Membrane Water Treatment, *Vol. 7*, *No. 5* (*2016*) *417-431*
DOI: http://dx.doi.org/10.12989/mwt.2016.7.5.417

Preparation and characterization of PVDF/alkali-treated-PVDF blend membranes

Q.F. Liu [1a], F.Z. Li [1b], Y.Q. Guo [1c], Y.L. Dong [1d],
J.Y. Liu [1e], H.B. Shao [*2,3] and Z.M. Fu [**1]

[1] *College of Environment and Resources*, *Inner Mongolia University*,
No. 235 West College Road, *Hohhot*, *Inner Mongolia*, *Hohhot 010021*, *China*
[2] *Key Laboratory of Coastal Biology & Bioresources Utilization*, *Yantai Institute of*
Coastal Zone Research (*YIC*), *Chinese Academy of Sciences* (*CAS*), *Yantai 264003*, *China*
[3] *Institute of Biotechnology*, *Jiangsu Academy of Agricultural Sciences*, *Nanjing 210014*, *China*

(*Received January 16*, *2015*, *Revised December 16*, *2015*, *Accepted May 08*, *2016*)

Abstract. Poly(vinylidene fluoride) (PVDF) powder was treated with aqueous sodium hydroxide to obtain partially defluorinated fluoropolymers with expected properties such as improving hydrophilicity and fouling resistance. Raman spectrum and FT-IR results confirmed the existence of conjugated carbon double bonds after alkaline treatment. As the concentration increased, the degree of defluorination increased. The morphology and structure of membranes were examined. The permeation performance was investigated. The results showed that membrane's hydrophilicity increased with increase of the percentage of alkaline treated PVDF powder. Moreover, in terms of the water contact angle, it decreased from 92° to a minimum of 68°; while water up take increased from 128 to 138%. Fluxof pure water and the cleaning efficiency increased with the increase of alkaline treated PVDF powder. The fouling potential also decreased with the increase of the percentage of alkaline treated PVDF powder. The reason that makes blending PVDF show different characteristics because of partial defluorination, which led the formation of conjugated C = C bonds and the inclusion of oxygen functionalities. The polyene structure followed by hydroxide attack to yield hydroxyl and carbonyl groups. Therefore, the hydrophilicity of blending membrane was improved. The SEM and porosity measurements showed that no obvious variations of the pore dimensions and structures for blend membranes were observed. Mechanical tests suggest that the high content of the alkaline treated PVDF result in membranes with less tolerance of tensile stress and higher brittleness. TGA results exhibited that the blend of alkaline treated PVDF did not change membrane thermal stability.

Keywords: PVDF; alkaline treatment; blend; hydrophilicity

∗Corresponding author, Professor, E-mail: shaohongbochu@126.com
**Corresponding author, Professor, E-mail: fuzhm2012@163.com
[a] Professor, E-mail: ndlqf@imu.edu.cn
[b] M.A., E-mail: 937366330@qq.com
[c] M.A., E-mail: guoyanqing563650@163.com
[d] M.A., E-mail: dongyilun1993@163.com
[e] M.A., E-mail: 59141643@qq.com

http://www.techno-press.org/?journal=mwt&subpage=7 ISSN: 2005-8624 (Print), 2092-7037 (Online)

1. Introduction

PVDF is one of the most widely used fluoropolymer due to its excellent mechanical/chemical properties. However, the hydrophobic property of PVDF limits its application in some fields, especially in the field of water treatment. Because the hydrophobic interactions between membrane and the particulates contained in feed water easily cause membrane fouling (Zhang *et al*. 2009). To improve hydrophilicity, various investigations have been carried out. Examples are plasma treatment (Wang *et al*. 2002), blending PVDF with hydrophilic polymers (Nunes and Peinemann 1992, Ochoa *et al*. 2003, Yang and Liu 2003, Li *et al*. 2015, Chang *et al*. 2014), chemical functionalization (Baroña *et al*. 2007), and radiation induced surface grafting (Rye 1993, Liu *et al*. 2007). Among them, the treatment with group I hydroxides has been carried by a few researches targeting the formation of expected properties based on the changes of its functional group and structure of the chain. Crowe and Badyal (1991) found that PVDF membrane can be partially defluorinated with treatment of aqueous lithium hydroxide. The introduction of oxygen-containing groups also was confirmed. Ross *et al*. (2000) compared the results of poly(vinyl fluoride) (PVF), PVDF and polytetrafluoroethylene (PTFE) membrane after treating with aqueous potassium hydroxide. PVDF and PVF membrane demonstrated significant changes in chemistry, but no chemical changes were observed for PTFE. In the cases of PVF and PVDF treated with alcoholic KOH, chemical changes were more marked with PVDF and alcohol further enhanced these trends. Brewis *et al*. (Brewis and Mathieson 1994 and Brewis *et al*. 1998) tried to enhance the effectiveness of the potassium hydroxide (KOH) treatments on the use of tetrabutylammonium bromide (TBAB). They found that TBAB greatly increased the effectiveness of KOH treatments in terms of joint strength improvement. Zhang *et al*. (2001) tried to degrade PVDF via mechanochemical solid-phase reaction between polyvinylidene fluoride and sodium hydroxide. They found that about 90% of fluorine in the PVDF sample can be converted into NaF by this process. Based on our previous work (Liu and Kim 2010), we proved that the hydrophilicity of the PVDF membrane can be improved and the anti-fouling potential of the treated membrane slightly increased after appropriate alkaline treatment. But pure water flux decreased. This may be attributed to the decrease of pore size and downward shifting of pore size distribution after alkaline treatment. In addition, extremely high alkali concentration can result in damage of membrane integrity.

To the author's knowledge, previous investigations are mainly focused on the treatment of preformed membranes. The membrane integrity under such severe oxidizing condition has to be seriously considered. In addition, to protect membranes, the treatment could not be conducted at high temperature and stirring conditions. This further slows down the process and even causes inhomogeneous reactions at different positions on the membrane surface.

So, in this study, we proposed a method that directly degrades PVDF powder with aqueous sodium hydroxide. As a result, the fear of damage of membrane integrity can be avoided. The degradation reaction was carried out in temperature controlled conditions with adjustable stirring speed. The degradation products are expected to consist mainly of non-thoroughly degraded PVDF powder, few polar based (OH based, carbonyl based etc.,) compounds and carbon-rich compounds. These newly formed materials blended with untreated PVDF are cast to form a membrane via the phase inverse process. The effects of blending ratio on characteristics of membranes were examined via SEM, contact angle, water uptake, mechanical properties, porosity, TGA, and FT-IR. The permeation performance in term of pure water flux, protein rejection, fouling potential and cleaning efficiency was also investigated.

The major concern in this study is to examine the process of the alkaline treatment of PVDF powder and further improve membrane hydrophilicity via blending with the PVDF powder after alkaline treatment. The main innovation is to treat PVDF powder instead of PVDF membrane.

2. Experimental

2.1 Materials

The PVDF (Solvey 6013/1001 Mw ca. 2.2×105 gmol-1) powder used in this study was received from Solvey Korea Co. Aqueous sodium hydroxide (NaOH) solutions were made up from Extra Pure grade pellets, supplied by Duksan Co., Ltd. Extra pure grade Ethyl acetate was purchased from Daejung chemicals & metals Co., Ltd. N,N-dimethylacetamide (DMAc) was purchased from Acros Organics, Inc., USA. Bovine serum albumin (BSA) was purchased from Aldrich.

2.2 Alkaline Treatment

Sodium Hydroxide pellets were dissolved in deionized (DI) water to prepare different concentrations of aqueous solution (2 M, 7 M, and 12 M). All solutions were put into Kontes round bottom flasks, which were placed on a heating mantles; and the temperature was set to 100°C by temperature controllers (CE. 5U, DX4, Hanyoung, Co.). PVDF powder were treated in the NaOH solution for 2 hours, then the solution were filtrated through glass microfiber filters (Whatman, GF/C, 47 mm) to separate solid and liquid phases. The solid particles were rinsed with 50 ml DI water for 3 times and dried at 100℃ for 2h. An extreme treatment condition was conducted as reference to compare the characteristics of the treated PVDF powder. The process was as follows: Initially, PVDF powder was added in 12 M NaOH solution at 100°C. With the reaction taking place, water gradually evaporated from the solution, which led to the increase in concentration of the solution over time. The reaction proceeded till the color of the solution changed to dark brown (ca. 30 hours), then we separated and treated the sample using the above mentioned method.

2.3 Preparation of PVDF/Alkaline treated PVDF-blend membrane

Membranes were prepared by phase inversion method. Adding mixed PVDF powder 15 wt.% to DMAc solution till totally dissolved at 80°C. Then casted it on a glass plate to form a flat membrane, which exposed to air for 20s at 20°C, then rinsed with DI water for 12 h, and dried in vacuum dryer at 60°C. The percentage of alkaline treated PVDF powder changed from 10 to 100.

Table 1 Preparation of membranes with different alkaline treatment conditions and blend ratio X

Percentage of alkaline treated PVDF powder	Type I (Treated with 2 M NaOH)	Type II (Treated with 7 M NaOH)	Type III (Treated with 12 M NaOH)
10	A10	B10	C10
20	A20	B20	C20
30	A30	B30	C30
50	A50	B50	C50
100	A100	B100	C100

Membranes were classified as type I, type II, and type III according to three different concentration of aqueous solutions (2 M, 7 M, 12 M) (Table. 1).

2.4 Mechanical analysis

Mechanical properties of alkalined-treated PVDF membrane were measured with universal testing machine (UTM LF Plus, Lloyd) at drawing speed of 10 mm/min, equipped with a 1 kN load cell.

2.5 Thermal gravimetric analysis

Thermal degradation of the membranes was measured using TGA (TG/DSC 92) by heating the samples from 60°C to 800°C at a heating rate of 10°C/min under nitrogen atmosphere.

2.6 Membrane morphology

Surface morphology of samples was observed using Hitachi S-3500N scanning electron microscopy (SEM) with accelerating voltage of 15.0 kV. For observing the cross-section of the membranes, samples were dried and then fractured using liquid nitrogen and coated with a thin layer of Pd/Au.

2.7 Pore size distribution

Membrane mean pore size distribution was measured based on the theory of bubble pressure method with capillary flow porometer (Porous Materials Inc., Model CFP-1200AE). Gas bubbles were blown through a capillary which is submerged in the sample liquid at constant rate. The pressure inside of the gas bubble continues to increase and the maximum value is obtained when the bubble has the completely hemispherical shape whose radius is exactly corresponding to the radius of the capillary. Then other pores were opened from big to small in turn with the increase of pressure. The air flow of wet membrane was measured when it reached steady state and the air flow of dry membrane was measured when all pores were opened. The flow ratio of wet and dry membrane and the distribution function were calculated separately.

2.8 Contact angle

Static contact angles of the membrane surface were measured based on the sessile drop method. A constant drop volume of 5 μl of DI water was perpendicularly deposited with a micro syringe onto a dry membrane surface in air and the contact angle was observed after 10 sec using Scalar video loupe (VL-11s) and the image was analyzed using the Sigma TV II program. The average value of five measurements was taken at different locations on the surface.

2.9 Water uptake property

The water uptake was measured using the method suggested by Baroña *et al.* (2007). The membrane samples were soaked in DI water for 24 h at room temperature until swelling equilibrium was achieved. The weight was recorded as wet weight W_w. Then the same sample was dried in vacuum at 60°C to obtain constant dry weight W_d. The water uptake was obtained through Eq. (1)

$$\text{water uptake (wt\%)} = ((W_w - W_d)/W_d) \times 100 \tag{1}$$

2.10 ATR-FTIR

Surface infrared spectra were recorded on a Varian 2000 FTIR spectrometer. For each measurement, 32 scans were performed at a resolution of 8 cm^{-1} in ATR mode. The IR penetration depth for this incident angle is 0.1-1 μm. Samples were dried in a vacuum oven overnight at room temperature before analysis.

2.11 Raman spectroscopy

The Raman spectra of the samples were recorded in backscattering geometry on a DILOR XY multichannel spectrometer using an excitation line at either 632 nm (out of resonance) of the He–Ne model 207B Spectra Physics laser (25 mW power at the laser head) or at 514.53 nm (resonance conditions) of a Ar^+ model 165 Spectra Physics laser (power less than 50 mW). Briefly the spectrometer consists of a triple monochromator used in subtractive mode to select a given spectral range followed by the spectrograph to complete the dispersion, and a Jobi-Yvon CCD (Charge Coupled Device) matrix thermoelectrically cooled. Using 200 μm slit widths, the spectral resolution was always better than 5 cm^{-1}.

2.12 Membrane performance

A dead-end magnetically stirred cell (Amicon Co., Ltd., Type 8050) with a 43 mm diameter and volume of 50 mL was used to evaluate the membrane performances. The cell was connected to a 3.5 L dispensing vessel. The effective membrane area (A) was 13.85 cm^2. The membranes were initially pressurized with distilled water at 2 bar for 30 min. Pure water flux tests were conducted by applying pressurized nitrogen gas at 1 bar. Permeate mass (M) was recorded by a digital balance (OHAUS Co., Ltd., Type Explorer. Pro). Membranes were soaked into DI water before use. Each test was conducted for at least 30 min. The flux was calculated using Eq. (2)

$$J_0 = M/(A*t) \tag{2}$$

where J is the membrane flux, M is accumulating mass, and t is filtration time.

To evaluate the fouling potential, a filtration protocol suggested by Zhang et al. (2009) was used in this study. The permeate flux with 0.1 wt% of BSA solution at pH 7.4 (adjusted by buffer solution) was measured at 1 bar for 6 h. Permeate mass was recorded by the digital balance every 30 sec. The initial flux was termed J_{p1} and the flux of the last 10 sec was termed J_{p2}. After protein solution filtration, the membrane was dismounted from the cell and cleaned three times with pure water in ultrasonic bath for 5 min before the water flux (J_1) was measured. Then the membrane was cleaned with 0.5 mol/L NaOH in ultrasonic bath for 30min and rinsed three times with pure water for 5 min before pure water flux (J_2) was measured. The measurement error for the flux was ±5 L/m^2 h. All filtration was performed at room temperature. $J_{p1}-J_{p2}$ is the flux loss due to fouling, J_1-J_{p2} is the pure water flux recovered by water cleaning, J_2-J_1 is the pure water flux recovered by caustic cleaning, and J_2-J_{p2} is the pure water flux recovered by both water and caustic cleaning.

The apparent rejection rate (R_{obs}) of the membrane was calculated by Eq. (3)

$$R_{obs} = \left(1-\frac{C_p}{C_b}\right)\times 100 \tag{3}$$

Where C_p and C_b represent protein concentrations in permeate and feed (mg/mL), which were determined spectroscopically at 280 nm with 752S UV/VIS spectrophotometer.

3. Results and discussion

3.1 Alkaline treatment

The investigation of the effect of concentration on the degree of alkalization was carried out by comparing the FTIR absorbance and color changes of treated PVDF. The result depicts that higher NaOH concentration led to products with darker color, which means more PVDF were degraded. However, there is no obvious difference that can be seen from the FTIR absorbance (the results are not presented here) for three different treatment conditions. To investigate the effects of concentration, more focus is placed upon the three types of membranes, which are discussed in the following sections.

3.2 Mechanical property

Tensile strength and elongation at break of the three types of membranes were shown in Fig. 1 and Fig. 2. Tensile strength slightly decreased with the increase of the Percentage of alkaline

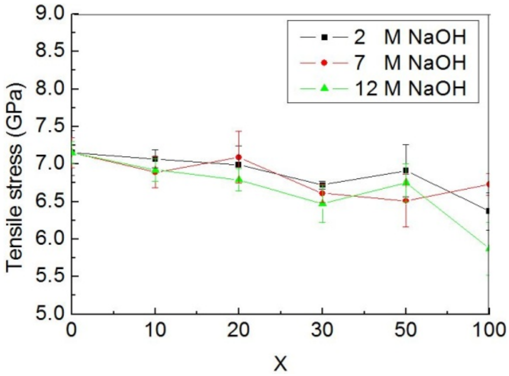


Fig. 1 Tensile stress of three types of membrane with different percentage of alkaline treated PVDF powder

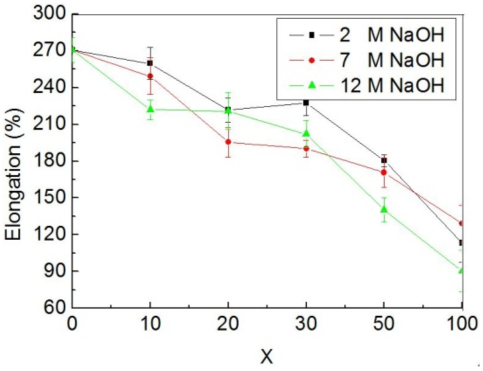


Fig. 2 Elongation of three types of membrane with differentpercentage of alkaline treated PVDF powder

treated PVDF powder. Elongation sharply decreased from 270% for pure PVDF membrane to 90% for pure alkaline treated PVDF membrane. This indicates that the high content of the treated PVDF might result in raising the brittleness of materials. In comparison, type Ⅲ membranes exhibited worse mechanical properties than type Ⅰ and type II membranes. This is believed to be due to effects of different concentrations of alkaline treatment conditions.Higher concentration led to more thorough defluorination of PVDF.

3.3 Thermal gravimetric analysis

Thermal stability of the blend membranes was evaluated by means of TGA technique. As shown in Fig. 3, the initial decomposition temperatures of all three kinds of membranes remained unchanged. This result exhibited that the blend of alkaline treated PVDF did not change membrane thermal stability.

3.4 Membrane morphology

The morphology of pure PVDF and the three types of alkaline treated PVDF blend membrane with different percentage of PVDF was observed with SEM. From Fig. 4, no significant change of the surface morphology was seen. The cross-section also did not show obvious variations of the pore dimensions and structures. All membranes exhibited a typical asymmetric structure composed of a thin and dense skin layer and a more porous bulk with finger-like pore structure.

3.5 Pore size distribution

Membrane pore size and pore size distribution (PSD) were reflected by bubble point pore diameter (maximum pore diameter), mean flow pore diameter, and diameter at maximal PSD. Fig. 5 showed that the mean flow pore diameter and diameter at maximal PSD did not change with the contents of alkaline treated PVDF. No considerable differences were observed in three types of membranes. Although the bubble point pore diameter showed big fluctuation, which may be due to the individual difference of the tested membrane samples. As results, a conclusion might be drawn that the addition of alkaline treated PVDF did not affect membrane pore structures.

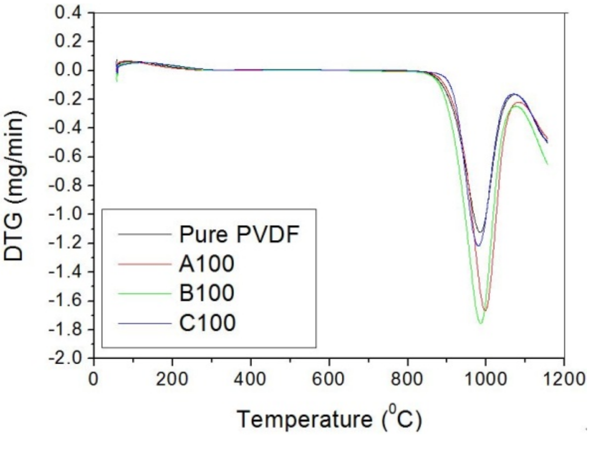


Fig. 3 TGA curves of membranes: pure PVDF, A30, A100, B30, B100, C30, and C100

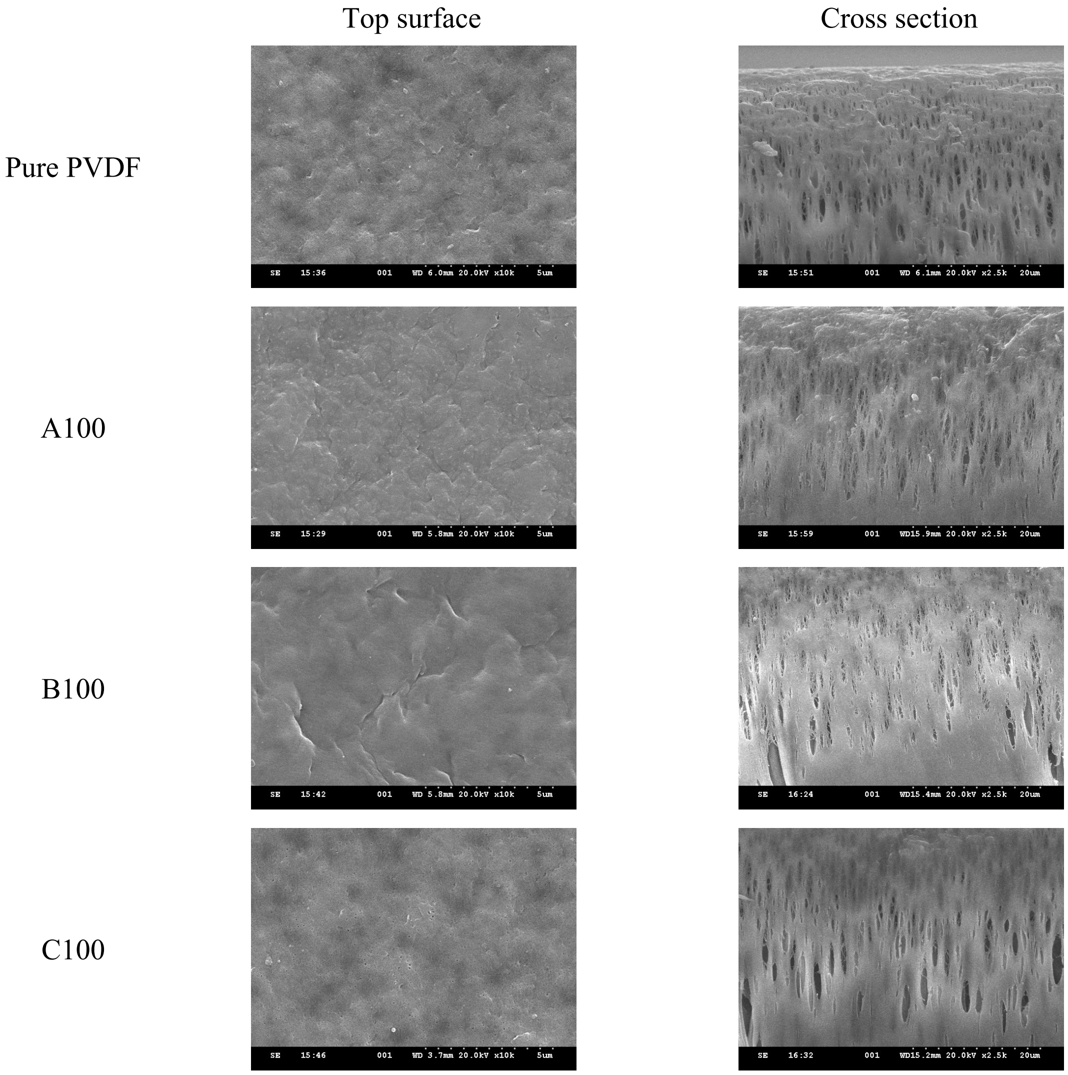
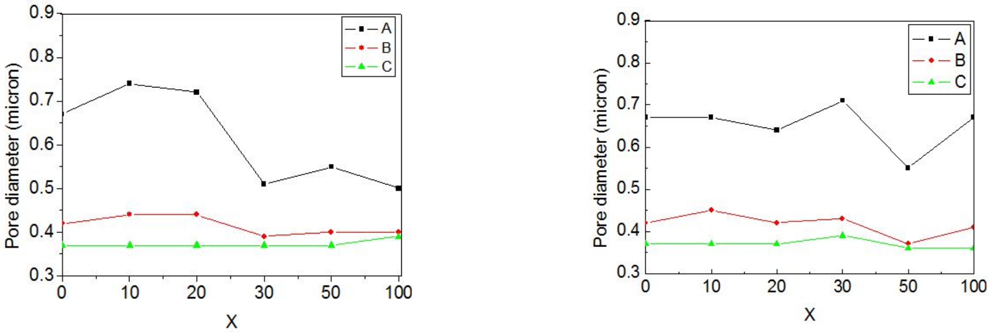


Fig. 4 SEM images of three types of membranes with different percentage of alkaline treated PVDF powder, (a) Top surface; (b) Cross section

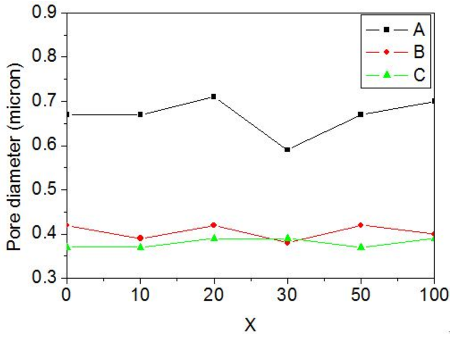
3.6 Contact angle

The contact angle between water droplets and membrane is an important parameter to measure surface hydrophilicity. Fig. 6 shows the values of contact angle of three types of membranes. For pure PVDF membrane, the surface is highly hydrophobic, has a contact angle of 92°. The contact angle decreased with increasing percentage of alkaline treated PVDF. From the figure, it can be seen that type I and type II membranes showed similar behaviors, and type III membranes showed lower contact angle values. It declined considerably to 68° when the membrane was made from the pure alkaline treated PVDF powder. These results confirmed that blending with alkaline treated PVDF can improve membrane hydrophilicity.



(a) Type I

(b) Type II



(c) Type III

Fig. 5 (a) Variations of bubble point pore diameter; (b) mean flow pore diameter, and (c) diameter at maximal PSD of three types of membranes with different percentage of alkaline treated PVDF powder

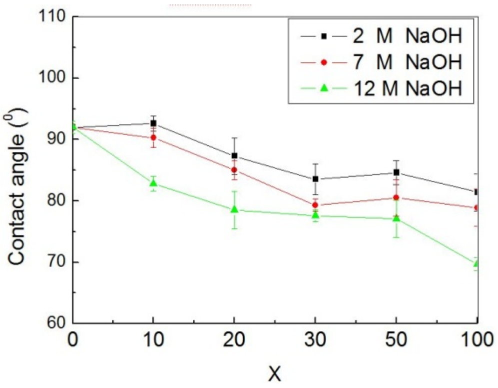


Fig. 6 The contact angle of three types of membrane with different percentage of alkaline treated PVDF powder

3.7 Water uptake property

The water content of the developed membranes was studied and the values are presented in Fig. 7. The water content of pure PVDF membrane was found to be 126%. When the percentage was

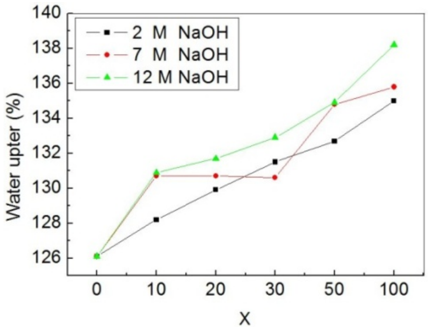


Fig. 7 The water uptake of three types of membranes with differentpercentage of alkaline treated PVDF powder

increased from 10 to 100%, the water content gradually increased from 128 to 138%, respectively. This result confirmed the increasing hydrophilicity and the existence of larger polymer chain segmental gap in the blend membranes.

3.8 ATR-FTIR

The FT-IR spectra of the pure PVDF membrane and three types of the blend membranes with different percentage of alkaline treated PVDF powder were shown in Fig. 8. All blend membranes showed a new weak absorbance peak at 1600 cm^{-1}, which can be assigned to conjugated carbon double bonds. According to Ross (Ross *et al*. 2000), this absorbance is weak as a result of the fact that the C = C bond is inactive in infrared (normally conjugated structures are not active in the infrared but are Raman active). The changes occurred at 1000 cm^{-1} may be due to the change of fluorine groups after alkaline treatment. There is no OH and C = O bands visible.

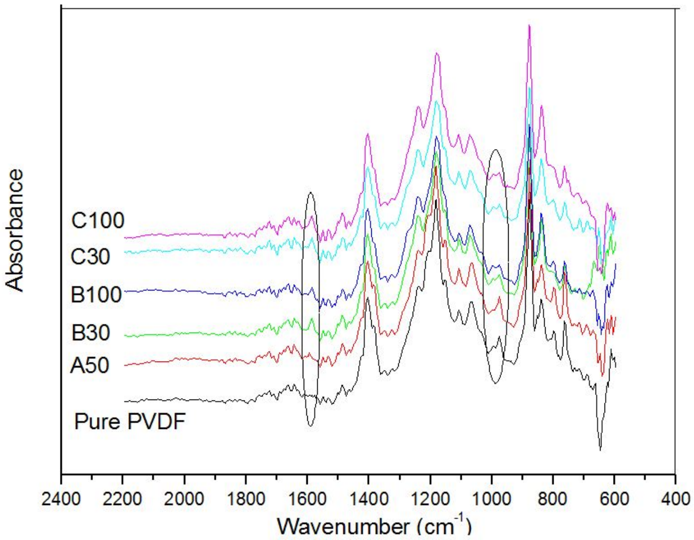
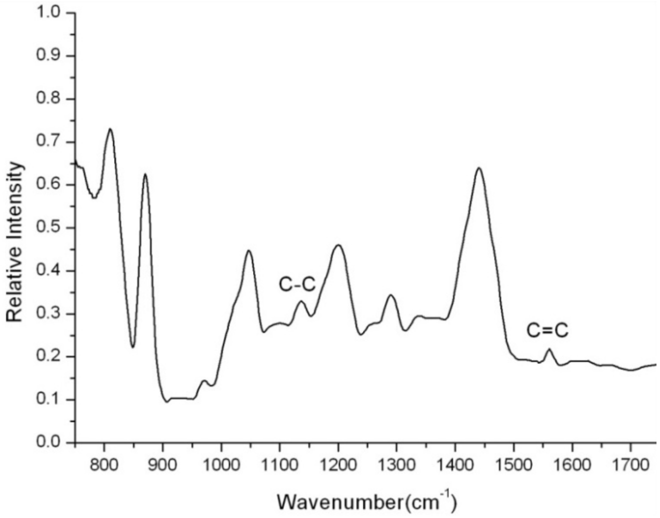
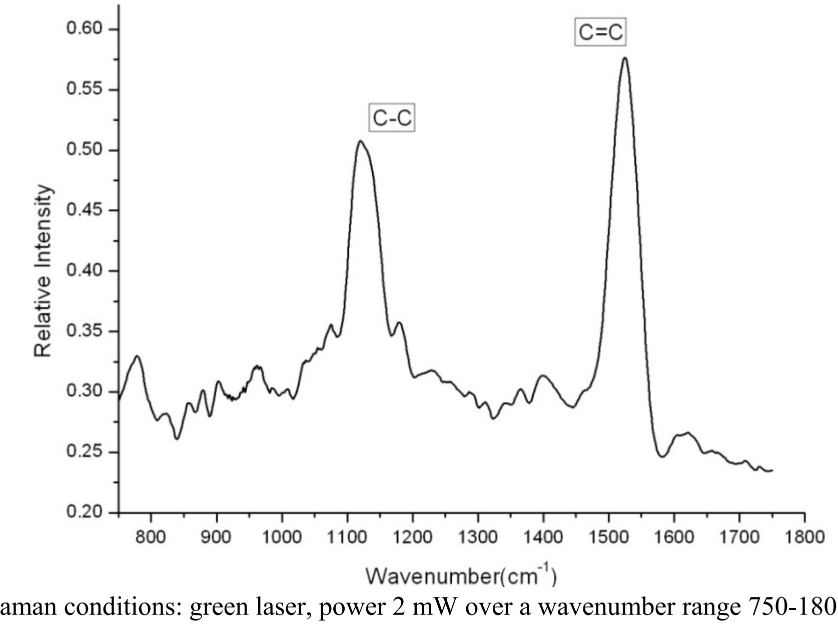


Fig. 8 FT-IR spectra of pure PVDF, A50, B30, B100, C30, and C100 membranes



(a) Raman conditions: green laser, 514.53 nm, power 200 mW over a wavenumber range of 750-1750 cm^{-1}



(b) Raman conditions: green laser, power 2 mW over a wavenumber range 750-1800 cm^{-1}

Fig. 9 Raman spectra of PVdF: (a) untreated (conditions: green laser, 514.53 nm, power 200 mW over a wavenumber range of 750-1750 cm^{-1}); (b) after 2 h treatment with 12 M NaOH at 100°C (conditions: green laser, power 2 mW over a wavenumber range 750-1800 cm^{-1})

3.9 Raman spectra

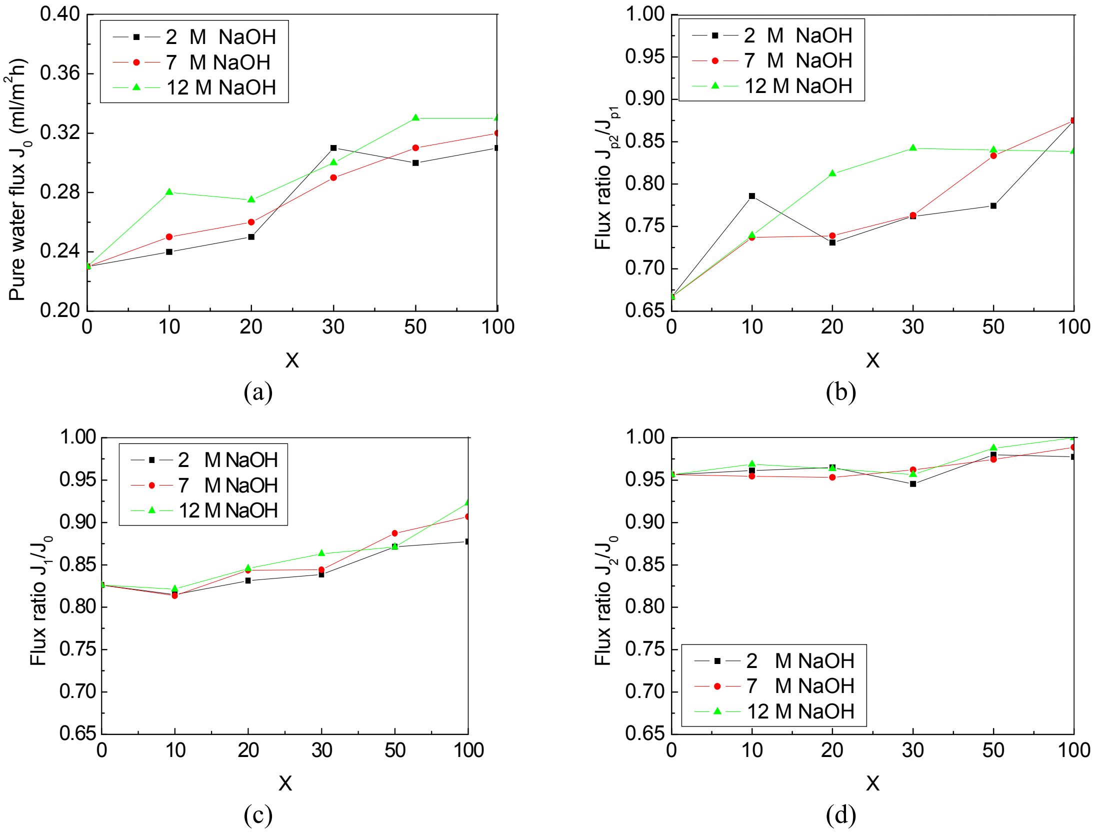
The Raman spectra of untreated and treated PVDF are shown in Figs. 9(a) and (b). After 2 hours treatment the spectra is completely different from the original spectra indicating a complete change in the chemical nature of the surface. The peaks at 1129 and 1525 cm^{-1} are representative of the C – C and C = C respectively. The spectra are similar to that of polyacetylene, which has a conjugated carbon double bond structure, the length of which can be estimated from the distance between the C – C bond peak and the C = C bond peak in the Raman spectra. After treatment there is no indication in the spectra of the presence of oxygen or fluorine groups, whilst fluorine is present, as expected, in the untreated spectra. The estimation of the conjugated chain length and the polydispersity of the polyene can be obtained from the wavenumber of the C = C band (around 1527 cm^{-1}). By use of the graph an estimation of conjugation length from our Raman results can be obtained. A separation of 399 cm^{-1} of the two Raman peaks represents a polyene with 8-9 C = C bonds present.

3.10 Membrane performance

The effects of alkaline treatment and blending ratio of PVDF on membrane performance were investigated by measuring the variation of pure water fluxes as a function of time. The dynamic anti-fouling properties were identified by filtration test of BSA model solution at a fixed pressure. The pure water flux J_0, flux ratio J_{p1}/J_{p2}, J_1/J_0, and J_2/J_0 were shown in Fig. 10(a), (b), (c), and (d), respectively. Here, J_{p1}/J_{p2} represents the anti-fouling ability of the membrane, J_1/J_0 represents the hydraulic cleaning efficiency, and J_2/J_0 represents the chemical cleaning efficiency. The pure water flux J_0 significantly increased with the increase of different percentage of alkaline treated PVDF powder, from 0.23 $\mathrm{ml \cdot m^{-2} \cdot h^{-1}}$ to about 0.30 $\mathrm{ml \cdot m^{-2} \cdot h^{-1}}$. This is attributed to the improvement of membrane hydrophilicity after blending with alkaline treated PVDF powder, which reduces the permeation resistance of water through the membrane. The flux ratio of J_{p1}/J_{p2} increased from 0.67 to about 0.87 when the membrane filtered the BSA solution (Fig. 10(b)). This result suggests that the membranes blended with alkaline treatment powder have obviously enhanced anti-fouling ability. The reason is because less protein is adsorbed on the membrane surface when membrane hydrophilicity is improved. In addition, the low hydrophilicity property of the membrane could lead to the membrane operating under low flux constantly for longer duration. After filtration of BSA solution, the membranes were cleaned with with pure water in ultrasonic bath. The flux ratio J_1/J_0 reflected this cleaning efficiency. From Fig. 10(c), the hydraulic cleaning became more efficient with the increase of different percentage of alkaline treated PVDF powder. This is because the protein has weaker mutual attraction with the low hydrophilic membrane. The chemical cleaning efficiency improved, with a flux recovery up to 97% for type I and type II membranes, and 100% for type III membrane when the percentage of the alkaline treated PVDF powder increased over 50%. The similar phenomena was explained by Zhang *et al.* (2009) that the BSA was not adsorbed by its hydrophobic parts (which would require a strong oxidative action) but by polar/ionic interactions which can be reversed by ionization of weak acid groups with alkaline media.

The rejection rate R_{obs} was calculated by Eq. (3). Three types of membrane showed similar trend that the R_{obs} slightly increased with increase of different percentage of alkaline treated PVDF powder (Fig. 11). We know that rejection is mainly membrane size dependent for a given solute. In our case, the variation of membrane pore size distribution and structure is not obvious with the variation of X. So the improvement of protein rejection must be related to the change of membrane surface properties. The increase of hydrophilicity of the membrane weakened the attraction of the hydrophobic protein. Thereby reduce the protein penetrating through the membrane.

In summary, the blended membrane with alkaline treated PVDF powder can effectively increase water permeate ability, reduce membrane fouling in filtration with BSA and slightly increase protein rejection rate. When fouling occurred for the blend membrane, the adsorbed



(a) (b)

(c) (d)

Fig. 10 (a) Pure water flux; and (b) flux ratio of J_{p1}/J_{p2}; (c) J_1/J_0; (d) J_2/J_0 as a function of blending ratio of alkaline treated PVDF powder

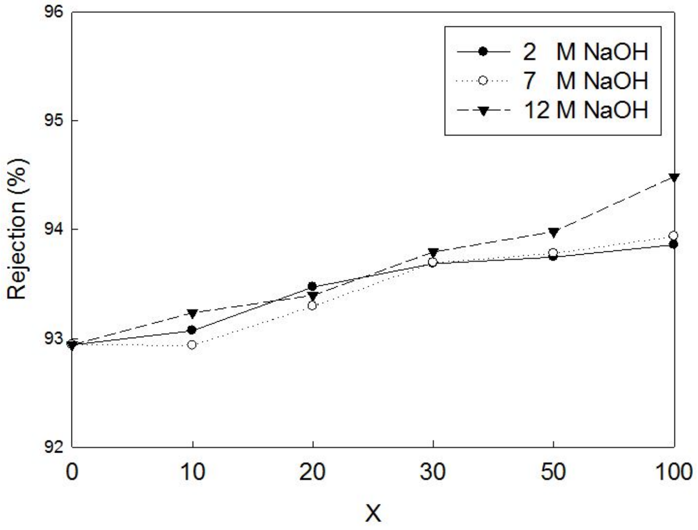


Fig. 11 Rejection of protein of three types of membranes with differentpercentage of alkaline treated PVDF powder

proteins could be more easily removed by pure water and or by mild cleaning with a dilute alkaline solution, in comparison with the pure PVDF membrane.

4. Conclusions

All results indicated that partial defluorination happened when PVDF powder treated with aqueous NaOH under certain condition. The hydrophilicity of blending membrane was improved based on the reasons that defluorinationlead the formation of conjugated C = C bonds and the inclusion of oxygen functionalities. Then, the polyene structure followed by hydroxide attack to yield hydroxyl and carbonyl groups, which are all hydrophilic groups. So, the fouling potential of the blend membrane decreased. The concentration of NaOH affects the characteristics of the final products. Extreme concentration leads to the products with darker color. In addition, the SEM and porosity measurements showed that no obvious variations of the pore dimensions and structures after treatment. The thermal stability also did not change based on the TGA results. Mechanical tests suggest that the high content of the alkaline treated PVDF result in membranes with less tolerance of tensile stress and higher brittleness.

Acknowledgments

This research was supported by the National Science Foundation of China (51108225; 51408320), and Natural Science Foundation of Inner Mongolia (2013MS0603), The College Scientific Research Projects of Inner Mongolia (NJZZ14002), Jiangsu Agriculture Science and Technology Innovation Fund [(JASTIF) CX(15)1005] and Shuangchuang Talent Plan of Jiangsu Province.

References

Brewis, D.M. and Mathieson, I. (1998), "Preatments of fluoropolymers: A review of studies between 1990 and 1995", *Proceedings of Adhesion Science and Technology 1st International Congress*, (M. Festschrift, W.J. Van Ooij, H.R. Anderson, Jr. Eds.), *VSP Publisher Inc.*, The Netherland, pp. 267-283.

Brewis, D.M., Mathieson, I. and Sutherland, I. (1994), "The effect of tetrabutylammonium bromide on the pretreatment of poly(vinyl fluoride) with potassium hydroxide", *J. Mater. Sci. Lett.*, **13**(1), 71-72.

Baroña, G.N.B., Cha, B.J. and Jung, B. (2007), "Negatively charged poly (vinylidene fluoride) microfiltration membranes by sulfonation", *J. Membr. Sci.*, **290**(1-2), 46-54.

Chang, H.H., Tsai, C.H., Wei, H.C. and Cheng, L.P. (2014), "Effect of structure of PVDF membranes on the performance of membrane distillation", *Membr. Water Treat.*, *Int. J.*, 5(1), 41-56.

Crowe, R. and Badyal, J.P.S. (1991), "Surface modification of poly(vinylidene difluoride)(PVDF) by LiOH", *J. Chem. Soc.*, *Chem. Commun.*, **25**(14), 958-959.

Li, H.B., Shi, W.Y., Zhang, Y.F and Zhou, R. (2015), "Comparison study of the effect of blending method on PVDF/PPTA blend membrane structure and performance", *Memb. Water Treat.*, *Int. J.*, **6**(3), 205-224.

Liu, Q.F. and Kim, H. (2010), "Performance evaluation of alkaline treated poly(vinylidene fluoride) membranes", *Sep. Sci. Tech.*, **45**(9), 1209-1215.

Liu, F., Du, C.H., Zhu, B.K. and Xu, Y.Y. (2007), "Surface immobilization of polymer brushes onto porous poly(vinylidene fluoride) membrane by electron beam to improve the hydrophilicity and fouling resistance", *Polymer*, **48**(10), 2910-2918.

Mathieson, I., Brewis, D.M., Sutherland, I. and Cayless, R.A. (1993), "Adhesion studies of fluoropolymers", *J. Adhes*., **41**(1-4), 113-128.

Nunes, S.P. and Peinemann, K.V. (1992), "Ultrafiltration membranes from PVDF/PMMA blends", *J. Membr. Sci*., **73**(1), 25-35.

Ochoa, N.A., Masuelli, M. and Marchese, J. (2003), "Effect of hydrophilicity on fouling of an emulsified oil wastewater with PVDF/PMMA membranes", *J. Membr. Sci*., **226**(1-2), 203-211.

Ross, G.J., Watts, J.F., Hill, M.P. and Morrissey, P. (2000), "Surface modification of poly(vinylidene fluoride) by alkaline treatment 1. The degradation mechanism", *Polymer*, **41**(5), 1685-1696.

Rye, R. (1993), "Spectroscopic evidence for radiation-induced crosslinking of poly(tetrafluoroethylene)", *J. Polym. Sci. Part B*: *Polym. Phys*., **31**(3), 357-364.

Wang, P., Tan, K.L., Kang, E.T. and Neoh, K.G. (2002), "Plasma-induced immobilization of poly(ethylene glycol) onto poly(vinylidene fluoride) microporous membrane", *J. Membr. Sci*., **195**(1), 103-114.

Yang, M.C. and Liu, T.Y. (2003), "The permeation performance of polyacrylonitrile/polyvinylidine fluoride blend membranes", *J. Membr. Sci*., **226**(1-2), 119-130.

Zhang, Q.W., Lu, J.F., Saito, F. and Baron, M. (2001), "Mechanochemical solid-phase reaction between polyvinylidene fluoride and sodium hydroxide", *J. Appl. Polym. Sci*., **81**(9), 2249-2252.

Zhang, M.G., Nguyen, Q.T. and Ping, Z.H. (2009), "Hydrophilic modification of poly (vinylidene fluoride) microporous membrane", *J. Membr. Sci*., **327**(1-2), 78-86.

CC