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Preparation of poly(vinylidene fluoride) microfiltration membrane with uniform surface-copolymerized poly(ethylene glycol) methacrylate and improvement of blood compatibility

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Abstract

This work describes the surface modification and characterization of poly(vinylidene fluoride) (PVDF) microfiltration (MF) membranes grafted with poly(ethylene glycol) methacrylate (PEGMA) via surface-activated ozone treatment and thermally induced graft copolymerization. The chemical composition and microstructure of the surface-modified PVDF membranes were characterized by Fourier transform infrared spectroscopy (FT-IR), contact angle, and atomic force microscopy (AFM) measurements. Blood compatibility of the modified membranes was evaluated by the biofouling property of the platelet adhesion observed by scanning electron microscopy (SEM) and the plasma protein adsorption determined by an enzyme-linked immunosorbent assay (ELISA). In general, the grafting density of the copolymerized PEGMA and the hydrophilicity on the surface of PVDF MF membranes increase with increasing macromonomer concentration of PEGMA in the reaction solution. The grafting distribution of PEGMA on the resulting membranes was found to form a uniform polymer hydrogel-like layer controlled by sufficient high content of PEGMA in the reaction solution, while their surface roughness was kept lower than that of the virgin membrane. For the platelet adhesion test, a remarkable suppression of the platelets adhered to the PVDF MF membranes grafted with PEGMA polymer was observed. In the water flux experiments, the PEGMA-grafted hydrophilic PVDF MF membranes exhibited good anti-fouling properties to substantially reduce the irreversible membrane fouling caused by platelet adhering and plasma protein adsorption as compared with the virgin hydrophobic PVDF MF membranes.

Keywords: Poly(vinylidene fluoride); Poly(ethylene glycol) methacrylate; Microfiltration membrane; Graft copolymerization; Blood compatibility

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a widely used material for the prepared membranes in microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) with excellent chemical resistance, good thermal, and mechanical properties [1–4]. One of the most important requirements for PVDF membranes in biomedical applications is to reduce the nonspecific adsorption of biomolecules when living systems encounter hydrophobic membrane surfaces. In general, biofouling of membranes prepared from hydrophobic materials will lead to a change in biomolecular structure selectively decreasing the permeate flux with time, especially in the filtration of protein, platelet, or cell-containing solutions. It is believed that the increase of hydrophilic moieties on a hydrophobic material surface can effectively reduce its membrane fouling as a consequence of the hydrophobic interactions between the biomolecules and the hydrophobic surface. Therefore, an ideal anti-fouling membrane should possess the excellent mechanical bulk properties of a hydrophobic material such as PVDF, and the anti-fouling characteristics of a hydrophilic surface on the membrane surface and pores. Several strategies [5–12] have been reported to improve the hydrophilicity of PVDF surface for extending this membrane material to more potential biomedical applications, such

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as low-fouling bio-separation, biomolecular immobilization and concentration, and stimuli-responsive controlled releases.

Fluro-based polymers such as PVDF have been widely studied to introduce various functional groups for altering their surface properties [13]. Surface modification is an effective approach to incorporate specific functionalities in the existing or commercial PVDF membranes through proper molecular design, while retaining its bulk properties. For improving the biocompatibility of fluro-based polymers, ester group in poly(ethylene glycol) (PEG)-based material is the ideal choice of surface functional moiety with anti-fouling characteristics [14–16]. PEG-based materials are the most commonly used synthetic materials to effectively resist nonspecific protein adsorption [17–19]. A series of attempts have been reported to improve the surface properties of PVDF with poly(ethylene glycol)-based polymers via physical blending [2,7], chemical coupling [6], and graft copolymerization [3,7,20,21]. For the general modification of membranes via surface graft copolymerization, reactive sites or groups on the membrane surface have to be introduced first by gas plasma, ozone, or UV treatment. In the following process, covalent immobilization of hydrophilic species such as PEG can be achieved with their monomers or macromonomers in solutions.

Kang and co-workers have developed PVDF microporous membranes with anti-fouling property via argon plasma-induced grafting of PEG polymer onto the membrane surface [6]. Here we report a different preparation approach to introduce PEG-based segments on PVDF membranes and evaluate their blood compatibility and biofouling property in detail. Surface-modified PVDF MF membranes were first prepared by the graft copolymerization with poly(ethylene glycol) methacrylate (PEGMA) macromonomer via the ozone treatment and thermal grafting polymerization. The PEGMA grafting density on PVDF membrane surface was controlled by different macromonomer concentrations in the reaction solution. Dense PVDF films without pore structures were also grafted with PEGMA to provide a study for the polymerized growth of polymer chains of grafting species in detail. The chemical composition and surface microstructure of the PEGMA-modified PVDF membranes were characterized by contact angle, Fourier transform infrared spectroscopy (FT-IR), and atomic force microscopy (AFM). The surface morphology of the modified PVDF membranes and the biofouling property of the platelet adhesion were studied by scanning electron microscopy (SEM). The amount of adsorbed plasma proteins was determined by an enzyme-linked immunosorbent assay (ELISA) to evaluate blood compatibility of the modified membranes. This work also demonstrates the degree of total water flux loss caused by platelet fouling and plasma protein adsorption from platelet rich plasma solution on the virgin and PEGMA-grafted PVDF membranes.

2. Materials and methods

2.1. Materials

PVDF microporous membranes with an average pore size of 0.1 μm, a thickness of about 110 μm, and a diameter of 47 mm were purchased from the Millipore Co. (VVHP04700 and VVLP04700) and were used as received. PVDF powder having a molecular weight of 370,000 was obtained from the commercial products of Kynar 760 and was washed with acetone. It was then dried at room temperature under vacuum prior to use. Dense PVDF films prepared from PVDF powder were cut into 4 cm^2 pieces for use as specimen in surface modification experiments. PEGMA macromonomer with a molecular weight of about 500 and an average number of ethylene glycol units of about 10 were purchased from Aldrich. Toluene was obtained from Aldrich and was used as a solvent for the ozone treatment and graft copolymerization. *N*,*N*-Dimethylaceramide (DMAc) for preparing the film casting solution was obtained from Aldrich. Phosphate buffer saline (PBS) was purchased from Sigma.

2.2. Surface copolymerization

PVDF MF membranes, which were commercially available, were obtained from Millipore Co. Ltd. Dense PVDF films were prepared by phase inversion from a NMP solution containing 15 wt% PVDF powder. After casting the solutions with a casting knife of 300 μm on a glass plate, the dense film was formed via solvent evaporation for 24 h at 50 °C. It was then left overnight in a vacuum oven to allow complete release of solvent. A schematic illustration is shown in Fig. 1. The commercial PVDF MF membrane of about 110 μm thickness and the dense PVDF film were both pretreated with a continuous stream of O_3/O_2 mixture. The O_3/O_2 mixture was bubbled through 30 mL isopropanol (IPA) solution with a flow rate of 360 L/h and ozone concentration of about 46 g/L at 25 °C which was generated from a custom-built ozone generator (Model OG-10PWA, Ray-E Creative Co., Ltd., Taiwan). After the ozone treatment, the glass reactor was cooled quickly in an ice box at 4 °C and then the ozone-treated PVDF membrane and film were transferred to the vacuum oven for 30 min at 25 °C to remove the residue IPA. The ozone-treated PVDF membrane and film were placed into a 30 mL toluene with PEGMA macromonomer content adjusted from 10 to 30 wt% to achieve the desired grafting density of PEGMA. The reactor flask with solution was saturated with purified argon for 5 min and then placed in an oil bath at 80 °C for 48 h under constant stirring. After the desired reaction time, the ozone-treated PVDF membrane and film were transferred into purified toluene. Unreacted macromonomers and homopolymers were extracted by soaking in methanol and distilled (DI) water three times and the residue solvent was removed in a vacuum oven. Both PVDF membranes and films on the surface modification with PEGMA polymer were performed under the same experimental conditions.

2.3. Surface characterization

The chemical composition of surface-modified PVDF membranes and films with PEGMA polymer was characterized using FT-IR spectrophotometer (Perkin-Elmer Spectrum One) and using Zinc Selenide (ZnSe) as an internal reflection ele-