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Journal of Membrane Science

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

Fabrication of polyvinyl chloride ultrafiltration membranes with stable antifouling property by exploring the pore formation and surface modification capabilities of polyvinyl formal

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ARTICLE INFO

Article history:

Received 18 January 2014

Received in revised form

29 March 2014

Accepted 4 April 2014

Available online 15 April 2014

Keywords:

Polyvinyl formal

Pore formation

Surface modification

Antifouling ultrafiltration membranes

Stability

ABSTRACT

Polyvinyl chloride (PVC) and polyvinyl formal (PVF) blend ultrafiltration membranes were fabricated by non-solvent induced phase separation (NIPS) method with different casting solution composition. The PVC/PVF membranes were characterized and evaluated by scanning electron microscopy (SEM), Fourier Transform Infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), water contact angle measurement and performance measurement. The results showed that PVF played the role of pore formation agent during the NIPS process, and both of porosity and the mean pore size of the membranes were increased with the increased dosage of PVF. Simultaneously, PVF was enriched to membrane surface via spontaneous surface segregation and the membrane surface hydrophilicity was greatly elevated, which implied the remarkably enhanced antifouling property. The robust residence of PVF on the membrane surface was confirmed by a long-term test of incubating membranes in deionized water, which revealed the stable antifouling property of PVC/PVF membranes. Therefore, PVF could be explored as a potential versatile modifier for fabricating high performance ultrafiltration membranes.

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1. Introduction

Membrane fouling is a major obstacle to the efficient application of membrane technology [1]. Membrane fouling is primarily caused by the accumulation of proteins, natural organic matter (NOM) and microorganisms during long-term operation [1,2]. The accumulation of foulants will lead to permeation flux decline, operation pressure increase, frequent physical and chemical cleaning and even a reduced membrane life. Therefore, the fabrication of antifouling membranes is one of the active and valid methods to overcome the bottleneck of large scale application of membrane technology.

Improvement in hydrophilicity of membrane surface is confirmed as an effective and popular method for fouling resistance [3]. Many attempts have been made to increase the membrane surface hydrophilicity by surface coating, surface grafting, surface segregation or other methods [3,4]. Surface coating can increase the hydrophilicity of membranes surface substantially, but the membrane pores are severely blocked and the coating layer is easily eluted after long-term

usage of membranes. Surface grafting is the most commonly utilized method to render the stable hydrophilic and fouling resistant membrane surfaces, and the relatively harsh reaction conditions, the membrane pore blockage as well as the un-modifiable internal pore surfaces hinder its working efficiency and applicability. Furthermore, as post-treatment approaches, both surface coating and surface grafting add extra step to membrane manufacturing cost [3–5].

Surface segregation, an in situ approach, has evolved as a facile and effective approach to improve the membrane surface hydrophilicity. Generally, in this approach, amphiphilic block copolymers, consisted of hydrophobic backbones and hydrophilic side chains, are added into membrane casting solution. Upon immersion into the coagulation bath, hydrophilic segments will spontaneously segregate to the polymer/water interface without leaching out from the membrane matrix for the reason of interfacial energy, and construct the hydrophilic fouling resistant layer on membrane surface and internal pore surface after the solidification of membrane materials. Moreover, the resultant surface is rendered with the unique self-healing and self-repairing properties [6].

The amphiphilic block copolymers with hydrophobic backbones and hydrophilic side chains, such as PES-g-PEGMA [5], PS-b-PAA [7] and PS-b-PDMAEMA [8], display the excellent application effect but the complicated synthesis and high price may prevent them from large scale application. Among various amphiphilic block copolymers,

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commercial triblock copolymer Pluronic F127, consisted of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) blocks, has a great potential as novel additives in antifouling membrane preparation [9,10], since Pluronic F127 can be easily obtained at a low cost. It has been demonstrated that the residence of Pluronic F127 on the membrane surface is ascribed to the hydrophobic–hydrophobic interaction between membrane matrix and PPO segments of Pluronic F127, rather than chain entanglement [10]. Nevertheless, the hydrophobic–hydrophobic interaction cannot ensure the completely stable presence of Pluronic F127 in the membrane matrix and thus may not be able to render the persistent antifouling property of the membranes, which remains the disputable issue for surface segregation method [10,11].

Polyvinyl chloride (PVC) is one of the most widely used polymer materials to fabricate ultrafiltration and microfiltration membranes, due to its robust mechanical strength, low-cost, and other excellent physical and chemical properties such as high resistance to acids, bases, solvents, and chlorine [2,12,19]. However, the relatively hydrophobic nature of PVC is an inherent obstacle to its efficient application in water treatment, because of the proneness to high degree of fouling. Therefore, surface segregation is considered as a facile and effective approach to enhance the hydrophilicity of PVC membrane surface.

In this study, polyvinyl formal (PVF) was blended into PVC with different ratios to fabricate PVC/PVF blend ultrafiltration membranes. PVF is manufactured by simultaneous hydrolysis and acetalization of polyvinyl acetate and can be easily obtained in quantity at a low cost. The hydrophilic PVF can enable membrane pore formation, increase membrane surface hydrophilicity and endow PVC/PVF membranes with excellent antifouling property. Simultaneously, the intense interaction of PVC and PVF, and the water-insoluble property of PVF ensure the stable residence of PVF on the membrane surface. In summary, the aim of this study was to develop a surface segregation modifier of both low cost and persistent antifouling property.

2. Experimental

2.1. Materials

Polyvinyl formal (PVF, M_w 35 kDa) with an average acetalization degree of 80% was purchased from Tokyo Chemical Industry Co. (Japan). Polyvinyl chloride (PVC) with average polymerization degree 800 was purchased from Dagu chemical factory (Tianjin, China). Both PVC and PVF resin were dried at 80 °C for 12 h prior to utilization. PEO–PPO–PEO triblock copolymer Pluronic F127 with a molecular weight of 12,600 and a PEO content of 70 wt% was purchased from Sigma. Humic acid (HA), polyethylene glycol 2000 (PEG2000) and N, N-dimethylacetamide (DMAc) were purchased from Kewei Chemicals Co. (Tianjin, China). Bovine serum albumin (BSA, M_w 66.4 kDa) was purchased from Institute of Hematology, Chinese Academy of Medical Science (Tianjin, China). Yeast (effective diameter 1.2 μm) was obtained from China General Microbiological Culture Collection Center, and then suspended in PBS prior to utilization.

2.2. Membrane preparation

PVC/PVF blend ultrafiltration membranes were prepared by non-solvent induced phase separation (NIPS) [12]. The formulations of casting solutions were given in Table 1. The casting solutions had a total polymer concentration of 16 wt%, while PVF content in the total polymer varied from 0 to 2, 4, 6, 8 wt%. Different amounts of PVC and PVF were dissolved in DMAc and stirred at 60 °C for about 4 h to ensure the homogeneous mixing,

Table 1

The composition of pure PVC membranes and PVC/PVF membrane casting solutions.

Membrane	Composition of casting solution			W_{PVF} (wt%)
	PVC (g)	PVF (g)	DMAc (g)	
1#	3.2	0	16.8	0
2#	2.8	0.4	16.8	2
3#	2.4	0.8	16.8	4
4#	2.0	1.2	16.8	6
5#	1.6	1.6	16.8	8

and then left for 8 h to allow complete release of bubbles. After cooled to room temperature, the solutions were cast on glass substrate with a steel knife, and then immersed in a coagulation bath of deionized water. Subsequently, the membranes were peeled off and washed thoroughly with deionized water to remove residual solvent. The control PVC/PEG membranes were prepared with 16 wt% PVC and 8 wt% PEG2000 in casting solution and PVC/Pluronic F127 membranes were prepared with 16 wt% PVC and 8 wt% Pluronic F127 in casting solution.

2.3. Membrane characterization

2.3.1. Membrane morphology and mechanical property

The surface and cross-section morphologies of PVC/PVF blend ultrafiltration membranes were observed using field emission electron microscope (FESEM, Nova Nanosem 430, FEI Co., USA). The PVC/PVF membrane samples freeze-dried with vacuum freeze dryer (FD-1C-50, Boyikang Co., China) were broken in liquid nitrogen and sputtered with gold for producing electric conductivity prior to SEM measurement.

The mechanical property was tested with a material-testing machine (AXM350-10KN, Testometric Co., UK). Prior to test, membranes were dried and cut into rectangle strips with a dimension of 50 mm \times 10 mm (length \times width). The stress–strain curve was obtained at an extension rate of 9 mm/min, from which the tensile strength, elastic modulus, and maximum elongation of the membranes were determined.

2.3.2. Membrane porosity and mean pore size

Membrane porosity and mean pore size were measured according to its dry–wet weight. Firstly, the membranes were weighed as the wet weight after mopping the excess water. Then the wet membranes were vacuum dried at 60 °C for 24 h and measured the dry weight. The porosity of membrane was calculated as [13–15]

$$\varepsilon(\%) = \frac{W_w - W_d}{\rho_w A \delta_0} \times 100 \quad (1)$$

where ε is the porosity of membrane, W_w (g) is the wet sample weight, W_d (g) is the dry sample weight, ρ_w (g/cm³) is the density of pure water, A (cm²) is the area of membrane in the wet state and δ_0 (cm) is the thickness of membrane in the wet state.

The mean pore size (nm) was calculated by Guerout–Elford–Ferry equation ((2)) on the basis of pure water flux and porosity data [14–16]:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\eta lQ}{\varepsilon \Delta P}} \quad (2)$$

where η is the pure water viscosity (8.9×10^{-4} Pa s), Q is the volume of the permeation of pure water per unit time (m³/s), and ΔP is the operation pressure (100 kPa).

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