Preparation and characterization of the antifouling porous membranes from poly(vinylidene fluoride)-graft-poly(N-vinyl pyrrolidone) powders Postprint

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Date: 2023-06-18T00:00:00+00:00

Abstract

Porous membranes were prepared using the phase inversion method from poly(vinylidene fluoride)-graft-poly(N-vinyl pyrrolidone) (PVDF-g-PVP) powders, which were synthesized via γ-ray induced graft polymerization (pre-irradiation). Chemical compositions, thermal behavior, morphology and hydrophilicity of the membranes were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, element analysis, thermalgravavimetric analysis, differential scanning calorimetry, scanning electron microscopy and contact angle measurements, respectively. Permeation experiments were conducted to evaluate the water flux, and the dynamic BSA fouling resistance performances were investigated, too. All the experimental results indicate that the PVDF-g-PVP membranes demonstrate better separation performances over the pristine PVDF membrane.

Full Text

Preamble

Preparation and characterization of antifouling porous membranes from poly(vinylidene fluoride)-graft-poly(N-vinyl pyrrolidone) powders

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(Received February 17, 2014; accepted in revised form May 12, 2014; published online October 6, 2014)

Porous membranes were prepared using the phase inversion method from poly(vinylidene fluoride)-graft-poly(N-vinyl pyrrolidone) (PVDF-g-PVP) powders, which were synthesized via γ-ray induced graft polymerization (pre-irradiation). Chemical compositions, thermal behavior, morphology and hydrophilicity of the membranes were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, scanning electron microscopy and contact angle measurements, respectively. Permeation experiments were conducted to evaluate the water flux, and the dynamic BSA fouling resistance performances were investigated as well. All experimental results indicate that the PVDF-g-PVP membranes demonstrate better separation performance than the pristine PVDF membrane.

Keywords: Poly(vinylidene fluoride)-graft-poly(N-vinyl pyrrolidone), Porous membrane, Characterization
DOI: 10.13538/j.1001-8042/nst.25.050303

Introduction

Poly(vinylidene fluoride) (PVDF) membranes are widely used in microfiltration and ultrafiltration processes due to their good thermal stability, chemical resistance, ultraviolet and radiation resistance, and well-controlled porosity [1-4]. However, because of the hydrophobic nature of PVDF, protein fouling often occurs both on the membrane surface and within the pores when the membranes are exposed to protein-containing solutions, which in turn restricts the applications of PVDF membranes [5, 6]. In recent years, membrane researchers have attempted to improve the hydrophilicity of PVDF membranes using grafting methods, such as surface living/controlled radical polymerization [7-9], plasma-induced grafting [10-12], UV-assisted graft polymerization [13-16], and radiation-induced graft polymerization [17-21]. Hydrophilic functional monomers are grafted onto PVDF main chains or membrane surfaces with these grafting methods, but grafting the membrane surface directly can change the membrane pore size and distribution, thereby reducing permeability [22, 23].

In this study, we propose a routine of graft polymerization of PVDF powders by ^{60}Co γ-ray pre-irradiation to fabricate porous membranes. The radicals formed in PVDF powders by γ-rays initiate the graft polymerization of vinyl monomers, and functional graft chains are introduced to endow PVDF with desirable properties [24-26]. In our previous work, hydrophilic poly(vinylidene fluoride)-graft-poly(N-vinyl pyrrolidone) (PVDF-g-PVP) powders were prepared by grafting N-vinyl pyrrolidone (NVP) onto PVDF powders using the pre-irradiation method [27]. In this paper, porous membranes are cast from PVDF-g-PVP powders of different degrees of grafting (DG) via the phase inversion method. The chemical compositions, thermal behavior, morphology and hydrophilicity of the membranes are investigated, and the antifouling property of the porous membranes is examined.

Experimental

Materials

PVDF powders (TA-6020) were purchased from Solvay Co. Ltd. (Brussels, Belgium). NVP of analytical grade was obtained from J&K Corp. (Shanghai, China). N-methyl pyrrolidone (NMP), hydrochloric acid of analytical grade, bovine serum albumin (BSA, Mw = 67,000 Da) and phosphate-buffered saline (PBS) were purchased from Sinopharm Reagent Co. Ltd. (Shanghai, China). All materials were used without further purification.

Membrane preparation

The porous membranes were prepared using the immersion precipitation phase inversion method. PVDF and PVDF-g-PVP powders of different DGs were dissolved in NMP (wt% = 16%) at 70 °C for 7 days to obtain a homogeneous solution. The solution was cast onto a glass plate at (24 ± 1) °C, which was then immersed in a precipitation bath of deionized water maintained at (16 ± 1) °C. The newborn membrane was evaporated in air for 20 s. The prepared membranes were immersed in fresh deionized water to remove all residual solvent before characterization.

Membrane characterization

Fourier transform infrared (FTIR) spectroscopy measurements The FTIR spectra were recorded on a TENSOR 27 FTIR spectrometer (Bruker Optics, Germany) in attenuated total reflection (ATR) mode. The samples were placed on the sample holder and all spectra were recorded in the wavenumber range of 4000–600 cm^{-1} by cumulating 32 scans at a resolution of 4 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) analysis XPS analysis was performed with a Kratos Axis Ultra DLD XPS instrument (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromatized Al Kα X-ray source at a constant dwelling time of 100 ms and a pass energy of 160 eV. The samples were vacuum-dried before measurement. Peak analysis software was applied to analyze the spectra.

Elemental analysis The bulk C, H and N contents of the membranes were determined on a Vario EL III elemental analyzer (Elementar Co., Hanau, Germany). Each membrane was measured twice.

Thermal behavior analysis Thermogravimetric analysis (TGA) was performed on a Pyris1 TGA thermogravimetric analyzer (Perkin Elmer, USA) between 50 °C and 800 °C. The samples were heated from 50 °C to 100 °C at a rate of 40 °C/min. To eliminate the influence of adsorbed water, all samples were kept at 100 °C for 5 min before they were heated to 800 °C at a rate of 10 °C/min for testing in an alumina crucible under nitrogen purging at 20 mL/min.

Differential scanning calorimetry (DSC) analysis was performed on a METTLER TOLEDO DSC822e DSC instrument (Mettler-Toledo International Inc., Zurich, Switzerland) from 25–250 °C at a heating rate of 10 °C/min under nitrogen gas atmosphere. To eliminate thermal history of the samples, scans were taken twice, and the second scan results were recorded.

Scanning electron microscopy (SEM) analysis Morphology of the porous membranes was studied on an LEO1530vp SEM (Zeiss, Germany). To obtain cross-section images, the membranes were immersed in liquid nitrogen and fractured. The samples were attached on carbon tape, coated with Au by sputtering, and scanned at 25 kV and 10 mA.

Contact angle measurements Contact angles of the membranes were measured on an Attention Theta system (KSV Instruments Ltd., Finland). A water drop (5.0 µL) was lowered onto the membrane surface from a needle tip. A magnified image of the droplet was recorded with a digital camera. Static contact angles were calculated from the images with software, and measurements at six points on a membrane were averaged as its contact angle.

Water flux measurements A self-made microfiltration cell apparatus [28] with an effective filtration area of 0.002 m^2 was used to measure the flux of the membranes. A sample membrane was mounted onto the filtration cell and precompacted at -10 kPa for a certain time until the flux maintained a constant value. The flux (J) was calculated by $J = V/(A \cdot \Delta T)$, where V is the volume of permeation water, A is the effective area of the membrane, and ΔT is the time of measurement.

Evaluation of antifouling property BSA was chosen as the model protein to evaluate the antifouling property of the membranes. After the water flux measurement, pure water was changed to 1 g/L BSA solution in PBS (pH = 7.4). The sample membrane was kept filtering for 4 h with BSA solution under stirring, and the permeate flux profile with time was recorded to determine the fouling resistance of the membrane. Filtration runs were performed with full recycle of penetrant to the feed tank to maintain the BSA concentration at a constant level.

Results and Discussion

FTIR-ATR spectroscopy

FTIR-ATR spectra of pristine PVDF membrane and PVDF-g-PVP membranes with different DGs are compared in Fig. 1 [Figure 1: see original paper]. A distinctive new band around 1670 cm^{-1} can be seen in the spectra of PVDF-g-PVP membranes, and the absorbance increases with DG. This band arises from characteristic vibrations attributed to C=O stretching in the grafted PVP chains. The results confirm the existence of PVP chains on the PVDF-g-PVP membrane surface.

XPS analysis

Surface compositions of the PVDF-g-PVP membranes were studied by XPS. Fig. 2 [Figure 2: see original paper] shows the wide-scan and C1s core-level spectra of the porous membranes. The wide-scan spectra show signals attributed to C, F and O elements in the PVDF-g-PVP membranes, and a new signal at 399.8 eV is attributed to the N element originating from the amide groups in PVP polymer chains. The minuscule amount of O element in PVDF powders may be due to remaining initiator and surfactant, but the supplier did not provide any information on these details.

In the C1s core-level spectrum of the pristine PVDF membrane, peaks at 286.4 eV and 290.8 eV represent CH_2 and CF_2 species, respectively, and the peak at 287.9 eV corresponds to CHF species. For the PVDF-g-PVP membranes, three new peak components appeared in the C1s core-level spectra, which are assigned to the grafted PVP polymer chains: binding energies at 287.9 eV for the N-C=O species, at 284.9 eV for the hydrocarbon of the PVP chains, and at 286.4 eV for the C-N species. The C-N and (CH_2) (PVDF) peaks overlap to form a single peak in Fig. 2, as do the CHF and N-C=O peaks.

Elemental analysis

The C, H and N contents of the PVDF-g-PVP membranes are listed in Table 1 . The bulk C, H and N contents were determined by elemental analysis, and the surface N contents were calculated from XPS spectra. From Table 1, the bulk and surface N contents increase with DG, and the surface N content of each grafted membrane is much higher than the corresponding bulk N content. That is to say, the PVP polymer concentration on the membrane surface is higher than that in the membrane bulk. This is attributed to surface segregation of the hydrophilic PVP graft chains during membrane fabrication by phase inversion in the aqueous medium, due to the relatively low interfacial energy between the PVP graft chains and water [29-31].

Thermal behavior analysis

Thermal behavior of the porous membranes was investigated by TGA and DSC measurements. Fig. 3 [Figure 3: see original paper] shows the TGA curves of two PVDF membranes. The pristine PVDF membrane has only one thermal decomposition step, commencing at about 460 °C, while the PVDF-g-PVP membrane (DG = 11.75%) exhibits a two-step thermal decomposition process. The first main weight loss starting at about 340 °C is attributed to degradation of the PVP side chains, while the second weight loss beginning at about 460 °C is attributed to decomposition of the PVDF main chains. The two-step decomposition of PVDF-g-PVP membranes suggests that the PVP grafts do not alter the inherent decomposition of the matrix PVDF.

Figure 4 [Figure 4: see original paper] shows the DSC curves of PVDF-g-PVP membranes of different DGs. The melting temperature of the porous membranes decreased slightly with increasing DGs, being 174.6 °C for the pristine PVDF membrane but 173.8 °C and 172.1 °C for the grafted membranes of DG = 6.06% and DG = 11.75%, respectively. This is because the proportion of PVP increases with DG, and PVP has a lower melting temperature than PVDF.

Surface hydrophilicity analysis

Surface hydrophilicity of the membranes was evaluated by contact angle measurement (Fig. 5 [Figure 5: see original paper]). The contact angle of the pristine PVDF membrane is 85° due to the intrinsic hydrophobicity of PVDF. Because of the existence of carbonyl groups in the PVP chains, the grafted membranes are relatively hydrophilic, and the contact angles decrease with increasing DGs, being 69° at DG = 17.43%. Thus, the hydrophilicity of PVDF-g-PVP membranes is obviously improved.

Morphology study

SEM images of the pristine and grafted PVDF membranes of different DGs are shown in Fig. 6 [Figure 6: see original paper]. From the surface images, it is evident that the number of pores in PVDF-g-PVP membranes is greater than that of the pristine membrane, and the pore sizes of PVDF-g-PVP membranes are larger than those of the pristine. This is due to the enhanced hydrophilicity of PVDF-g-PVP powders, which is beneficial for pore formation during the membrane fabrication process. However, when DG is higher, the number of pores decreases, especially the smaller pores. The grafted PVP chains may plug or cover the membrane pores, resulting in decreased surface porosity [1, 32].

As evident from the cross-section SEM images, an asymmetric morphology with a skin layer and macrovoids in the support layer can be observed for both the pristine and grafted membranes. However, the pore connectivity of PVDF-g-PVP membranes is greater than that of the pristine. The thickness of PVDF-g-PVP membranes changed slightly from that of the pristine. This change may be due to a variable exchange rate between water and the solvent [33]. Also, the angle from which the SEM image was taken may cause differences in apparent membrane thickness.

Water flux

Figure 7 [Figure 7: see original paper] shows the water flux of the porous membranes as a function of DG. The water flux of PVDF-g-PVP membranes is higher than that of the pristine, but it decreases with increasing DGs, being

79.91 $L/(m^2 \cdot h)$ at DG = 6.06% while just 18.14 $L/(m^2 \cdot h)$ at DG = 17.43%. In general, water flux of membranes is mainly controlled by membrane hydrophilicity and membrane structure. With improved hydrophilicity, a greater number of pores of larger pore size are beneficial for flux improvement [28]. Although the hydrophilicity of PVDF-g-PVP membranes increases with DG based on the contact angle results, the surface SEM images show that the porosity of the grafted membranes reduces with increasing DG. Obviously, the membrane structure influences water flux significantly in this case. Consequently, the water flux of PVDF-g-PVP membranes decreases with increasing DG.

Antifouling property analysis

Antifouling behavior of the porous membranes was investigated with respect to dynamic BSA fouling. The results in terms of permeate flux relative to pure water flux are shown in Fig. 8 [Figure 8: see original paper]. It can be seen that both the pristine and grafted membranes exhibit flux decline resulting from fouling. In comparison, the flux decline of PVDF-g-PVP membranes is rather mild. For example, after 4 h of continuous filtration, the flux of the pristine membrane and the PVDF-g-PVP membrane of DG = 11.75% dropped to 52.78% and 82.54% of their initial pure water flux, respectively, indicating improved antifouling property of the grafted PVDF membrane. However, the flux of the PVDF-g-PVP membrane of DG = 17.43% dropped to 75.58% of its initial pure water flux, which is lower than that of the PVDF-g-PVP membrane of DG = 11.75%. Both hydrophilicity and pore size distribution affect BSA fouling on the membrane surface [7, 34-36]. The PVDF-g-PVP membrane of DG = 17.43% shows the highest hydrophilicity and should exhibit the best antifouling property. However, its mean pore size is the largest of all the porous membranes, which can influence fouling resistance significantly. Considering these two factors, the PVDF-g-PVP membrane of DG = 11.75% exhibits the best antifouling property.

Conclusion

Porous membranes were cast from pristine PVDF and PVDF-g-PVP powders with different DGs by the phase inversion method. The existence of PVP graft chains in PVDF-g-PVP membranes has been demonstrated by FTIR-ATR and XPS spectroscopy. The hydrophilicity of PVDF-g-PVP membranes was improved compared to the pristine PVDF membrane due to the presence of hydrophilic PVP graft chains, which consequently led to reduced contact angles. Furthermore, the hydrophilicity of PVDF-g-PVP membranes was intensified with increasing DG. The different PVP polymer concentrations in the membrane bulk and on the membrane surface confirmed surface segregation of the hydrophilic PVP polymer in the surface region. Thermal behavior analysis showed that PVDF-g-PVP membranes exhibited a two-step thermal decomposition process, and the melting temperature of PVDF-g-PVP membranes was slightly decreased compared to the pristine one. SEM images demonstrated that the PVDF-g-PVP membrane with a DG of 6.06% exhibited the greatest porosity, which led to the highest water flux, and the pore connectivity of PVDF-g-PVP membranes was greater than that of the pristine PVDF membrane. Filtration performance evaluation indicated that PVDF-g-PVP membranes had better fouling resistance than the pristine one, and the PVDF-g-PVP membrane with a DG of 11.75% exhibited the best antifouling property.

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