

Preparation of Temperature Sensitive Poly(vinylidene fluoride) Hollow Fiber Membranes Grafted with *N*-isopropylacrylamide by a Novel Approach

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ABSTRACT: In the present study, the temperature sensitive PVDF-*g*-NIPAAm HFM was prepared by grafting *N*-isopropylacrylamide (NIPAAm) on poly(vinylidene fluoride) (PVDF) hollow fiber membrane (HFM) using a novel approach, alkaline treatment method. The structures of PVDF-*g*-NIPAAm HFM were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), respectively. The effects of alkaline treatment time and grafting yield on the mechanical prop-

erties of PVDF HFM were measured and analyzed. In addition, the temperature sensitive behavior of PVDF-*g*-NIPAAm HFM and the effect of grafting yield on the temperature sensitive behavior were investigated by the flux of pure water and the rejection of ovalbumin. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 833–837, 2006

Key words: poly(vinylidene fluoride); *N*-isopropylacrylamide; membranes; hydrogels; temperature sensitive

INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPAAm) has been extensively studied because of its temperature sensitive properties. It exhibits a lower critical solution temperature (LCST) behavior at around 32°C in aqueous solutions. PNIPAAm chains hydrate to form an expanded structure in water when the solution temperature is below its LCST and dehydrate to form a compact structure when heated to above the LCST. However, applications of PNIPAAm hydrogel have been limited because of its low mechanical strength in a highly swollen state. The limitation can be overcome by grafting NIPAAm on the membrane substrates, thus temperature sensitive polymeric membrane can be obtained, and there are some studies that have been reported about temperature sensitive membranes by grafting NIPAAm on various existing porous membranes such as Poly(propylene) membrane,^{1,2} Poly(vinyl alcohol) and the copolymer membrane,³ nonwoven polyester,⁴ and Poly(vinylidene fluoride) (PVDF) membranes.^{5–9}

Among these membrane substrates, PVDF has many advantages and widely applied in microfiltration (MF) and ultrafiltration (UF). To obtain tempera-

ture sensitive PVDF-*g*-NIPAAm membrane, various methods have been used for making NIPAAm grafted onto the PVDF membrane: electron beam grafting,⁸ phase inversion process^{5–7} and plasma treatment.¹⁰

Here we report a novel approach (alkaline treatment) for grafting NIPAAm on PVDF hollow fiber membrane (HFM). In this study, the effects of alkaline treatment time and grafting yield on the mechanical properties of PVDF HFM were analyzed. The temperature sensitive behavior of PVDF-*g*-NIPAAm HFM and the effect of grafting yield on the temperature sensitive behavior were investigated by the flux of pure water and the rejection of ovalbumin.

EXPERIMENTAL

Material

Poly(vinylidene fluoride) (PVDF) hollow fiber membranes were obtained from Tianjin Polytechnic University Membrane Company. *N*-isopropylacrylamide (NIPAAm) was used as a graft monomer and was supplied by Kohjin co. Ltd., Japan; *N,N'*methylenebisacrylamide (MBAA) and K₂S₂O₈ were purchased from Tianjin chemical reagent co., China as a crosslinking agent and initiator, respectively. Tetrabutylammonium bromide (TBAB) (Shanghai chemical reagents co., China) use as phase transfer catalyst. Ovalbumin (Sigma, Grade V, 98% purity, M_w = 45,000). All chemicals were analytic grades and were used as received without further purification.

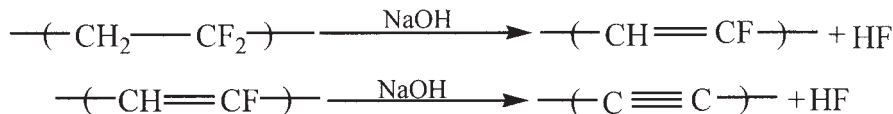
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Alkaline treatment of PVDF HFM

PVDF HFM was immersed in 10 wt % NaOH solution containing 0.05 wt % tetrabutylammonium bromide (TBAB) with different time at 60°C. After treat-

ment, PVDF HFM was washed with pure water so as to remove the alkali solution. The reaction mechanism of alkaline treatment is depicted in following formula:



Double bond was formed within the molecule in consequence of dehydrofluorination, and two dehydrofluorination processes would lead to the formation of carbon-carbon triple bonds.

Preparation of PVDF-g-NIPAAm HFM

Alkaline-treated PVDF HFM was soaked in 10 wt % NIPAAm aqueous solution containing 10 vol % dimethylformamide (DMF) at room temperature. After immersion for 3 h, PVDF HFM was taken out, wiped with a filter paper to remove solvent on the surface of membrane and was immersed in MBAA aqueous solution with various concentration for 30 min under the protection of nitrogen gas. After reaction for 1 h at 60°C in a seal condition, the PVDF-g-NIPAAm HFM were washed with high purity water within an ultrasonic bath to eliminate the unreacted monomer and the homopolymer probably formed on the surface of HFM. PVDF-g-NIPAAm HFM was dried in vacuum at 80°C for 2 h and weighed.

Test and analysis

Grafting yield of NIPAAm

Grafting yield of NIPAAm (G) was measured by a weighting method.

$$G = (m_1 - m_0) / m_0 \times 100\%$$

Where m_0 represents the mass of the pristine PVDF HFM and m_1 represents the mass of the grafted. In the present work, various grafting yield were obtained by changing the concentration of MBAA.

Flux of pure water and rejection of ovalbumin

Flux experiments through the PVDF HFM were carried out using distilled water under a pressure of 0.01 kg/cm², and solute rejection was measured by analyzing the concentration of ovalbumin in the feed and permeates. During the measurement, the cell and permeating solution were kept in a thermostat water bath, allowing the exact control of the temperature. Flux (J , L/(m² h)) was calculated as

$$J = V / (At)$$

Where V is the volume of liquid (L), A is effective area of HFM (m²) and t is time (h). The solute rejection, R , was calculated as

$$R\% = 100(C_0 - C_1) / C_0$$

Where C_0 and C_1 are the concentration of ovalbumin in the feed and permeate, respectively. The solutions of ovalbumin were prepared by dissolving the ovalbumin in a 0.05 mol/L phosphate-buffered solution (disodium hydrogen phosphate + potassium dihydrogen phosphate, pH 7.0). The concentration of ovalbumin in the feed was 0.2 g/L and the concentration of ovalbumin in the permeates were measured by a UV spectrophotometer (UV-2401, Shimadzu) at the wavelengths of 280 nm.

FTIR analysis

The pristine PVDF HFM, alkaline-treated PVDF HFM, and PVDF-g-NIPAAm HFM were powdered and ground with KBr. The FTIR spectra were recorded on Bruker spectrophotometer (Tensor 37 model).

Morphology of PVDF-g-NIPAAm

The cross section of pristine PVDF HFM, alkaline-treated PVDF HFM and PVDF-g-NIPAAm HFM were observed by SEM (Quanta 200).

Mechanical analysis

Mechanical properties of alkaline-treated PVDF HFM and PVDF-g-NIPAAm HFM were measured with tensile test machine (PC/LLY-06, Lanzhou electron instrument, China) at drawing speed of 20 mm/min. All measurements were performed five times for each sample for an average.

RESULTS AND DISCUSSION

FTIR analyses

Figure 1 shows FTIR spectra of the pristine PVDF HFM, alkaline-treated PVDF HFM, and PVDF-g-

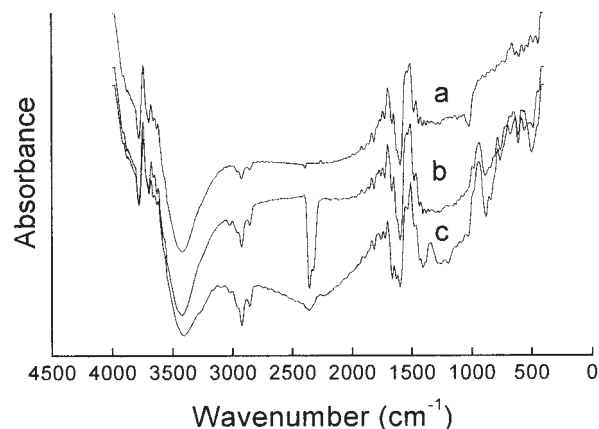


Figure 1 FTIR spectra of (a) the pristine PVDF HFM, (b) alkaline-treated PVDF HFM, (c) PVDF-g-NIPAAm HFM.

NIPAAm HFM, respectively. By comparison with curve *a*, the weak absorbance at 1680 cm^{-1} and strong absorbance at 2250 cm^{-1} in curve *b* indicate the formation of $\text{C}=\text{C}$ double bonds and $\text{C}\equiv\text{C}$ triple bonds, which support the mechanism of alkaline treatment mentioned earlier. Curve *c* presents two main differences with respect to curve *b*. The $\text{C}\equiv\text{C}$ stretch bands around 2250 cm^{-1} become weak, suggesting NIPAAm grafting on the alkaline-treated PVDF HFM. Meanwhile, the absorption band at 1655 cm^{-1} was attributed to the stretching vibrations of $\text{C}=\text{O}$ groups in NIPAAm; 1150 cm^{-1} vibration and 1380 cm^{-1} framework vibration were designated to the isopropyl ($\text{CH}(\text{CH}_3)_2$) in NIPAAm, which indicate that NIPAAm have been grafted onto the alkaline-treated PVDF HFM.

Morphologies of PVDF-g-NIPAAm HFM

SEM can be used to elucidate the structure of HFM. Figure 2 shows the morphology of cross section of various PVDF HFMs. It could be clearly seen from Figure 2(a) that the pores of the pristine PVDF HFM were distributed uniformly. After alkaline-treated at first stage, as shown in Figure 2(b), the structural integrity of PVDF HFM was not destroyed and pores still distributed uniformly as pristine PVDF HFM. However, extending the alkaline treatment time continuously would make the pores of HFM destroyed. (Fig. 2(c)). After grafting, PNIPAAm gel can be observed obviously on both surface and pores of the PVDF-g-NIPAAm HFM (Fig. 2(d)).

Mechanical properties of PVDF-g-NIPAAm HFM

Figure 3 shows the average tensile elongation and tensile strength of PVDF HFM as a function of alkaline treatment time, respectively. With the increase in alkaline treatment time, the average tensile elongation

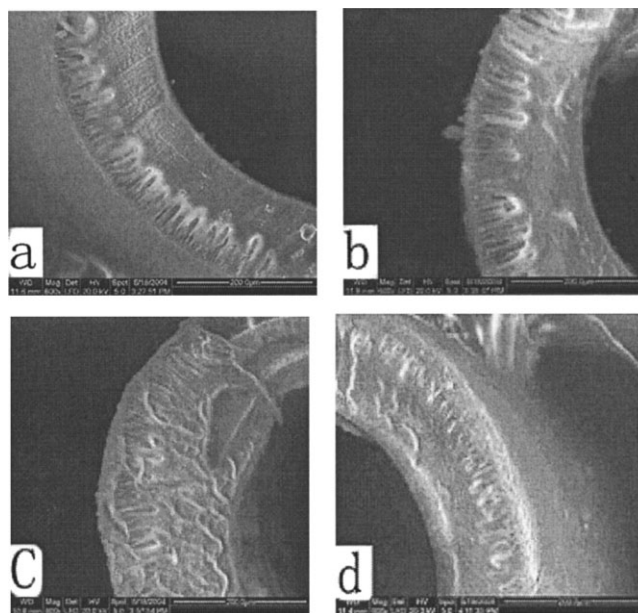


Figure 2 SEM pictures of various HFM: (a) the pristine PVDF HFM, (b) alkaline-treated PVDF HFM with 4 min, (c) alkaline-treated PVDF HFM with 10 min, and (d) PVDF-g-NIPAAm HFM (alkaline treatment time was 4 min).

markedly decreased and the average tensile strength increased at first, then dramatically decreased. This is attributed to $\text{C}=\text{C}$ double bond forming within the molecule of alkaline-treated PVDF, which caused the flexibility of PVDF HFM to be impaired. However for the average tensile strength, at the first stage of alkaline treatment, $\text{C}=\text{C}$ double bond was formed only on the surface of PVDF HFM, and the structural integrity of HFM was not destroyed. In addition, bond energy of $\text{C}=\text{C}$ double bond is stronger than $\text{C}-\text{C}$ bond. Therefore the average tensile strength of PVDF HFM did not decrease by alkaline treatment but, on the contrary increase during the first stage of alkaline treatment. However, extending the alkaline treatment time continuously could cause the formation of $\text{C}=\text{C}$

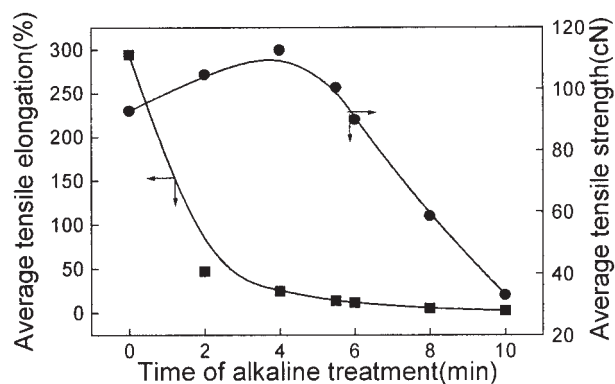


Figure 3 Effect of alkaline treatment time on average tensile elongation and strength.

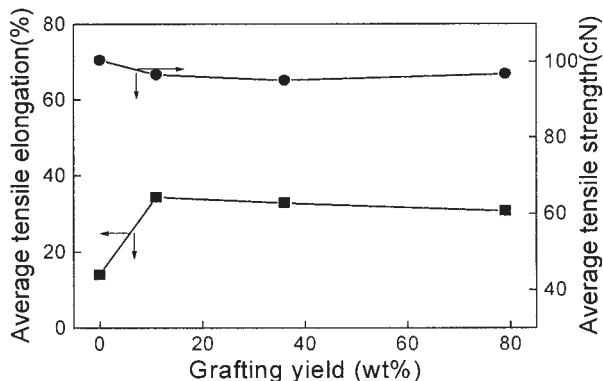


Figure 4 Effect of grafting yield on average tensile elongation and strength.

double bond and $C\equiv C$ triple bond also in the interior of PVDF HFM, which caused the impairment of the structural integrity of HEM, resulting in marked decrease in the average tensile strength, as shown in Figure 3. Therefore, from the viewpoint of mechanism of alkaline treatment and maintaining the mechanical properties of PVDF HFM, time of alkaline treatment was fixed at 4 min in this work.

The mechanical properties of PVDF-g-NIPAAm HFM as a function of grafting yield are showed in Figure 4. Compared with that of the alkaline-treated PVDF HFM, the average tensile strength of PVDF-g-NIPAAm decreased a little initially, and the average tensile elongation increased at first, then kept steadily. This result can also be attributed to the amount of $C=C$ double bond. With the increase in the grafting yield, the amount of $C=C$ double bond decreased, resulting in the increase in flexibility and decrease in average tensile strength

Temperature sensitive behavior of PVDF-g-NIPAAm HFM

Effect of temperature on the flux of pure water and the rejection of ovalbumin through pristine PVDF HFM and various grafted PVDF-g-NIPAAm HFMs were shown in Figure 5 and Figure 6, respectively. The pristine PVDF HFM exhibited almost constant values of the flux of pure water and rejection of ovalbumin, indicating that the pristine PVDF HFM did not show temperature sensitive behavior. In contrast to pristine PVDF HFM, there were differences in PVDF-g-NIPAAm with grafting yield of 11 and 36%, which showed that the flux of pure water and rejection of ovalbumin changed with temperature. It could be considered that PNIPAAm hydrogel is covalently tethered both on the surface and into the pores of PVDF HFM. Therefore the permeability of PVDF-g-NIPAAm depends on the conformation of the PNIPAAm hydrogel grafted onto the pores of PVDF hollow fiber. Below

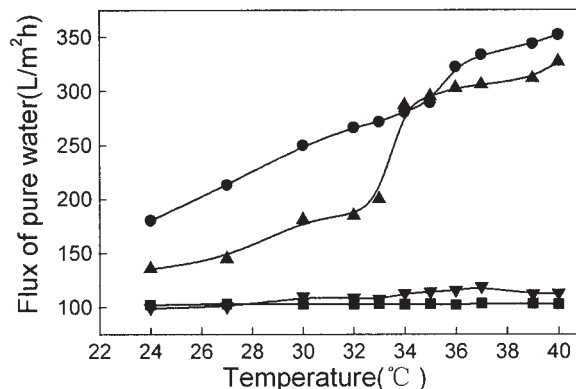


Figure 5 Effect of temperature on the flux of pure water through pristine PVDF HFM (■), 11% grafted PVDF-g-NIPAAm HFM (●), 36% grafted PVDF-g-NIPAAm HFM (▲), and 79% grafted PVDF-g-NIPAAm HFM (▼).

the LCST, the PNIPAAm hydrogel is in the swollen state in the pores, and making pores of PVDF hollow fiber close. As a result, the flux of pure water decreased and the rejection of ovalbumin increased. Above the LCST, PNIPAAm hydrogel grafted onto the pores of PVDF HFM shrink, and thus the pores in PVDF hollow fiber are left open, making the flux of pure water increasing and the rejection of ovalbumin decreasing. Therefore, the PNIPAAm hydrogel grafted onto the pores of PVDF hollow fiber acts as a sensor of temperature and as a valve to regulate the filtration rate of the membrane.

In addition, grafting yield of NIPAAm is another important factor that affects the temperature sensitive behavior of PVDF-g-NIPAAm HFM. As shown in Figure 5 and Figure 6, when the grafting yield was 11 and 36% respectively, the flux of pure water and rejection of ovalbumin of PVDF-g-NIPAAm HFM changed with temperature, indicating that PVDF-g-NIPAAm HFM with 11 and 36% grafting yield are temperature

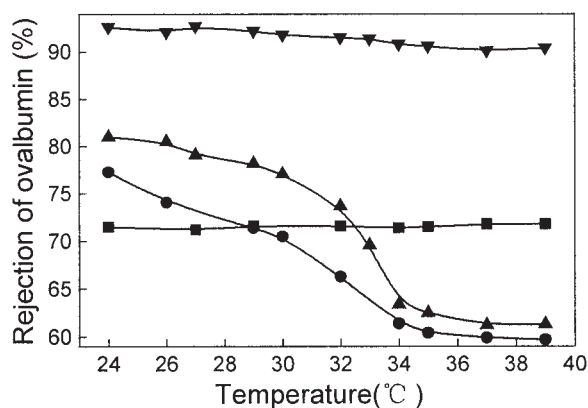


Figure 6 Effect of temperature on the rejection of ovalbumin through pristine PVDF HFM (■), 11% grafted PVDF-g-NIPAAm HFM (●), 36% grafted PVDF-g-NIPAAm HFM (▲), and 79% grafted PVDF-g-NIPAAm HFM (▼).

sensitive HFMs. The differences are that the curve of 11% grafting yield changed gradually at around 32°C, while the curve of 36% grafting yield changed markedly at around 32°C because of the different swelling behavior of the grafted PNIPAAm hydrogel. However, for HFM with 79% grafting yield, the flux of pure water and rejection of ovalbumin did not exhibit a temperature sensitive behavior. This might be associated with the formation of a dense skin of PNIPAAm hydrogel on the wall of the pores, and it would fill up the pores of PVDF HFM, even the temperature is above LCST. As a result, the flux of pure water and the rejection of ovalbumin cannot be changed with temperature. Therefore, it can be inferred that PVDF-g-NIPAAm HFMs with various grafting yields had different thermal sensitive behavior. It is possible to control the flux of pure water and ovalbumin across the PVDF-g-NIPAAm HFM by changing the grafting yield.

CONCLUSIONS

Alkaline treatment method is an effective way of grafting NIPAAm on the chains of PVDF hollow fiber. FTIR support the mechanism of alkaline treatment, i.e., dehydrofluorination and two dehydrofluorination lead to the formation of C=C and C≡C, respectively. Meanwhile, we measured and analyzed the effect of alkaline treatment time on the mechanical property of

PVDF HFM and found that a suitable alkaline treatment time was 4 min under our experimental condition. The flux of pure water and rejection of ovalbumin were used in the studies of temperature sensitive behavior and the result showed that the PVDF-g-NIPAAm HFMs prepared by alkaline treatment method were temperature sensitive membranes and the grafting yield also has an important role in controlling the flux of pure water and the rejection of ovalbumin.

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