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Microfiltration membranes prepared from acryl amide grafted poly(vinylidene fluoride) powder and their pH sensitive behaviour

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ABSTRACT

Acryl amide (AAm) was grafted onto poly(vinylidene fluoride) (PVDF) powder by a pre-irradiation induced graft polymerization technique. The chemical structure of AAm grafted PVDF powder (denoted as PVDF-g-PAM powder) was characterized by FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis. Then, the microfiltration (MF) membranes were cast from PVDF-g-PAM powder with different degrees of grafting (DG) using a phase inversion method. The contact angle of those modified MF membranes decreased with increased DG, indicating the enhanced hydrophilicity of modified MF membranes due to the existence of PAM side chains. The morphology of MF membranes was studied by scanning electron microscopy (SEM), pore size and distribution was determined by mercury porosimetry analysis, and water filtration properties was tested at different pH values. The results showed that MF membranes made from PVDF-g-PAM powder have better water flux performance than that of the pristine one due to the enhanced hydrophilicity. Moreover, modified MF membranes showed certain pH sensitivity behaviour with high DG, where the flux changes with the pH value of fed aqueous solution and it is reproducible during the 12 times cyclic test.

1. Introduction

Stimuli-responsive materials, which are also called smart materials, are sensitive to external stimuli and capable of altering their properties in response to external stimuli [1,2]. The majority of known smart materials including polymeric solutions, gels, surfaces and interfaces, is designed to be dependent on changes in pH, temperature, and electrolyte concentration [3,4]. Furthermore, microfiltration (MF) membranes and ultrafiltration (UF) membranes for emerging applications including responsive biological interfaces, controlled release, and drug delivery [5–9], are also required to be stimuli-responsive.

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline membrane material that has attracted much research interest due to its good thermal stability, chemical resistance, ultraviolet light and radiation resistance, and excellent processability [10–13]. However, filtration membranes prepared from pristine PVDF are usually not stimuli-responsive due to the lack of functional groups. Therefore, PVDF membranes are often modified by chemical or physical methods in order to satisfy the requirements of specific applications.

It is well known that surface grafting techniques of functional monomers onto membranes are common methods used to prepare pH sensitive MF and UF membranes [14,15]. However, surface grafting methods which are directly grafted on the membrane may change the membrane pore size and distribution, and then reduce the membrane permeability [16]. Therefore, a process of modifying the polymer powder before fabricating it into membrane was proposed. We adopted the pre-irradiation induced graft polymerization method to functionalize the polymer powder, where the radicals were formed in the polymers by γ-rays or electron-beam irradiation which were used to initiate many kinds of vinyl monomer graft polymerization, so as to endow the material with desired properties [17–19].

In our previous work, MF membranes were prepared from acrylic acid and methacrylic acid grafted polyethersulfone powders, and the resulting MF membranes showed pH sensitive properties, where the flux was dependant on the pH value of the solution [17,18]. Acryl amide (AAm) is a hydrophilic monomer [20–24], and poly(acryl amide) (PAM) is a biocompatible water-soluble polymer [25,26]. Moreover, PAM is used as a polymeric flocculant in waste-water treatment [26–30]. In this work herein, AAm grafted PVDF powder was prepared under a pre-irradiated

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induced graft polymerization technique, then MF membranes were cast from PVDF-g-PAM powders with different degree of grafting (DG) under a phase inversion method. The morphology and properties of the modified MF membranes were characterized. It was shown that the PVDF-g-PAM membrane had pH sensitive properties.

2. Experimental

2.1. Materials

PVDF powder with a diameter of 0.1 mm was purchased from Solvay Chemicals Company, Belgium. AAm, 1-methyl-2-pyrrolidone (NMP), and poly(vinyl pyrrolidone) (PVP) K30 (M_w = 50,000) were purchased from Sinopharm Reagent Co. Ltd., Shanghai, China. PE non-woven fabric (TYVEK 1057 D) was obtained from DuPont Co., U.S.A. All materials were used without further purification.

2.2. Pre-irradiation induced graft polymerization and preparation of MF membranes

PVDF powder was irradiated in air by γ-rays from a ^{60}Co source at room temperature, and then stored in a refrigerator at −24 °C before use. AAm concentrations from 10% to 40% were prepared by adding the monomer into water solution under stirring in a 300 mL Erlenmeyer flask. Irradiated PVDF powder (10 g) was added to the flask and bubbled with nitrogen gas for 20 min to remove oxygen. Then it was sealed and then heated in a water bath to initiate the graft polymerization at 65 °C under continuous stirring. After a period of reaction from 1 to 6 h, the grafted powder was filtered and washed by deionized water. The filtered and washed grafted powder was extracted by deionized water in a Soxhlet extractor for 72 h to thoroughly remove the residual monomer and homopolymer. Finally, PVDF-g-PAM powder was dried in a vacuum oven at 60 °C until weight was constant. The DG values of the PVDF-g-PAM powder were determined by fluorine elemental analysis as described in our previous paper [31]. MF membranes cast from PVDF-g-PAM powder with different DG were prepared using the phase inversion method as described in our previous paper [17,18,32].

2.3. Infrared spectroscopy measurement

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

2.4. X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis was performed with a Kratos Axis Ultra instrument using monochromatic Al Kα radiation. Wide scans were carried out in the range of 1100–0 eV, and narrow scans were performed for the C 1s region and N 1s region of PVDF-g-PAM. Pristine and grafted PVDF powders were vacuum-dried and then XPS spectroscopy was taken. Peak analysis software was applied to analyze the spectra. All binding energies (BE) were correct by assuming the BE as 286.44 eV for the C 1s hydrocarbon peak of PVDF according to the standard spectra [33].

2.5. Contact angle measurement

The contact angles of the MF membranes were measured on an Attension Theta system (KSV Instruments Ltd., Finland). A 5 μL water drop from a needle tip was lowered onto the membrane's surface. A magnified image of the droplet was recorded by a digital camera. Static contact angles were determined from these images with calculation software supplied. Every sample membrane was measured at 7 different points separated from each other with the distance of 2 cm, and the contact angle was the average of these data.

2.6. Morphology study and pore size measurement in desiccated surface

Scanning electron microscope (SEM) images of the cross-section and surface of MF membranes were taken on an ULTRA 55 SEM (Zeiss, 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. The cross-section images were amplified to 2000× and surface images were amplified to 30,000×. Pore size measurement was determined by mercury porosimetry (Autopore 9500, Micromeritics, America). Every sample membrane was dried in a vacuum oven at 60 °C. Pore size distribution and porosity were evaluated by measuring digitally.

2.7. pH sensitive behaviour determination

2.7.1. Swelling measurement at different pH value

The weight change during swelling in aqueous solutions with different pH value was applied to determine swelling behaviour of MF membranes as reported in our previous work [17,18,32].

MF membranes rinsed in deionized water were dried in a vacuum oven for 24 h at 60 °C and then immersed in aqueous solutions with different pH value (3, 5, 7, 9, 11) for at least 24 h. The swollen MF membranes were taken out and the excess water on the surfaces was gently removed. After that, the weight of swollen membrane (W_{wet}) was quickly measured. At last MF membranes were dried in a vacuum oven for 24 h at 60 °C again to obtain the weight of dry membrane (W_{dry}) and the degree of swelling was calculated by the following formula:

$$\text{Degree of swelling}(\%) = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100 \qquad (1)$$

2.7.2. Pore size measurement at different pH value

The pore size of the MF membrane was measured by the bubble point analysis, which was also reported in our previous work [17,18,32]. The MF membranes were immersed in aqueous solution with prescribed pH value for 24 h. 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 slowly and continuously. When the first bubble appeared on the membrane's surface, the gas pressure was recorded, which indicated the maximum pore size. The result is governed by the Washburn equation [17,18,32]:

$$Pr = 2\gamma \ \cos\theta \qquad (2)$$

where P is the N_2 pressure, r is the pore radius of the sample, $\gamma\cos\theta$ is the Wilhelmy surface tension, and θ is the contact angle. Here the wetting agent was deionized water, and the contact angle in the Washburn equation was zero according to the ASTM standard F316-03.

2.7.3. Flux measurement at different pH values

A home-made filtration system was used to characterize the flux of the MF membranes, which was described previously [17,18,32]. The sample membrane was immersed in aqueous solutions with specific pH value overnight prior flux measurement. Then the membrane was mounted on a microfiltration cell (an effective area of