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Antifouling microfiltration membranes prepared from acrylic acid or methacrylic acid grafted poly(vinylidene fluoride) powder synthesized via pre-irradiation induced graft polymerization

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ABSTRACT

This study describes the manufacture, characterization and evaluation of microfiltration membranes with antifouling properties. Poly(vinylidene fluoride) (PVDF) powder was grafted with acrylic acid (AAc) or methacrylic acid (MAA) via a pre-irradiation induced graft polymerization technique. The presence of graft chains was proven by FT-IR spectroscopy. Then, microfiltration (MF) membranes were cast from AAc or MAA grafted PVDF powder with different degree of grafting (DG) using phase inversion methodology. The contact angle, mean pore size and water uptake of MF membranes were measured. The morphology of MF membranes was studied by scanning electron microscopy (SEM), and water filtration properties were tested. The antifouling performance of those MF membranes cast from AAc or MAA grafted PVDF powder was characterized by means of measuring the recovery percentage of pure water flux after the membranes were fouled by bovine serum albumin (BSA) aqueous solution. After the antifouling performance test, BSA absorbed onto the surfaces of MF membranes was characterized by FT-IR spectroscopy in ATR mode. The experimental results show that MF membranes made from grafted polymer powder have elevated water flux performance and antifouling properties.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is widely used in the preparation of microfiltration (MF) and ultrafiltration (UF) membranes due to its good thermal stability, chemical resistance, excellent processability, and convenience in controlling the porosity and morphology [1,2]. However, applications of these membranes have been limited due to the hydrophobic nature of PVDF, where protein fouling occurs on membranes' surfaces and pores when those membranes are exposed to protein-containing solutions [3,4].

In recent years, hydrophilic MF and UF membranes prepared from chemically or physically modified PVDF have been widely studied and reported [5–7]. Several approaches have been developed to endow the membranes with hydrophilic properties, such as surface coating or surface grafting [3,8]. And those modified membranes showed improved antifouling properties imparting an enhanced interfacial energy with water-rich media which can reduce biomacromolecule adsorption [4,9,10].

Nevertheless, coating or surface grafting directly on a pre-prepared membrane has some shortcomings. For example, the coated surface layer is physically absorbed on membrane's surface therefore it is easy to be washed off [2,9]. And surface grafting of pre-prepared membranes is likely to be accompanied by changes in membrane pore size and distribution, which results in reduced permeability [3,4].

Therefore, we proposed to modify polymer powder, rather than as prepared membranes, by a pre-irradiation induced graft polymerization technique and then fabricated the modified polymer powder into MF membranes. By pre-irradiation induced graft polymerization, the polymer was irradiated by γ-rays or electron-beams, forming radicals in polymeric materials which can initiate graft polymerization of various vinyl monomers, so as to impart the material with desirable properties [11,12].

In this work, PVDF powder was firstly irradiated in air using a ^{60}Co γ-ray source, and then, hydrophilic monomers of acrylic acid (AAc) or methyl acrylic (MAA) were grafted onto it. AAc or MAA grafted PVDF powders with different degree of grafting (DG) were cast into MF membranes under phase inversion. The structures and properties of those modified MF membranes were then investigated. Especially, the antifouling properties were studied using bovine serum albumin (BSA) as a model contaminator.

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2. Experimental

2.1. Materials

PVDF in powder form with diameter of 0.1 mm was purchased from Solvay Chemicals Company, Belgium. 1-Methyl-2-pyrrolidone (NMP), poly(vinyl pyrrolidone) (PVP) K30 ($M_w = 50{,}000$), BSA ($M_w = 67{,}000$), AAc, and MAA were purchased from Sinopharm Reagent Co. Ltd., Shanghai. PE non-woven fabric, labeled as TYVEK 1057 D, was obtained from DuPont Co., U.S.A. All of the materials were used without further purification.

2.2. Pre-irradiation induced graft polymerization

PVDF powder was irradiated to 15 kGy in air using γ-ray from a ^{60}Co source at room temperature, and then stored at −24 °C in a refrigerator before use.

In a 300 mL Erlenmeyer flask, 140 mL deionized water, 20 g irradiated PVDF powder, and 60 mL AAc or MAA were added and mixed by ultrasonication. The flask was then bubbled with nitrogen for 15 min to remove oxygen. After that, it was sealed, and graft polymerization was started at 60 °C under continuous stirring.

After a defined period, graft polymerization was stopped, and the grafted PVDF powder was filtered and washed. Then it was washed with 1 M NaOH solution at 60 °C under stirring for 2 h. During the wash, NaOH solution was replaced three times to ensure all of the homopolymers were completely removed. After that, the powder was filtered and recovered by excessive 1 M HCl solution. Then the powder was washed repeatedly with deionized water until the pH value of the exhausted liquid was 7.0. Finally, the PVDF-g-PAAc or PVDF-g-PMAA powder was dried at 60 °C in a vacuum oven until a constant weight was obtained.

The DG values of PVDF-g-PAAc or PVDF-g-PMAA powder were determined by acid–base back titration as described in our previous papers [11].

2.3. Infrared spectroscopy measurement

Pristine and grafted PVDF powders were pressed into pellets with KBr. Then FT-IR spectra were taken on a Nicolet Avatar 370 FT–IR spectrometer by the culmination of 32 scans at a resolution of 4 cm^{-1}.

The surface chemical structure of the MF membranes was analyzed in ATR mode with the SMART Accessory by pressing the sample over a Zn–Se crystal. All spectra in the ATR mode were recorded from 3600 cm^{-1} to 650 cm^{-1}, with a resolution of 4 cm^{-1} and using 32 scans.

2.4. Membrane preparation

MF membranes were prepared using the phase inversion method as follows:

Pristine or grafted PVDF powder and PVP were dissolved in NMP at 70 °C with a weight ratio of 12.5:3:84.5 for 6 days. Before membrane casting, the solution was ultrasonicated for 30 min to eliminate bubbles. After that, the solution was cast onto non-woven fabric taped on a stainless steel plate. Then, the newborn membrane was immersed in deionized water to set at 25 °C. When the membrane was fully solidified, it was taken out and rinsed with deionized water for several times to thoroughly wash off the remaining solvent and then it was kept in fresh deionized water for further characterization.

For clarity, MF membranes cast from pristine PVDF powder are termed pristine membranes, while MF membranes cast from PVDF-g-PAAc or PVDF-g-PMAA powder are termed modified membranes in the following paragraphs.

2.5. Contact angle measurement

The contact angles of the MF membranes were measured on a JCW-360a system (Chengde Experiment Equipments Co. Ltd., China). A water drop (~5 μL) was lowered onto the sample membrane's surface from a needle tip. A magnified image of the droplet was recorded by a digital camera. Static contact angles were determined from these images with calculation software. The contact angle measurement was taken as the mean value of 10 different points on every MF membrane.

2.6. Pore size measurement

Using laboratory-designed apparatus, the pore size of the MF membrane was measured under bubble point analysis, as reported in our previous work [11,12].

Before the measurement, the MF membranes were immersed in aqueous solution for 24 h and then in ethanol for 30 min. One MF membrane was mounted on a sample holder with an effective area of 3.14 cm^2 in a sealed container. N_2 gas was charged and the gas pressure increased continuously at the set speed of about 0.03 MPa/min. When the first bubble was observed on the membrane's surface, the gas pressure was recorded, which indicated the maximum pore size. When the last bubble was observed on the surface of membrane, the highest pressure was recorded as an indication of the minimum pore size.

The result is governed by the Washburn equation [13,14]:

$$Pr = 2\gamma\ \cos\theta \tag{1}$$

where P is the N_2 pressure, r is the average pore radius of the sample, and $\gamma\cos\theta$ is the Wilhelmy surface tension. Here the contact angle used in the Wilhelmy surface tension was zero contact angle according to the ASTM standard F316-03.

The average value of the maximum pore size and the minimum pore size was recorded as the mean pore size.

2.7. Water uptake measurement

The water uptake (WU) of the MF membranes was determined by measuring the weight change after soaking in deionized water.

MF membranes were rinsed with deionized water, and then dried in a vacuum oven at 60 °C for 24 h. After that, the dried membranes were immersed in deionized water for at least 24 h. Then the swollen membranes were taken out, and the excess water on the surfaces gently removed by just putting a blotter in contact with the membranes. Swollen membrane weights were quickly measured before drying the membranes under vacuum at 60 °C for 24 h. The dried membranes were quickly weighed and the WU was calculated according to the following formula:

$$\text{water uptake}\,(\%) = \frac{W_s - W_d}{W_d} \times 100 \tag{2}$$

where W_s and W_d were the weights of swollen and dry MF membranes, respectively.

2.8. Morphology study

Scanning electron microscope (SEM) images of the cross-section and surface of MF membranes were taken on a LEO1530vp SEM (Germany). Samples were attached using carbon tape and sputtered with gold. The voltage was set at 25 kV and the current was set at 10 mA. To obtain the cross-section images, membranes were immersed in liquid nitrogen and fractured before measurement.