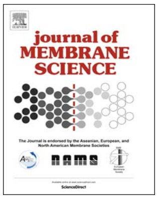
Journal of Membrane Science 539 (2017) 421–431

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci



Dopamine-induced nonionic polymer coatings for significantly enhancing separation and antifouling properties of polymer membranes: Codeposition versus sequential deposition

Yang He[a], Lihao Xu[a], Xia Feng[a], Yiping Zhao[a,*], Li Chen[a,b,**]

[a] State Key Laboratory of Separation Membranes and Membrane Processes, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China
[b] School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

ARTICLE INFO

Keywords:
Nonionic polymer
Polydopamine
Hydrogen-bonded interaction
Hydration capability
Antifouling property

ABSTRACT

Nonionic polymers (i.e., poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), poly(*N*-vinyl pyrrolidone) (PVP), and poly(*N*-acryoyl morpholine) (PACMO)) have been reported as promising antifouling materials for membrane surface modification. Better understanding of similarity and difference for the nonionic polymers in terms of hydration capability and antifouling property will benefit the design and development of antifouling surfaces. Herein, two simple and scalable methods yielded composite coatings on the hydrophobic polymer membrane surfaces: (i) a codeposition of polydopamine (PDA) with PEG (or PVA) (labeled as $M_{PDA\text{-}PEG}$ and $M_{PDA\text{-}PVA}$), and (ii) a sequential deposition featuring dopamine polymerization followed by the self-assembly of PVP (or PACMO) (labeled as $M_{PDA\text{-}PVP}$ and $M_{PDA\text{-}PACMO}$) via hydrogen-bonded interactions. The results suggested that hydrophilicity and surface free energy of all modified membranes were significantly enhanced after introducing PDA and nonionic polymers. The order of improved initial water flux of these modified membranes was $M_{PDA\text{-}PEG} > M_{PDA\text{-}PVP} \approx M_{PDA\text{-}PVA} > M_{PDA\text{-}PACMO}$. It was appeared that the codeposited membranes ($M_{PDA\text{-}PEG}$ and $M_{PDA\text{-}PVA}$ membrane) with excellent hydration capability and permeability had better antifouling property. However, antifouling property and durability were remarked for the sequentially deposited membranes ($M_{PDA\text{-}PVP}$ and $M_{PDA\text{-}PACMO}$ membrane) in comparison to the codeposited membranes as evaluated in protein filtration, oil/water emulsion filtration, and humic acid filtration. The hydration capability of hydrogen-bonded PDA-PVP (or PDA-PACMO) coating endows the sequentially deposited membranes with robust and comprehensive performance. This work systematically demonstrates that coating architecture is a vital role in the design of the nonionic polymer modified membranes.

1. Introduction

Water scarcity and energy consumption have been regarded as two inexorably intertwined challenges to global prosperity, health, and security [1]. Today, membrane technology has been anticipated a dominant position for water purification because it is excellent separation efficiency, relatively energy-saving characteristics, environmental friendliness, and ease of scale-up [2]. However, membrane fouling due to both temporary and permanent deposition of retained various foulants (such as proteins, natural organic matters, and oils) is still a bottleneck restricting the sustainability of membrane technology [3,4]. The ubiquitous phenomenon in turn leads to a significant permeability and selectivity decay, an increase in transmembrane pressure, and a shortened membrane lifespan. Therefore, the modification of membrane materials with antifouling ingredients to effectively alleviate or even prevent fouling is a pressing demand in maintaining the filtration performance and tailoring membranes with desirable properties. Recently, nonionic polymers, including poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), poly(*N*-vinyl pyrrolidone) (PVP), and poly(*N*-acryoyl morpholine) (PACMO), have been intensively studied as a promising class of antifouling agents in a range of membrane separation field [5]. It is generally accepted that the low fouling property of the nonionic polymers origins from their strong surface hydration, which forms on the nonionic material surfaces via hydrogen bonding with surrounding water molecules [6,7]. This tightly hydration layer serves as a steric and energetic barrier against hydrophobic foulants attachment.

---

[*] Corresponding author.
[**] Corresponding author at: School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.
E-mail addresses: yipingzhao@tjpu.edu.cn (Y. Zhao), tjpuchenlis@163.com (L. Chen).

http://dx.doi.org/10.1016/j.memsci.2017.06.028
Received 12 March 2017; Received in revised form 1 June 2017; Accepted 12 June 2017

Common strategies include blending modification, surface-initiated polymerization, and physical coating have been achieved to incorporate nonionic polymers into and/or onto polymer membranes [8–12]. Nonionic polymers as main hydrophilic agents are mostly used for the blending with membrane preparation. However, the nonionic polymers are more like pore forming agent rather than hydrophilic agent through an immersion precipitation method, because the water soluble nonionic polymers can be eluted out during the preparation and operation process. Faced with the limitations of simple blending modification, a few of amphiphilic polymers containing nonionic polymer moieties have been developed to endow more stable hydrophilic membranes via surface-initiated polymerization [13–15]. Nevertheless, the existing strategy often meets the demand for substrate specific and extra pretreatment, some of their intricate syntheses are merely effective for small scale development in laboratories [16]. Inspired by the mussel proteins, dip-coating modification with polydopamine (PDA) is exploited since 2007 as a more universal tool for membrane modification platform, while the high reactivity of the PDA facilitates its use as an intermediate layer for anchoring nonionic polymers [17,18]. For example, Freeman et al. [19] fabricated antifouling membranes by dip-coating a PDA layer and then grafting methyl-terminated PEG, and confirmed that the modified membranes could improve fouling tolerance. Li et al. [20] modified PES membranes by dip-coating a PDA layer and then grafting glycine-functionalized PVA, and found that the pure water flux was remarkably enhanced. Although the immobilization of nonionic polymers onto the PDA intermediate layer via grafting reaction is very popular, selected nonionic polymer requires synthesis of suitable pendant groups prior to the grafting approach. It is difficult to directly employ commercial nonionic polymers without active groups, because they further require multiple organic steps or complex operations under an inert atmosphere. In addition, the nonionic polymers still suffer from the difficulty to controllable graft density and uniform porosity on the PDA intermediate layer. Therefore, it remains a challenge to develop a versatile, simple and scalable fabrication method for constructing antifouling membranes with nonionic polymers.

In complementary approaches, hydrogen-bonded interactions provide a facile and universal approach to anchoring nonionic polymers for antifouling materials [21,22]. The hydrogen-bonded interactions are noncovalent self-assembly, do not involve intricate chemical reactions and damage the bulk properties of membranes during modification processes, and can be precisely controlled at the nanoscale by varying process parameters (hydrogen bonding density, ingredient concentration and self-assembly time). Jiang and co-workers [23] used m-trihydroxybenzene as hydrogen bond donor to construct the hydrogen-bonded interactions between PEG and PES substrate membranes. PEG was robustly resided onto the PES membrane surfaces, endowing the membrane surface with higher wettability. Wang and co-workers [24] employed a metal-polyphenol precursor layer to immobilized PVP on the polyamide reverse osmosis membrane surface by the hydrogen-bonded interactions between the PVP and the precursor layer. In terms of PDA coatings, Stadler and co-workers [25] demonstrated that PEG and PVA can be participated using a codeposition method with PDA to form a composite coating without the need for a covalent group (such as an amine or thiol group), while PVP as a strong hydrogen bond acceptor was found to suppress PDA formation. Taking advantage of the strong hydrogen-bonded interactions between PVP and PDA, Zhu and co-workers [26] immobilized a PVP layer on the PDA-coated polypropylene microfiltration membrane surface using a sequential deposition method, endowing the membranes with enhanced hydrophilicity, permeation and protein resistance. As a matter of fact, the sequential deposition method needs a two-step in this case, but the obtained coating is similar to a self-assembled monolayer. The generated coating structures can be delicately well-controlled by the coating density of the nonionic polymers, which resulted in membranes with both high permeability and antifouling property.

However, few works have been done to systematically compare the antifouling properties of the nonionic polymers; it is still unknown whether the most hydrophilic surfaces are the most excellent antifouling ones. Furthermore, it has never been analyzed whether there is a synergistic effect between the hydration capacity and coating architecture for immobilization of nonionic polymers, conferring membranes with robust hydrophilic and low fouling on the water/membrane interface. Therefore, the antifouling property of the nonionic polymer on the membrane surface needs a comprehensive insight underlying hydration capability and coating architecture. Starting from this point, we employ PDA-nonionic polymer coatings in the codeposition and sequential deposition method to modify PVDF membrane surfaces. PDA-PEG (or PDA-PVA) is codeposited to construct a mixed coating on the PVDF membrane surfaces, while PVP (or PACMO) is sequentially deposited to construct a hierarchical coating on the as-prepared PDA-coated PVDF membrane surfaces. The hydrophilicity and surface free energy of these membranes were contrastively analyzed, and the results were combined with corresponding total interfacial free energy of cohesive by the extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory to investigate the role of hydration capability between the membrane surfaces and the BSA protein molecules. This provided a theoretical basis for speculation and comparison of the permeate flux decline phenomenon during the filtration process. Filtration experiments using different foulants (include BSA protein, oil/water emulsion, and humic acid, respectively) were conducted with the pristine and modified PVDF membranes to evaluate the effects of hydration capability and deposition pattern. The sequentially deposited PDA-PVP (or PDA-PACMO) coating was found to strongly affect the antifouling property and long-term durability of the modified PVDF membranes, although the effect of hydration capability was indeed prominent. Our results revealed that the sequentially deposited PVDF membranes in the hydrogen-bonded manner were an attractive strategy to mitigate membrane fouling during the filtration process.

2. Experimental

2.1. Materials and reagents

PVDF powders (Solef 1010, $M_w = 3.52 \times 10^2$ kg mol^{-1}, $M_w/M_n = 2.3$) were purchased from Solvey Company of Belgium. Lithium chloride (LiCl) and humic acid (HA, 10–30 kDa) were bought from Guangfu Fine Chemical Research Institute (Tianjin, China). N, N-dimethylformamide (DMF, Guangfu Technology Development Co. Ltd., Tianjin, China) was used as the solvent. Dopamine hydrochloride was obtained from Ouhe Technology Development Co. Ltd., Beijing, China. Tris(hydroxymethyl) aminomethane (TRIS) was purchased from Sigma-Aldrich, pH value of prepared TRIS buffer is 8.5. PEG (MW 8 500–10 150 Da), PVA (polymeriazation degree of 1750 ± 50 and alcoholysis degree of 98%), PVP K30 (MW 48,000 Da) were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). *N*-acryoyl morpholine (ACMO) was purchased from MAYA Reagent Co., Ltd., Zhejiang, China. PACMO homopolymers were synthesized by free radical polymerization method, the weight-average molecular weight and polydispersity index of homopolymers were 21,600 Da and 1.79, respectively. Bovine serum albumin (BSA) having a molecular weight of 68,000 Da was purchased from Solarbio Science & Technology Co. Ltd., Beijing, China. Rice oil (Golden Dragon Fish) was purchased from a local supermarket. Other reagents were all analytical grade and used without further purification.

2.2. Coating of PVDF membranes using nonionic polymers

The PVDF flat membrane (labeled as $M_{Pristine}$) was fabricated via the immersed phase inversion method. The casting solution of the $M_{Pristine}$ membrane as follows: 8 g PVDF powder and 4 g LiCl were dispersed in 63 g DMF by vigorous stirring at 60 °C. After degassed for 6 h, the solution was cast on a glass plate using a 200 μm steel knife, and then the