,000 Da	25322-68-3	Fluka Chemie AG, Buchs, Switzerland
PEG, typical M_w of 400, 1000, 4000 and 10,000 Da	25322-68-3	Sigma Chemical Company, St. Louis, MO, USA
1-Methyl-2-pyrrolidinone (NMP), anhydrous 99.5%	872-50-4	Aldrich Chemical Company, Inc., Milwaukee, WI, USA
Ethylene glycol, anhydrous, 99.8%	107-21-1	Sigma–Aldrich, Inc., St. Louis, MO, USA
Diiodomethane, ReagentPlus, 99%	75-11-6	Sigma–Aldrich, Inc., St. Louis, MO, USA

[a] Weight average molecular weight (M_w) = 30,800 ± 800 Da with polydispersity of 1.55 ± 0.45, measured by multiple angles laser light scattering (MALLS) with refractive index (RI) detector equipped with Tosoh TSK gel GMHHR-H_xZ column, mobile phase 10 mM LiBr in dimethylformamide (DMF) and flow rate 1 ml/min.

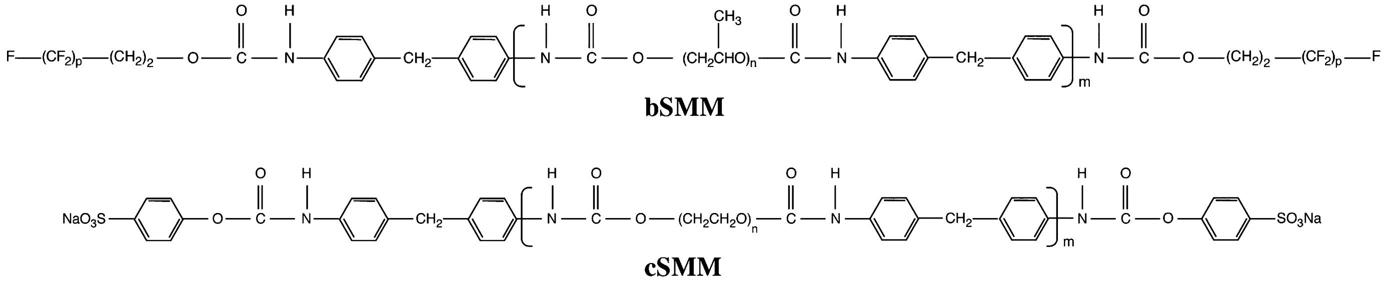

Fig. 1. The chemical structure of bSMM and cSMM.