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Surface modification of a polyamide reverse osmosis membrane for chlorine resistance improvement

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ABSTRACT

A surface modified polyamide (PA) thin film composite (TFC) membrane was prepared using in-situ polymerization of sorbitol polyglycidyl ether (SPGE) on the membrane surface immediately after interfacial polymerization of TFC membranes. This modification was conducted to protect the chlorine-sensitive sites of the PA membrane using a chlorine-resistant hydrophilic SPGE polymer. The optimum preparation condition of the modified PA TFC reverse osmosis membranes was investigated, and then the successful modification of the membrane was confirmed using various analytical tools including Fourier transform infrared spectroscopy, a zeta potential analyzer, a contact angle analyzer, X-ray photoelectron microscopy, scanning electron microscopy, and atomic force microscopy. The modification converted the surface of the membrane to a more neutral, hydrophilic, and smooth surface. With increasing SPGE concentration in the coating solution, molecular overlapping of the coating polymer led to a denser coating layer, which resulted in declined flux but increased salt rejection. Chlorination tests showed that the modification of the membrane using SPGE ring-opening polymerization improved chlorine stability.

1. Introduction

Reverse osmosis (RO) is a membrane-based desalination process in which relatively pure water is transported across the membrane by the pressure gradient between the feed and permeate water, while dissolved organics and inorganics are rejected due to the chemical nature of the membrane material and the physical structure of the membrane [1]. Since the development of composite polyamide (PA) membranes using interfacial condensation method by Cadotte [2], drastic progress in RO membrane technology has been made. However, widespread use of the membrane is limited due to the adsorption of retained organic and/or inorganic materials and the subsequent decline in performance [3]. Fouling, which is defined as the (ir)reversible deposition of retained materials, can be mitigated through pretreatment of feed water before the membrane filtration and minimized by a physical or chemical cleaning process after filtration. Among the techniques controlling membrane fouling, the addition of chlorine to the feed water is one of most convenient method and has been adopted in many RO applications for deactivating microorganisms causing membrane biofouling. Since the PA membrane is reported to be very sensitive to chlorine [4–8], reducing agents need to be used in the dechlorination process. Partial failure of the dechlorination process can result in the deterioration of PA membranes, making the whole membrane useless.

Various approaches have been devised to develop chlorine-resistant membrane by eliminating chlorine-sensitive sites of the PA membrane or protecting the sensitive sites using chlorine-resistant coating materials. Amide nitrogen and aromatic rings of the PA membrane are sites that can be easily attacked by chlorine. Kawaguch and Tamura [9] chlorinated secondary and tertiary amide to investigate chlorinating behavior in the presence or absence of amidic hydrogen and demonstrated that the amide nitrogen is a key chlorination reaction site. Uemura and Kurihara [10] observed that a cross-linked N-substituted PA TFC membrane is more chlorine tolerant compared to a typical cross-linked PA TFC membrane. Glater and Zachariah [11] investigated the effect of chlorine on a PA membrane and concluded that chlorine attacks on aromatic rings change the hydrogen-bonding forces. Chlorination of the aromatic ring in the PA membrane can be blocked by the substitution of a deactivating functional group such as $-NO_2$ or $-SO_3H$ at the ring position [12]. Son and Jegal [13] developed TFC RO membranes using several different amines and trimesoyl chloride (TMC) and showed that the m-phenylene diamine (MPD) derivative with functional groups such as $-CH_3$ and $-OCH_3$ has better chlorine tolerance. Surface modification such as grafting or physical adsorption is a potential technique to improve chlorine resistance of commercially available PA membranes. Du and Zhao [14] prepared poly (N,N-dimethylaminoethyl methacrylate) (PDMAEMA) positively charged nanofiltration membranes using an interfacial cross-linking reaction and demonstrated that the membrane was stable

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during 28-days storage in 5 ppm NaOCl preservatives. Based on the results of Du and Zhao, Kang et al. [15] coated PA RO membranes with the PDMAEMA and demonstrated that the coated membrane shows better chlorine resistance. Polyvinyl alcohol (PVA) is a hydrophilic and electric neutral polymer that has been applied to the RO membrane to improve hydrophilicity and, thus, antifouling properties. Furthermore, the PVA coating was reported to provide enhanced chlorine resistance to the membrane [16]. Considering long-term stability, the cross-linked structure of these coating materials is desirable. However, modification using a grafting or physical adsorption method requires another cross-linking step, which might be economically undesirable. Therefore, it is economically favorable to form the cross-linked coating using only one step.

The objective of this study was to develop a novel method that is suitable for surface modification of an aromatic PA RO membrane to improve its chlorine tolerance. Cross-linked sorbitol polyglycidyl ether (SPGE) was polymerized on the PA RO membrane surface via in situ ring-opening polymerization. N,N-dimethylaminopropylamine (DMAP) and glycerol were used as a ring-opening agent and a humectant. The physicochemical properties of the membrane surface were analyzed using various analytical tools and compared before and after the coating process. Permeability and selectivity of the virgin and modified membranes were evaluated by filtration of a 2000 ppm NaCl aqueous solution at 25 °C under the operating pressure of 1.5 MPa. Exposures of the membranes to 100 ppm free chlorine solutions during various exposure times were carried out to evaluate membrane chlorine resistances.

2. Experimental materials and methods

2.1. Chemicals and reagents

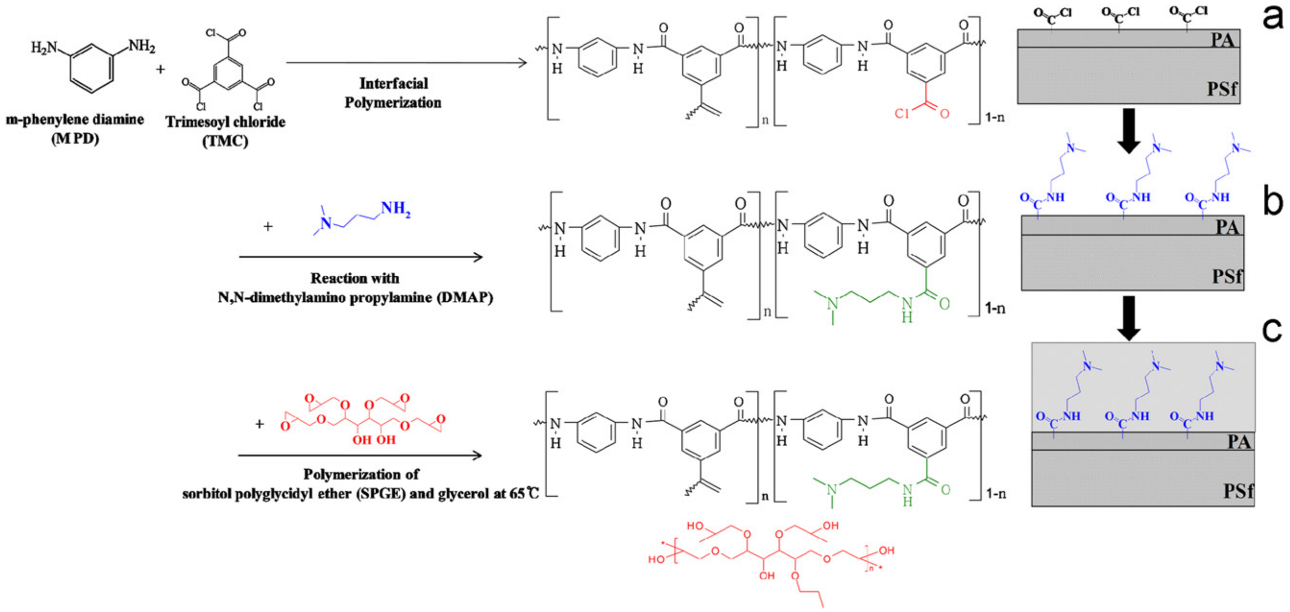
Polysulfone layer on a nonwoven fabric was prepared using polysulfone beads with a number average molecular weight of 35,000 Da (Solvay Advanced Polymers, L.L.C., USA) and N,N-dimethyl formamide (DMF) (Acros Organics, USA). The chemicals used in the PA skin layer formation include 2.25 wt% m-phenylene diamine (MPD) (Sigma-Aldrich) dissolved in deionized (DI) water and 0.06 wt% trimesoyl chloride (TMC) (Sigma-Aldrich). A proprietary organic solvent, Isol-C (SK Chemical Inc., Korea), was selected to dissolve the acid chloride and prepare the organic phase solution for the interfacial polymerization. The reaction time for the interfacial polymerization was 90 s. N,N-dimethylamino propylamine (DMAP) (Acros Organics, USA) and sorbitol polyglycidyl ether (SPGE) (JSI Co., Ltd., Korea) were used to modify the PA membrane surface.

2.2. Modification of PA membranes

The top layer of the PA TFC membrane has residual carboxylic acids (–COOH) [17]. The formation of the carboxylic acid is due to the hydrolysis of acyl chloride groups (–COCl) that were remained after the reaction with amine. Therefore, further modification of nascent TFC membrane is possible through a chemical reaction between the unreacted acyl chloride groups and other amine-containing chemicals when the further reaction is conducted before hydrolysis of the acyl chloride is complete [18]. After the interfacial polymerization reaction between TMC (0.06 wt%) and MPD (2.25 wt%), excess hydrocarbon solution was removed and the membrane was subsequently dipped into a solution of DMAP in DI water for 5 min. The membranes were rinsed with DI water to remove the residual DMAP solution and then the membrane was dipped into a solution containing SPGE and glycerol. The glycerol worked as a humectant, while the DMAP, a tertiary amine, was used as both an anchor to hold the SPGE to the membrane surface and a ring-opening agent since tertiary amine can initiate ring opening of the epoxy moiety of the SPGE polymer [19]. The ring-opening polymerization reaction of SPGE was carried out in a convection oven at 60 °C for 5 min, and the glycerol prevented the membrane from drying out in the oven (Scheme 1). All of the membranes were thoroughly washed with and stored in DI water before test.

2.3. Membrane surface characterization and performance evaluation

The chemical composition changes after modification of the PA membrane that confirm the successful coating of the DMAP and SPGE on the PA TFC membrane were investigated using Nicolet Magna 550 Fourier transform infrared spectroscopy (FTIR) (Midac, USA) and SIGMA PROBE X-ray photoelectron spectroscopy (XPS) (Thermo VG



Scheme 1. Schematic drawing of the surface modification process: (a) polyamide (PA) thin film composite (TFC) membrane, (b) DMAP-treated TFC membrane and (c) SPGE-treated TFC membrane.