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Preparation of polyelectrolyte multilayer films consisting of sulfonated poly (ether ether ketone) alternating with selected anionic layers

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ABSTRACT

We have developed a new approach involving the use of pressure during the alternating physisorption of oppositely charged polyelectrolytes on porous supports. For example, new polyelectrolyte multilayers (PEMs) as selective skins in composite membranes for NF were prepared by alternating layer-by-layer deposition of sulfonated poly (ether ether ketone) (sPEEK) and branched polyethyleneimine (PEI). During this electrostatic self-assembly deposition, it was demonstrated that the use of pressure could increase the salt rejection of the PEMs by one to two times. The effect of polymer charge density on membrane performance, e.g. sulfonation degree of sPEEK, was also studied. By depositing the sPEEK dissolved in methanol and branched PEI dissolved in water, the rejection of the PEMs could be further increased. The rejection is about 89% and very close to that of current commercially successful polyamide membranes, which is about 96%. The antifouling property of the PEMs has also been studied. Our membranes have a better antifouling property in comparison with commercial membranes, NTR 7450.

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1. Introduction

The alternating physisorption of oppositely charged polyelectroytes on porous supports is a relatively new technique that provides a simple way to create ultrathin polyelectrolyte multilayers (PEMs). In the late 1960s, Iler first reported the alternate self-assembly of charged colloidal particles and suggested the idea of building a multilayer structure from polycations and polyanions by electrostatic interaction [1]. In 1991, Decher and Hong first deposited charged polymers alternately to form thin multilayer films by this method [2,3]. In comparison with Langmuir–Blodgett (LB) or conventional spin coating and casting techniques, the electrostatic self-assembly has several advantages: (1) the films are mechanically stable because of a strong electrostatic interaction; and (2) there are no pinholes and other defects as in LB films. In addition, this process can be carried out under ambient conditions using economically available raw materials [4].

PEMs, typically <1 μm thick, are created by alternately exposing a substrate to positively and negatively charged polyelectrolyte with an interval process, e.g. the rinse of water and/or drying. The amount of adsorbed polyelectrolyte and the layer structure (conformation of the attached chains) are governed by parameters such as the charge density of the polyelectrolyte, the sign and the density of the surface charge, and the ionic strength of the depositing solution [5–7]. As illustrated in Fig. 1, in general, higher charge density of the polymer results in a more compacted conformation. When salts are added, the charge of the polymer will be screened to some extent. This is the same effect as the reduction of charge density of the polymer, i.e. layer becomes thicker and more polymer segments are adsorbed.

The method of polyelectrolyte self-assembly has now been adopted in many applications including controlled drug delivery, molecular sensors, artificial muscles, solid battery electrolytes, and separation membranes. Despite the enormous research activities in the field of polyelectrolyte multilayers, only a small number of publications involved this simple technique for the preparation or modification of membranes, especially for NF membranes [4,8]. However, there are several advantages of PEM films for NF membranes [9]. First, PEM films have high water adsorption. It was reported that from 6 to 10 water molecules were associated with each ionic group (regardless of sign) in a neutral polyelectrolyte complex. This number corresponds to the first hydration sphere around ions. Since these water molecules can be considered as bound water instead of free water, it is possible to achieve a high selectivity in the passage of water relative

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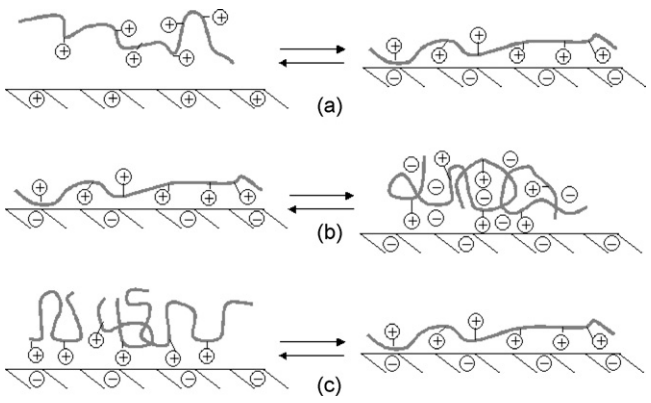

Fig. 1. Schematic description of the adsorption of a charged homopolymer at a solid surface. Effects of (a) surface charge, (b) electrostatic screening and (c) charge density of the polymer on the amount and the structure of the adsorbed polyelectrolyte [4].

to the passage of salt. Second, the proximity of ionic groups facilitates the transport of water. Finally, for non-neutral complexes, the presence of immobilized ions in NF membranes will suppress the imbibing of ions from solution due to the Donnan exclusion effects. In addition, this "layer-by-layer" or "electrostatic self-assembly" (ESA) method affords control over thickness, charge density, and composition of the selective skin layer in NF membranes. Moreover, a wide range of polyelectrolytes is available to form PEM films. Therefore, flux, selectivity and possibly fouling rates of NF membranes could be tailored by judicious selection of constituent polyelectrolytes. Despite the versatility of PEM films, studies for NF application thus far primarily focused on poly (styrene sulfonate)/poly (allylamine hydrochloride) (PSS/PAH) [10], PSS/chitosan [11], PSS/poly(diallyldimethylammonium chloride) (PDADMAC) [11], hyaluronic acid (HA)/chitosan [11], and poly (vinyl amine)/poly (vinyl sulfate) [12]. The highest rejection among the PEM films reportedly Bruening and coworkers was only around 40% for a feed concentration of 0.01 M NaCl [10,11]. Although Tieke and coworkers achieved 84% rejection for 0.01 M NaCl, the flux was relatively low (~0.013 $m^3\,m^{-2}\,day^{-1}$ at 5 bars) in his case he deposited 60-bilayer poly (vinyl amine)/poly (vinyl sulfate) films on PAN/PET supporting membranes [12]. In addition, all these PEM films were prepared in water. The formation of PEM films in organic solvents for NF application has received much less attention.

Our study demonstrates the preparation of PEM films having a high salt rejection (up to 89%) with only several bilayers (below 5 bilayers) of sulfonated poly (ether ether ketone) (sPEEK) and branched polyethylenimine (PEI). The typical structure is shown in Fig. 2. It was found that the salt rejection could be increased two or three times by pressing water through the membrane during the film deposition. The effect of pressure during the formation of PEMs has been mentioned by Zhang et al. [13]. However, their study focused on pervaporation membrane, which operated at pressure of 0.001 bar, while NF membranes usually operate at the pressure from 4 to 14 bar. In addition, the pressure they used during the deposition of PEMs was only one bar, while we studied the pressures above 6.89 bar. Zhang et al. also reported the reduced swelling during the preparation of PEM from poly (acrylic acid) aqueous solution and polyethylenimine (PEI) ethanol solution [14]. However, the PAA and PEI are soluble in water and the corresponding PEM will still swell a lot in water. Therefore, we proposed to use sPEEK, the solubility of which varied with different degree of sulfonation [15]. For example, sPEEK is insoluble in common solvents at moderate temperatures below 30% sulfonation. Above 30%, sPEEK is soluble in hot DMF, NMF, DMAc and DMSO, above 40%, in the same solvents at room temperature; above 70%, in methanol and at 100% in hot water. By using the special sPEEK insoluble in water, the back dissolution effect of sPEEK on contact with PEI aqueous solution during the deposition of PEMs can be reduced. The swelling of the final PEM can also be reduced. We have prepared PEM films consisting of sPEEK in different organic solvents such as methanol and N-methylformamide (NMF). We have also prepared PEM films from sPEEK and poly (4-vinylpyridine) (P4VP) in methanol, where the salt rejection was 62%.

2. Experimental

2.1. Materials

PAN (homopolymer, T_g = 85 °C, average M_w 150,000), polyvinylpyrrolidone (PVP, M_w = 29,000), branched polyethylenimine (PEI, typical M_n = 10,000 (GPC), typical M_w = 25,000 (LS)), low molecular weight polyethylenimine (typical M_n = 600 (GPC), typical M_w = 800 (LS), branched), and poly (4-vinylpyridine) (P4VP, typical M_w = 160,000, T_g = 142 °C (onset, annealed)) were received from Aldrich. Poly (ether ether ketone) (PEEK) pellets was purchased from Polysciences Inc.

2.2. Preparation of asymmetric hydrolyzed PAN UF membranes for substrate membranes

The UF membranes were prepared by the phase separation technique using water as a coagulant. PAN was used as a membrane material and PVP as an additive to make the membrane more porous. PAN and PVP powder were dissolved at 80–90 °C with stirring in DMF to form a 15:5 wt.% PAN:PVP casting solution. The solution was cast onto a Hollytex® polyester non-woven fabric using a laboratory membrane-casting machine (Separation Systems Technology, USA). The nascent membrane was immersed in a room temperature tap water coagulation bath without evaporation of solvents in the air. After precipitation, the membrane was kept in a water bath for several days and then washed with deionized water before further experiments. The substrate membrane

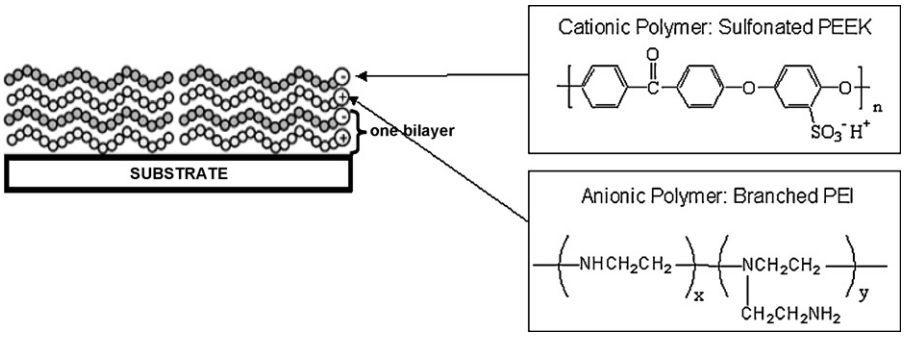

Fig. 2. Layer-by-layer electrostatic assembly of sPEEK and PEI.