Preparation of a PVDF Membrane with Antifouling and Anticoagulant Activities via Blending and PDA-initiated ATRP

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Introduction

Dopamine (DA) is a kind of neurotransmitter. Under oxidation condition, it undergoes an oxidation-crosslinking reaction, forming polydopamine (pDA) particles and aggregates in the reaction solution. The hydroxyl groups at the surfaces of pDA particles are able to react with 2-bromoisoburyryl bromide (BIBB), which allows initiating atom transfer radical polymerization (ATRP) of zwitterionic sulfobetaine methacrylate (SBMA).

The number of surface pores and pore sizes of the PVDF membrane increased after blending modification. However, surface-initiated ATRP of SBMA make the membrane surface dense significantly (Figure 3).

This work aims to prepare a modified poly(vinylidene fluoride) (PVDF) membrane via blending and pDA-initiated ATRP of SBMA, and offers a versatile approach to improve the biocompatibility of hydrophobic polymer membranes for their biomedical and blood-contacting applications.



3. Membrane hydrophilicity and permeation properties



Figure 4. (a) Contact angle and (b) BSA retention of pure and modified PVDF membranes.

The modified membrane showed better hydrophilicity and higher protein retention (Figure 4), and was possessed of improved anti-fouling properties (Table 1).

Table 1. Permeation flux and anti-fouling performance of pure and modified PVDF membranes.^a

Membrane ID. –	Permeation Flux (L•m ⁻² •h ⁻¹ •bar ⁻¹)			Degree of Water Flux Recovery and Loss (%)			
	J _{W0}	J _{P0}	J_{W1}	FR _w	R_t	R _r	R _{ir}
PVDF	5.87	0.93	2.58	43.95	84.16	28.11	56.05
PVDF/pDA	27.49	7.46	15.94	57.98	72.86	30.85	42.02
PVDF/pDA-pSBMA ₁	1.85	0.59	1.64	88.65	68.11	56.76	11.35
PVDF/pDA-pSBMA ₂	26.99	7.48	18.36	68.03	72.29	40.31	31.97



Figure 1. Scheme for preparation of PVDF/pDA-pSBMA membranes via two methods.

a. PVDF/pDA membranes were prepared by blending pDA with PVDF casting solution. Subsequently, pSBMA was grafted on the surfaces of PVDF/pDA blend membranes via pDA-initiated ATRP;

b. pSBMA-grafted pDA particles (pDA-pSBMA) were synthesized in advance, then the resultant particles were blended with PVDF casting solution to produce PVDF/pDA-pSBMA blend membranes.

Results and Discussions

1. Analysis of chemical compositions



^a Here, J_{WO} is the initial water flux, J_{PO} is subsequent permeation flux of BSA solution, and J_{W1} is water flux after membrane cleaning process. FR_w is water flux recovery. R_t is total protein fouling, and R_r and R_{ir} represent reversible and irreversible protein fouling ratio, respectively.

4. Platelet adhesion



Figure 5. Morphologies of platelets on pure and modified PVDF membranes.

The platelet adhesion and activation were notably suppressed on the modified membrane surface, which indicated satisfying anticoagulant activity (Figure 5).

Conclusion

PVDF/pDA-pSBMA₁ membrane has higher surface density of pSBMA and shows the best hydrophilicity, protein retention, anti-fouling and anticoagulation activities, while the water flux greatly reduced as surface pores are covered. Blending with pDA-pSBMA to prepare PVDF/pDA-pSBMA₂ membrane may avoid this disadvantage while the comprehensive properties lowered as a result.

Figure 2. FTIR spectra of (a) synthesized pDA-pSBMA and (b) PVDF/pDA-pSBMA membranes.

2. Membrane surface morphology



Figure 3. Surface SEM images of pure PVDF, PVDF/pDA and PVDF/pDA-pSBMA membranes.

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