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Construction of microgels embedded robust ultrafiltration membranes for highly effective bioadhesion resistance

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ABSTRACT

Effective and robust anti-bioadhesion ultrafiltration membranes were fabricated in this paper via physically blending of anti-bioadhesion microgels. The microgels were synthesized by one-step cross-linking of antifouling segment, poly(ethylene glycol) methacrylate (PEGMA), and electrostatic repulsion segment, methylacrylic acid (MAA). Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) results indicated that large amounts of PEGMA and MAA polymers had been enriched on the membranes surface. Scanning electron microscope (SEM) indicated that the spherical PEGMA-MAA (PM) microgels might form interpenetrating structure with the membrane matrixes, and substantially increased the pore size of the membranes. Water contact angle (WCA), pore size distributions and ultrafiltration tests suggested that the hydrophilicity, porosity, water flux, and antifouling property for the modified membranes were significantly enhanced. More importantly, systematic anti-adhesion investigations of plasma proteins, platelets, bacteria and vein endothelial cells confirmed that the modified membranes owned strong resistance capability to the bioadhesion of various organisms. The results revealed that highly robust and effective anti-bioadhesion ultrafiltration membranes could be prepared via the proposed blending of PM microgels with membrane matrix, thus this approach should be potential in various biomedical or industrial filtration fields where anti-bioadhesion properties were highly demanded.

1. Introduction

During the last thirty years, polymeric membranes have been extensively employed in blood purification (hemodialysis, plasmapheresis and plasma collection), separation (microfiltration, ultrafiltration, and gas separation), tissue engineering and regenerative medicine, and so on [1–6]. Among various widely used polymeric membrane materials, polyethersulfone (PES) shows good mechanical and film-forming properties, remarkable oxidative, thermal and hydrolytic stabilities [7]; therefore, PES has become the star membrane matrix in considerable fields, such as hemodialysis, artificial liver and water purification [8–10]. Nevertheless, owing to the main handicap of the hydrophobic property for PES membrane, fouling usually occurs and may lead to serious flux decline during the actual feeding operation as time elapses [11,12]. In particular, the adsorption of proteins and thus caused adhesion of platelets, bacteria, and even cells may seriously pollute membrane surfaces and in return caused dramatically declined performances in flux and separation [12,13].

The principal types of biofouling for PES membranes can be included as the adhesion and accumulation of various biocomponents, organisms and also the formation of bacterial biofilms [14]. Periodical washing with chemicals, like sodium hypochlorite, can reduce biofouling; however, it can deteriorate the membrane matrix simultaneously [15]. When membranes are used in pressure-driven processes, bio-organism fouling may seriously hamper their applications. Additionally, membrane fouling often leads to substantial energy consumption and significant operational cost, hence, fouling has become a headache problem [15]. To solve this problem, a variety of methods have been used to enhance the antifouling property and to overcome the inherent drawbacks of polymeric membranes [3,16–18], such as surface grafting [19], surface coating [20], physical blending [21], and etc. Surface grafting can construct highly stable antifouling layer via covalently tethering of functional polymers onto membrane substrates; however, the modification process is relatively complex, and hazardous

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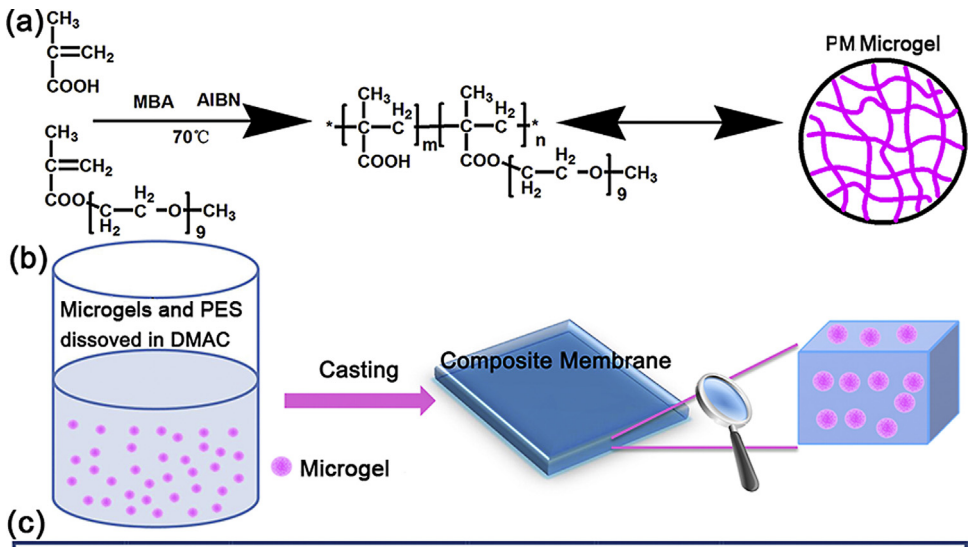

(c)

Samples	PES (g)	PM microgels/ (Needed microgels solution in DMAc) (g)	DMAc (g)	Total mass (g)	Concentration of PM microgels in bulk membrane (wt. %)
M-0	1.80	0 / 0	8.20	10	0
M-2	1.80	0.20 / 0.77	7.43	10	10.00
M-4	1.80	0.40 / 1.54	6.66	10	18.18
M-6	1.80	0.60 / 2.31	5.89	10	25.00

Fig. 1. (a) The synthetic process of PM microgels and the suggested chemical structure; (b) The preparation process of microgels blended membranes; (c) Weight ratios of the casting solutions and concentration of PM microgels in bulk membrane.

reagents may be used during the synthetic process. Surface coating is convenient but maybe less stable, which is not capable to meet long-term demands of filtration applications. Thus, these methods are restricted for the scalable application in membrane surface modification; therefore more facile and efficient approaches to construct antifouling PES membranes are highly required. Compared with surface grafting and coating, directly physical blending has always been considered as an easier and more convenient way to enhance the antifouling property of polymeric membranes [22–26].

One of the major problems in physical blending is that most of the antifouling polymers are hydrophilic compounds, such as the poly(ethylene glycol) (PEG), polyvinylpyrrolidone, polyglycerol and their derivatives. Thus, the elution of these antifouling reagents is inevitable during membrane preparation and filtration processes. The elution of hydrophilic compounds may have great influence on the membrane surface property and porosity, and the antifouling capability may also decline during long-term usage. Most recently, Ran et al. synthesized an amphiphilic triblock co-polymer of PVP-b-PMMA-b-PVP to improve the antifouling property of PES membrane by physical blending method [27]. Cheng et al. enhanced the PES membrane property by blending an amphiphilic terpolymer P(St–AA–NVP) [28]. Ma et al. reported that physically blending of heparin-mimicking polyurethane (HMPU) with PES matrix could significantly enhance the hemocompatibility of PES membrane [29]. The elution problem of these hydrophilic chains has been greatly suppressed in these studies; while, obvious phase separation between the synthesized polymers and PES matrix has also been observed due to the poor miscibility, which may affect the mechanical and surface properties for the modified membranes. To solve this problem, some approaches have been tried, such as synthesizing more compatible or miscible polymers with PES matrix; however, most of these methods reveal tedious chemical process and high preparation cost [30,31]. Therefore, it is still a bottle-neck to fabricate highly chemical and structure stable antifouling-membranes via physical blending methods.

In the present study, we report a highly efficient, universal and convenient protocol to fabricate effective anti-bioadhesion ultrafiltration membranes via physically blending of hydrophilic microgels. The microgels were synthesized by one-step cross-linking of antifouling segment, poly(ethylene glycol) methacrylate (PEGMA), and negatively charged segment, methylacrylic acid (MAA). Dynamic light scattering (DLS) were used to investigate the particle size and size distribution of the PEGMA-MAA (PM) microgels, the microgel morphology was observed by scanning electron microscope (SEM). High effective anti-bioadhesion ultrafiltration membranes were fabricated by blending the PM microgels with PES in casting solution. The surface chemical components of the membranes were examined by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS); the surface and cross-section morphologies of composite membranes were observed by SEM. Then, the membrane hydrophilicity, porosity and permeation flux were carefully examined; meanwhile, the antifouling property during ultrafiltration process was tested by using a model organic foulant. The anti-bioadhesion properties of the membranes were evaluated by systematic adsorption or adhesion investigations of protein, platelet, bacteria and vein endothelial cells on the composite membrane surfaces.

2. Experimental

2.1. Materials

PEGMA (average Mw ~475), MAA, N,N′-Methylidenebis(acrylamide) (MBA) and 2,2-Azobisisobutyronitrile