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Facile *in situ* PEGylation of polyamide thin film composite membranes for improving fouling resistance

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ABSTRACT

We report a novel approach for *in situ* PEGylation of thin film composite (TFC) reverse osmosis (RO) membrane for sustained performance. The approach was based on use of end-functionalized polyethylene glycol (MPD-PEG-MPD or MeO-PEG-MPD) with end groups structure resembling the structure of *m*-phenylenediamine (MPD), commonly used for preparation of TFC membrane. Michael addition reaction between MPD and acrylate-terminated-polyethylene glycol (AA-PEG-AA or MeO-PEG-AA) produces such type of end-functionality for further use in interfacial polymerization (IFP) with conventionally used trimesoyl chloride (TMC). PEGylated TFC membranes exhibited superior antifouling property during water desalination in presence of fouling agent (protein) compared to non-PEGylated TFC membrane. The best results were obtained with the membranes prepared by addition of 0.25–0.5% (w/v) of AA-PEG-AA or MeO-PEG-AA to the MPD solution (2% w/v in water) for Michael addition reaction prior to IFP with TMC (0.125% w/v in hexane) in as much as the antifouling property was enhanced and the performance (salt rejection efficiency and flux) remained almost unaffected. TFC membranes were characterized by Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), contact angle (θ), scanning electron microscope (SEM), atomic force microscope (AFM) and CHN analyses. The incorporated PEG remained stable in the polyamide network and is mainly attributed to the participation of both MPD and MPD-PEG-MPD or MeO-PEG-MPD in the IFP process.

1. Introduction

Numerous publications, patents and field studies have witnessed significant progress of use of TFC membranes for water desalination, water purification, nanofiltration applications and separation of organics from aqueous streams [1–9]. TFC membranes are usually prepared *via* IFP between water soluble aromatic diamines, preferably MPD and hexane soluble aromatic multifunctional acid chloride, preferably TMC [1–5]. Subsequently, efforts were also made to enhance the performance of TFC membranes [6–9]. IFP reaction takes place in the interface between water and organic, preferably towards the organic phase due to limited diffusion of aromatic acid chloride towards water. This innovative route is extremely successful for the preparation of TFC membranes owing to fast reaction between amines with acid chlorides, limited diffusion of amine and acid chloride monomers towards the interfacial zone, unique cross-linked network formation with network pore size smaller than NaCl and larger than water and finally, formation of thin film (thickness ~100–200 nm). The main reason of thin film formation is the limited diffusion of reactive monomers towards the interfacial zone. Varieties of acid chlorides such as 5-isocyanato-isophthaloyl chloride, 5-chloroformyloxy-isophthaloyl chloride, cyclohexyl tricarboxylic acid chloride, and 2,4,6-pyridinetricarboxylic acid chloride were also used for the preparation of TFC membrane to study the effect of structure on the performance of the resultant TFC membranes [5,10–12]. Further, TMC was reacted with mixture of MPD+*m*-phenylenediamine-5-sulfonic acid or MPD+2,2′-benzidinedisulfonic acid for the preparation of TFC membranes [13,14]. These studies revealed structure–property relationship of the prepared membranes.

Although, TFC RO membranes show great promises where purification, especially water purification is required, however, the RO technology is greatly limited by fouling, which is a major obstacle for membrane application [4,5]. The performance of fouled RO membrane can partially be restored by appropriate cleaning process. However, such cleaning processes inevitably increase operation difficulty and decrease membrane′s life time, which turn enhance the overall cost. Hence efforts were made to design membranes with enhanced antifouling property by

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various means [15]. To mitigate membrane fouling, and to provide long-term solution, a convenient way is the surface modification to prepare antifouling membrane by enhancing hydrophilicity on the membrane surface. Surface modification of TFC membrane can be categorized into two major classes: (i) physical adsorption or coating over the surfaces and (ii) covalent attachment of antifouling polymer chains on the TFC membrane surfaces [16–25]. Grafting of polymer chains by surface initiated polymerizations, covalent grafting methods and chemical coupling are the examples of covalent attachment of hydrophilic polymers. Such approaches are promising and enhance the antifouling property. However, one drawback of post-surface modification technique is the lowering of flux of resultant membranes for many cases. Moreover, controlling the polymerization parameters for maintaining proper grafting density for antifouling property is also difficult.

PEG is hydrophilic and well known for imparting antifouling property on membrane surface. Besides surface initiated polymerization on membrane surface, immobilization of PEG on TFC polyamide membrane was achieved by treating the premade polyamide surface with amine-terminated PEG and glycidyl ether-terminated PEG [18,26]. Amine-terminated PEG and glycidyl ether-terminated PEG react with available –COCl and $-NH_2$ groups of the polyamide network respectively. Thus the grafting density of the immobilized PEG chains depends on the concentration of unreacted –COCl or $-NH_2$ groups present in the polyamide film. Zou et al. reported the modification of TFC membrane by PEG-like hydrophilic polymer, *via* plasma polymerization to reduce organic fouling [27]. Hydrophilic surface modifying macromolecules such as combination of reactive diisocyanate and PEG were reported to enhance the antifouling property of the membranes when added into the TMC solution before IFP [28]. Addition of polyvinyl alcohol into the piperazine solution during IFP produced nanofiltration membranes with enhanced antifouling property and nanofiltration performance [29]. Zhang et al. reported preparation of nanofiltration membrane on the surface of modified pluronic/polyethersulfone ultrafiltration membranes by the IFP between piperazine and TMC. This approach resulted TFC membrane with antifouling property due to exposure of polyethylene oxide segments [30]. Coating of silver-PEGylated dendrimer nanocomposite on the surface of TFC membrane was reported to enhance the antifouling property of the resulted membrane [31]. Surface initiated atom transfer radical polymerization (ATRP) of sulfobetaine methacrylate on aromatic polyamide TFC membrane surface resulted grafting of TFC membrane by fouling resistant zwitterionic poly(sulfobetaine methacrylate) polymer. This approach was based on post-attachment of ATRP initiator on membrane surface followed by metal catalyzed ATRP [32]. Hence, in order to mitigate membrane fouling, design of novel low fouling TFC membranes without much compromising the performance is highly desirable.

Herein, we report a novel and convenient approach for *in situ* hydrophilization of TFC-RO membranes by IFP between TMC and mixture of MPD+premade Michael adduct (formed by the reaction between MPD and AA-PEG-AA or MeO-PEG-AA). The mechanism of incorporation of polyethylene oxide (polyether) type of oligomeric/polymeric chains into the polyamide network has been investigated. It is demonstrated here that the reaction between excess MPD and AA-PEG-AA or MeO-PEG-AA produced MPD-PEG-MPD or MeO-PEG-MPD which participates in the IFP with TMC in similar way as MPD. Under certain concentration of MPD-PEG-MPD or MeO-PEG-MPD, obtained TFC membranes exhibited enhanced antifouling property and similar performance compared to TFC membrane prepared with neat MPD and TMC. The advantages of this approach have been discussed.

2. Experimental

2.1. Materials

Polysulfone (PSf, Udel P-3500, Solvay Polymers) was dried at 80 °C for 2 h prior to the preparation of the casting solution in dimethylformamide (DMF). TMC (98%), MPD (98%), poly(ethylene glycol)diacrylate (AA-PEG-AA, $M_n=700$ g/mol) and poly(ethylene glycol)methyl ether acrylate (MeO-PEG-AA, $M_n=480$ g/mol) all from Aldrich were used as received. Amine terminated poly (ethylene glycol) (H_2N-PEG-NH_2) was prepared by the reported procedure [18]. DMF (99.5%), dichloromethane (DCM), hexane and bovine serum albumin (BSA) from Spectrochem, India, were of analytical grade and used without further purification. Non-woven polyester fabric (Nordlys, TS100) was used as received.

2.2. Preparation of PSf support membrane

The PSf support membrane was prepared on non-woven fabric by phase inversion method using semi-automated casting machine as described earlier [12]. Briefly, PSf was dissolved in DMF at concentration of 15% (w/v) under stirring at 70 °C to prepare the casting solution. The solution was settled for 12 h at room temperature to allow complete release of bubbles. After that, the PSf solution was cast on the non-woven fabric by semiautomatic blade casting machine at 4 m/min. The gap of the blade from the platform surface was adjusted such that the thickness of the membranes was 30–40 μm excluding fabric thickness. The humidity and temperature inside the casting chamber were 13–14% and 33–35 °C respectively. The fabric was then passed through a gelation bath of temperature 24–25 °C and containing 0.1% (w/v) sodium lauryl sulfate in H_2O/DMF (H_2O:DMF=96:4 v/v). The cast PSf was then washed with water and stored in RO-filtered water. The water flux of the membranes was found to be $\sim 430\ L\,m^{-2}\,h^{-1}$ at 0.35 MPa and at temperature 28 °C.

2.3. Preparation of TFC membranes

Table 1 summarizes abbreviations and concentrations of components used for the preparation of different TFC membranes. First, separate MPD solutions were prepared by dissolving MPD in water containing AA-PEG-AA ($M_n=700$ g/mol), MeO-PEG-AA ($M_n=480$ g/mol), and H_2N-PEG-NH_2 (400 g/mol). A representative example of preparation of TFC membrane (Table 1) with MPD solution containing AA-PEG-AA (1% w/v) is as follows. MPD (20 g) was dissolved in water (300 mL) and AA-PEG-AA (10 g) was added into it. After purging with nitrogen, the mixture was stirred at 70 °C for 4 h to obtain MPD+MPD-PEG-MPD mixture. Next, water (686 mL), DMSO (10 mL) and glycerol (4 mL) were added into the

Table 1
Concentration of constituents used for the preparation of select TFC membranes and their abbreviations. [TMC]=0.125% (w/v) in hexane; curing temperature and curing time for all the cases were 70 °C and 2 min respectively.

Abbreviation	MPD (%)	X-PEG-X (%)	DMSO (%)	Glycerol (%)
$TFC_{PEG\text{-}0}$	2	0	1	0.5
$TFC_{AA\text{-}PEG\text{-}AA(0.25\%)}$	2	0.25	1	0.5
$TFC_{AA\text{-}PEG\text{-}AA(0.5\%)}$	2	0.5	1	0.5
$TFC_{AA\text{-}PEG\text{-}AA(1\%)}$	2	1	1	0.5
$TFC_{MeO\text{-}PEG\text{-}AA(0.25\%)}$	2	0.25	1	0.5
$TFC_{MeO\text{-}PEG\text{-}AA(0.5\%)}$	2	0.5	1	0.5
$TFC_{MeO\text{-}PEG\text{-}AA(1\%)}$	2	1	1	0.5
$TFC_{H_2N-PEG-NH_2(0.5\%)}$	2	0.5	1	0.5

X=–AA, $-NH_2$; concentrations in all cases were in % w/v.