Chemical Engineering Journal 145 (2008) 218–224

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Plasma surface modification of polypropylene microfiltration membranes and fouling by BSA dispersion

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ARTICLE INFO

Article history:
Received 20 November 2007
Received in revised form 15 March 2008
Accepted 10 April 2008

Keywords:
Antifouling characteristics
Low temperature NH_3 plasma treatment
Polypropylene microfiltration membrane
Surface modification

ABSTRACT

Fouling is the major obstacle in membrane processes applied in protein filtration. To overcome the problem, the polypropylene microfiltration membranes (PPMMs) were surface-modified by low temperature NH_3 plasma treatment. Structural and morphological changes on the membrane surface were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The change of surface wettability was monitored by contact angle measurements. The pore size and distribution were evaluated by mercury porosimetry. The static water contact angle of the modified membrane reduced obviously. The relative pure water flux of the modified membranes had a maximal value for the plasma treatment time of 1 min. To assess the relation between the plasma treatment and the membrane fouling by bovine serum albumin (BSA), the filtration and the adsorption of BSA experiments were carried out. It was found that the surface modified membranes showed better regeneration performances, i.e. higher flux recoveries after water and caustic cleaning than those of the nascent PPMM. Flux recoveries after water and caustic cleaning for the NH_3 plasma treated PPMM for 1 min were 51.1 and 60.7%, respectively higher than those of the virgin membrane. The results demonstrated that the bovine serum albumin adsorption was suppressed significantly by plasma surface modification.

1. Introduction

Membrane filtration is increasingly used for the separation and purification of protein-containing dispersions [1–3]. But fouling is one of the critical factors determining the effectiveness of the membrane process [4,5]. This fouling is mainly attributed to the concentration polarization and protein deposition on the membrane surface [6]. Concentration polarization, resulting from concentration gradient due to solute accumulation near the membrane surface, is reversible in nature and independent of the properties of the membrane. However, the protein adsorption, which leads to significant loss of membrane performance, is irreversible in nature [7].

The fairly good properties of polypropylene microfiltration membrane (PPMM), including high void volumes, well-controlled porosity, chemical inertness, good mechanical strength and low cost, make it a promising membrane material [8]. Unfortunately, PPMM lacks functional groups, which leads to hydrophobicity, poor biocompatibility, and also no reactivity. In some cases, the antifouling characteristics for hydrophilic membrane are better than those of hydrophobic one [9]. As a result, modification of polypropylene microfiltration membrane from hydrophobicity to hydrophilicity is very important [10]. Different methods such as UV irradiation, plasma treatment, gamma irradiation, and chemical reaction have been employed to modify the membrane surface [11,12].

Among the various surface-modification techniques, low temperature plasma treatment is regarded as a favorable one. The properties of the membrane surface can be tailored to satisfy a particular request without affecting the bulk of the polymer [13–16]. Intensive researches on the surface modification of PPMMs by plasma treatment have been conducted; the fouling of bovine serum albumin was greatly reduced after the plasma treatment [17]. In our previous work, PPMM was surface modified by NH_3 plasma treatment [18], and the antifouling characteristics of the membranes in a submerged membrane bioreactor during the filtration of activated sludge were investigated. The modified membranes showed better filtration behaviors in the submerged membrane bioreactor than the unmodified membrane, and flux recovery after water cleaning was higher. The irreversible fouling resistance decreased after plasma treatment.

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doi:10.1016/j.cej.2008.04.007

The objective of this study is to investigate the effects of low temperature NH_3 plasma treatment on the membrane fouling during the filtration of BSA dispersion.

2. Materials and methods

2.1. Materials

Polypropylene microfiltration membrane (PPMM) with a porosity of 45–50% and an average pore diameter of 0.10 μm were prepared in our laboratory. The inner and outer diameters of PPMM were 240 and 290 μm, respectively. Bovine serum albumin (BSA, purity >98%, pI = 4.8, M_w = 66 kDa) was purchased from Sino-American Biotechnology Co. and used as received. BSA dispersion was prepared in a phosphate buffered saline (PBS) solution at pH 7.4.

2.2. Membrane surface modification by low temperature NH_3 plasma treatment

Before surface modification, membrane samples were washed with acetone, dried in a vacuum oven at room temperature for 24 h, and stored in a desiccator.

A plasma generator from Peking KEEN Co. Ltd. (China) was used. Tubular type Pyrex reactor (10 cm × 150 cm) was rounded with a pair of copper electrodes. These two electrodes were powered through a matching network by a 13.56 MHz radio-frequency generator. U-shaped membrane modules and the polypropylene flat microfiltration membrane samples were fully stretched out in a rectangular frame using rubber bands, then the frame was put in the center of the plasma reactor chamber. Before plasma treatment, the chamber was purged four times with NH_3 and evacuated to a pressure of 5.0 Pa. The working pressure was then adjusted to 10 Pa. On the basis of systematic experiments considering surface etching and modification induced by plasma, 30 W was chosen as the applied radio-frequency power. Treatment time was changed in the range of 0–8 min. Finally, the membrane was taken out of the chamber and used for characterization and/or filtration measurement.

2.3. Characterization of the membrane surface

XPS is very powerful in identifying specifies present at the surface/interface and atoms and functional groups [19]. With its capability to make qualitative and quantitative elemental analysis and to detect the chemical environment of each element through the “chemical shift” and “binding energy”, it can provide very complete chemical information about the first 10–20 layers of a flat surface [20]. In the present work, chemical composition of the PPMM surface was analyzed by XPS with a PHI 5000c XPS spectrometer (PerkinElmer Instruments, U.S.A.). All the results presented here corresponded to the use of the Al Kα radiation (1486.6 eV). The background pressure was 1×10^{-5} Pa. A pass energy of 150 eV was used to obtain the wide scan spectra, while 25 eV pass energy and 45° take-off angle were used for the high-resolution spectra of C1s. The signal of C1s, 284.7 eV, was selected for energy calibration. The C1s envelopes were analyzed and peak-fitted after subtraction of a Shirley background using a Gaussian–Lorenzian peak shapes obtained from the Casa XPS software package.

Surface morphologies of the unmodified and modified PPMMs were observed by scanning electron microscope (SEM) with a S-570 system (Hitachi, Japan) operating with an accelerating voltage of 20 keV. Prior to SEM analysis, the membrane was affixed to a standard sample stub by double-sided carbon conductive tape (Ted-Pella). To prevent surface charging, a thin film (5 nm) of Au was sputtered onto all samples by an Anatech sputter coater prior to imaging.

To evaluate the hydrophilicity changes of the membrane surface, polypropylene flat microfiltration membrane with almost similar average pore size and porosity was treated with NH_3 plasma under the same condition. Then, the samples were kept in air at room temperature for about 24 h before the contact angle measurements were conducted. Water contact angle on the membrane surface was measured by the sessile drop method by using a DATA Physics System (OCA20, Germany) at a constant temperature (25 °C). The liquid drop of 1 μl was placed onto the membrane surface by a micro-syringe. To avoid the penetrating of the water drop into the membrane pores, the drop image was immediately captured, then recorded by a video camera and digitalized. The average value was obtained from at least 10 measurements tested for each membrane. The standard deviation was about 1–3°.

An Autoscan 3310X Porosimeter (Porous Materials Inc.) was used to measure the pore diameter and porosity of the studied membranes. The apparatus has an available pressure range of 0–3300 psi (absolute). A weighed amount of membrane was introduced into the chamber filled with mercury. When the maximum pressure is achieved, the extrusion curve starts by slowly reducing the applied pressure. From the data, on intruded volume versus applied pressures, the porosity and pore size were obtained according to a procedure outlined elsewhere [21].

A versatile materials experimental instrument (RG2000-10, Shenzhen, China) was used to estimate the mechanical properties after NH_3 plasma treatment, the grip distance was 50 mm and the velocity of elongation was 100 mm/min. At least 10 measurements were taken to calculate the mean values.

2.4. Permeation and antifouling properties

The permeation properties of the unmodified and modified PPMMs were examined by using a permeation cell equipped with a peristaltic pump under constant pressure. All the membranes were wetted with ethanol for 30 min before flux measurements. The filtration protocol used in this work, was similar to Shim et al. [22]. Each membrane was first pre-compacted for 30 min at 60 kPa with the flow from-out-to-in. Then, the pressure was lowered and the de-ionized water flux ($J_{0,u}$) was obtained at 40 kPa by measuring permeate until the consecutive five recorded values (1 h for each record) differed by less than 2%. After surface modification, the de-ionized water flux ($J_{0,m}$) was also obtained by the same procedure. Subsequently, 1 g/l BSA dispersion was permeated through the membrane at 40 kPa and the flux at the end of the BSA filtration was recorded as J_p. To confirm the water flux recovery property of these BSA-permeated membranes, the membranes were cleaned with de-ionized water, and then the de-ionized water flux (J_1) was measured. Finally PPMMs were cleaned with a 0.1 M NaOH solution on a vibrator for 4 h and the pure water flux (J_2) was measured again. The volumetric flux was determined through the timed collection of permeate, and adjusted to a reference temperature of 20 °C by accounting for the changes in water viscosity [23].

The antifouling characteristics, such as reduction from pure water flux, flux ratio after fouling, flux recovery after water and caustic cleaning, were described by the following equations:

$$\text{Reduction from pure water flux} = \left(\frac{1 - J_p}{J_{0,u}}\right) \times 100\% \qquad (1)$$

$$\text{Flux ratio after fouling} = \frac{J_{p,m}}{J_{p,u}} \qquad (2)$$

$$\text{Flux recovery after water cleaning} = \left(\frac{J_1}{J_{0,\mathrm{u}}}\right) \times 100\% \quad (3)$$

$$\text{Flux recovery after caustic cleaning} = \left(\frac{J_2}{J_{0,\mathrm{u}}}\right) \times 100\% \quad (4)$$

where the subscripts m and u refer to the modified and unmodified membrane.

BSA was used as a model protein to evaluate the protein-resistant characteristics of the unmodified and modified membranes. The studied membranes with about 100 cm^2 of external surface area were immersed in ethanol for 30 min followed in PBS solution for 30 min to prewet the membrane surface. Then each sample was put into a tube containing 10 mL of BSA dispersion with various concentrations whose pH was adjusted to 7.4 with phosphate buffer solution. The mixture was incubated at 30 °C for 24 h to reach an adsorption–desorption equilibrium. The amount of adsorbed BSA was determined by measuring spectrophotometrically the difference between the concentrations of BSA in the dispersion before and after contact with the membranes. The spectroscopic analytical method utilized in this work for protein dosage was based on the reaction of albumin with Coomassie brilliant blue (Fluka) dyestuff to record the absorbance of the albumin-Coomassie brilliant blue complex according to Bradford's method [24]. A calibration curve between the spectrophotometric absorbance and the BSA concentration was established to reduce the effect of protein adsorption on the surface of the experimental device for the adsorption measurement. The reported data were the mean value of triplicate samples for each polymer membrane.

3. Results and discussion

3.1. Characterization

PPMMs were treated with NH_3 plasma for a specified time (0–8 min). To analyze the chemical composition of the membrane surface, XPS survey scans for the membranes were conducted (Fig. 1). Compared with the virgin PPMM (Fig. 1(a)), it can be clearly seen that after NH_3 plasma treatment (Fig. 1(b)), two obvious peaks, namely the peak at 531.6 eV corresponding to O1s and the peak at 402.3 eV corresponding to N1s, appear. The N1s peak can be designated to the $-NH_2$ groups generated by NH_3 plasma treatment, while the O1s peak can be ascribed to hydroxyl/carbonyl groups, which were formed by the residual water in ammonia and the post-reaction of surface radicals with oxygen when the samples were taken out from the plasma reactor [25].

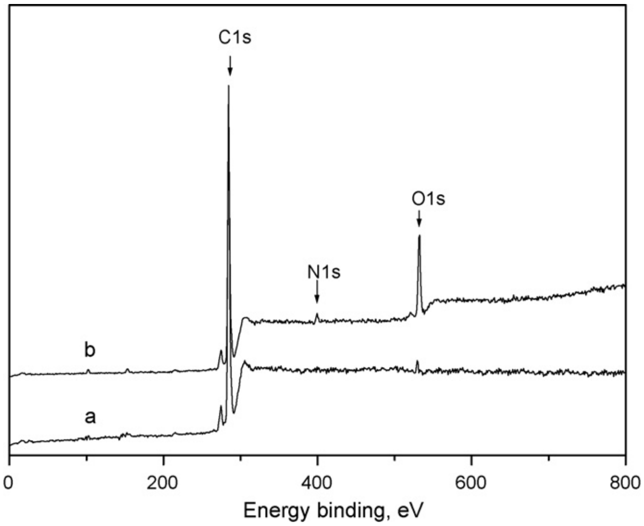

Fig. 1. XPS spectra of PPMMs for the virgin (a) and 4 min NH_3 plasma treated PPMM (b).

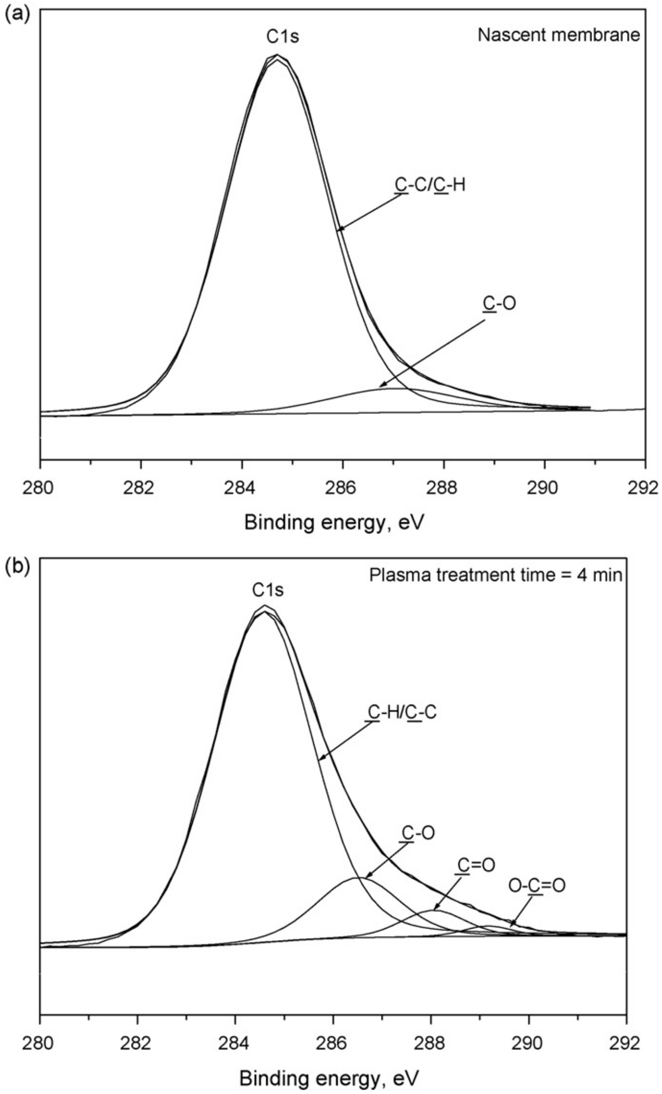

Fig. 2. Resolved XPS spectra of C1s for (a) the virgin and (b) 4 min NH_3 plasma treated PPMM.

Fig. 2 shows typical high-resolution XPS spectra of C1s (a) and (b) spectra measured by regional scans to distinguish different types of functional groups on the membrane surface. C1s spectrum for the virgin PPMM (Fig. 2(a)) has peaks assigned to C—C or C—H (284.7 eV) and C—O (286.7 eV), the C—O may come from the oxygen contamination on the membrane surface [26]. The binding energies at 284.7 eV for C—C/C—H, 286.7 eV for C—O, 287.9 eV for C=O and 289.1 eV for O—C=O for the NH_3 plasma treated PPMM appear (Fig. 2(b)) [27].

The elemental composition of the NH_3 plasma treated PPMMs for 0, 4 and 8 min is shown in Table 1. It can be seen that with the increase of plasma treatment time, the atomic ratio of O/C increases from 2.8 to 12.9 mol%, N/C increases from 0 to 1.4 mol%. This results indicate that prolonged plasma treatment time will introduce more O and N onto the membrane.

The morphological changes of the virgin and modified PPMM were observed by SEM. Typical images are shown in Fig. 3. It can be found that, with the increase of NH_3 plasma treatment time, the

Table 1
Elemental content of the PPMM surfaces

Plasma treatment time (min)	Content (mol%)			Atomic ratio (%)	
	C	O	N	O/C	O/N
0	97.3	2.7	0	2.8	0.0
4	90.7	8.4	0.9	9.3	1.0
8	87.5	11.3	1.2	12.9	1.4

Table 2
Pore size and porosity of the nascent and modified PPMMs

Plasma treatment time (min)	Average pore size (μm)	Porosity (%)
0	0.11 ± 0.03	45.9 ± 2.5
0.5	0.12 ± 0.05	48.7 ± 2.8
1	0.15 ± 0.05	50.4 ± 2.3
2	0.14 ± 0.02	48.9 ± 2.5
4	0.13 ± 0.03	44.6 ± 3.2
8	0.10 ± 0.02	44.4 ± 2.7

pore size on the PPMM surface is enlarged to some extent at first and then decreases.

Three main phenomena affecting membrane properties take place normally during plasma treatment [28]. First, ablation and etching result in the increase of pore diameter and porosity. Second, chemical changes on the surface layer introduce various functional groups that can be further used for chemical reaction or hydrophilization, depending on the plasma conditions. Third, the deposition of polymer fragments formed by the gas used, and/or by the volatile products produced from the etched surface, can result in lower porosity. Therefore, the pore size and porosity of a plasma treated membrane can become larger or smaller, depending on which of the two competing processes prevails (ablation or deposition). To ascertain whether the plasma adversely altered the physical properties of the membrane, the pore size and porosity of the virgin and modified PPMMs were determined by mercury porosimetry. Typical results are shown in Table 2. It can be found that the pore size and porosity increase with plasma treatment time up to 1 min and then decrease with the increase of plasma treatment time.

Contact angle measurements have been commonly used to characterize the hydrophilicity of membrane surfaces. However, such measurements are difficult to definitely interpret the surface property for porous membranes because of capillary forces within pores, contraction in the dried state, heterogeneity, roughness, and restructuring of the surfaces [29–31]. But the relative hydrophilicity or hydrophobicity of each membrane can be easily gained by this measurement. Water contact angles on the unmodified and modified membrane surfaces are shown in Fig. 4. It can be found that the static water contact angle decreases evidently from about 128.2° to 53.7° with the increase of plasma treatment time from 0 to 8 min.

Variation of water contact angle with storage time was also performed, the typical results are shown in Fig. 5. The water contact angle for the modified membranes decreases up to 5 d, then it increases steadily. The decrease in the water contact angle may be due to the following reason.

In the case of NH_3 plasma treatment, polypropylene membrane surface interacted with N ion and electrons that are activated species in the plasma to make bond scission of C—H and C—C bonds. As a result, hydrogen atoms will be removed from the polymer chain, and carbon radicals will be formed at the polymer chain. These carbon radicals will be successively oxidized into oxygen functional groups such as hydroxyl, carbonyl, carboxyl groups, etc., when the membrane is taken out from the plasma reactor [25].

However, the water contact angle increases with the increase of storage time. It is commonly known that hydrophilicity gained by plasma modification is not stable; the effect can get lower and even disappear completely, namely “hydrophobic recovery”. This phenomenon can be attributed to the following reasons: mobil-

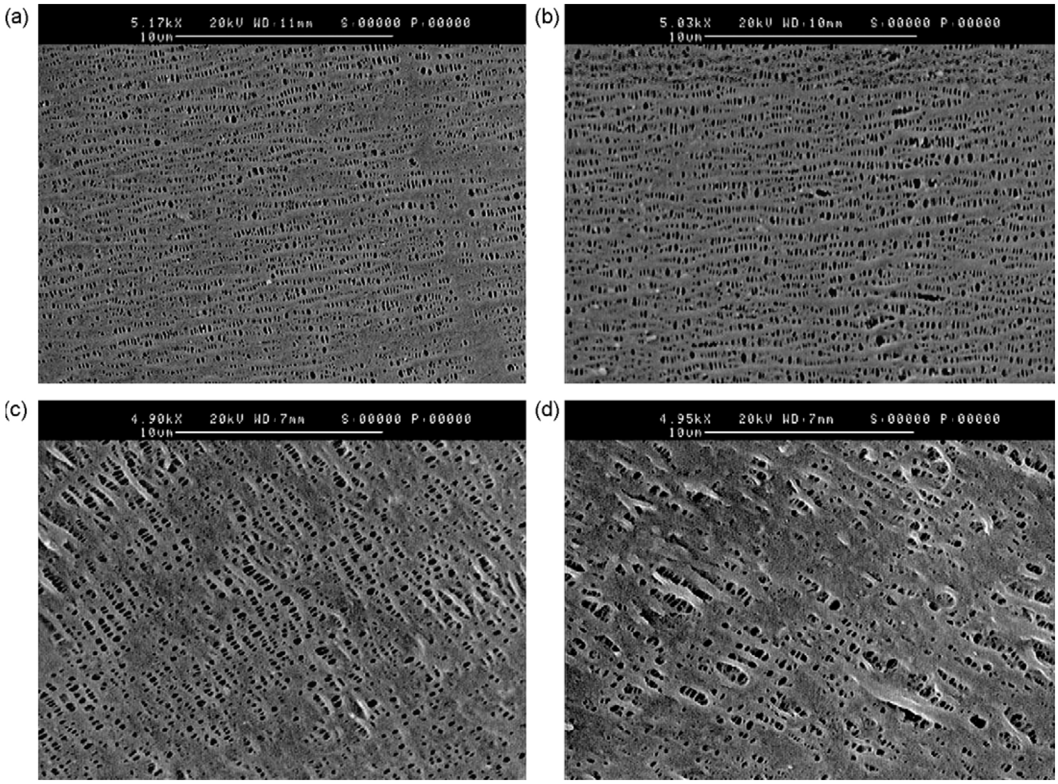

Fig. 3. SEM images of the PPMMs (5000×). (a) Virgin PPMM; (b)–(d) NH_3 plasma treated PPMMs for 1, 4 and 8 min, respectively.

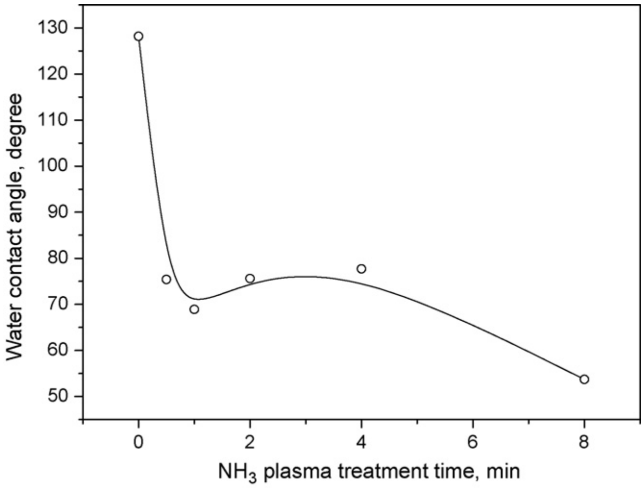

Fig. 4. Effect of the plasma treatment time on the water contact angle of the studied PPFMMs.

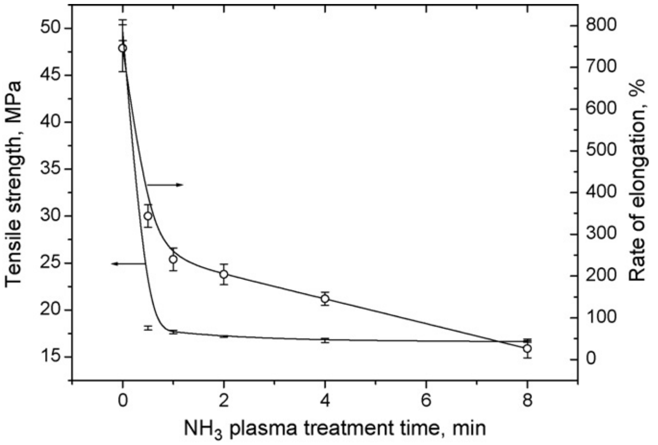

Fig. 6. Effect of the NH$_3$ plasma treatment time on tensile strength and rate of elongation at break of the PPMMs.

ity of surface functionalities (surface rebuilding), or sorption of hydrophobic moieties appearing in laboratory air. After 30 d of storage, the surface wettability clearly changes. This is in good agreement with the assumption [14]: some polar functionalities move towards bulk polymer, the rest of them modify the surface properties to make them different from which virgin samples have. In the present work, the membranes were used in contact with water, surface hydrophilicity will not disappear, as a result, the plasma modified membranes would be more fouling resistant over realistic operating times [25].

The change of mechanical properties after plasma treatment is also an important factor in practical membrane application processes such as backwashing and chemical cleaning. Therefore, the mechanical properties (tensile strength and rate of elongation at break) of the virgin and NH$_3$ plasma treated PPMMs were measured as a function of plasma treatment time. The results are shown in Fig. 6. It can be seen that both the tensile strength and the rate of elongation at break decrease quickly with the increase of plasma treatment time to 1 min. Prolonged treatment time cause no further effect on the tensile strength but the rate of elongation at break of the membrane decreases gradually. The decrease of tensile strength and the rate of elongation at break can be attributed to the scission of the molecular chains [28] on the membrane surface. This is a negative result due to the surface etching phenomenon during plasma treatment.

3.2. Filtration and antifouling properties of the membranes

To investigate the permeation properties of the studied membranes, ultra pure water and BSA dispersion filtration experiments were carried out. The relative pure water flux through the membrane was measured as a function of plasma treatment time, the typical results are shown in Fig. 7. The relative pure water fluxes for all the NH$_3$ plasma treated PPMMs are higher than that for the untreated PPMM. The relative pure water flux increases quickly with the increase of plasma treatment time up to 1 min, then falls down with the further increase of plasma treatment time. The increase of the permeation before plasma treatment time of 1 min could be explained by the increase of membrane surface hydrophilicity. Apart from that, enlargement of membrane pore size and/or the increase of porosity after plasma treatment play important roles for the enhancement of membrane permeability [32]. The decrease of the permeation after plasma treatment of 1 min could be explained by the following reasons. As mentioned above, the membrane pores are enlarged to some extent when the

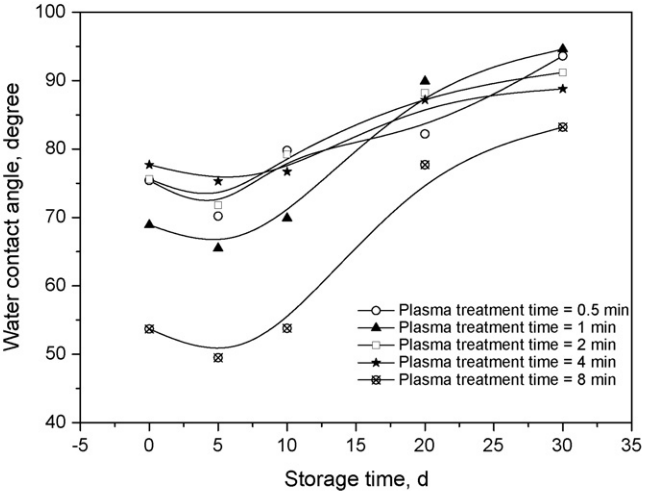

Fig. 5. Variation of water contact angles on the membrane surfaces with storage time (d).

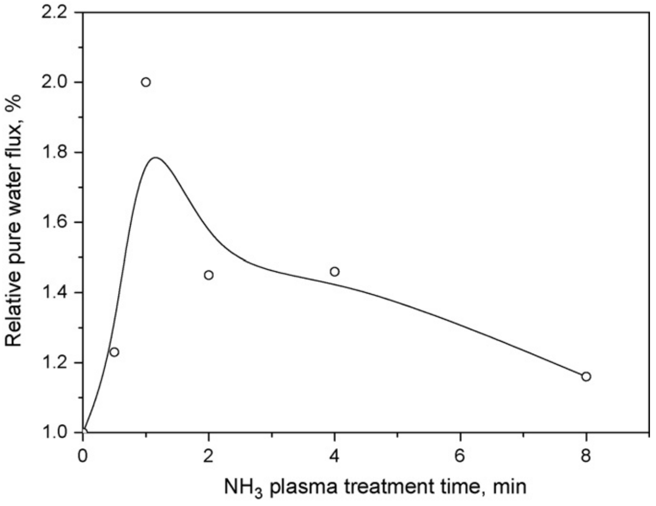

Fig. 7. Dependence of relative pure water flux through the PPMMs on NH$_3$ plasma treatment time.

Table 3
Reduction from pure water flux, flux ratio after fouling, flux recoveries after water and caustic cleaning, for the unmodified and modified PPMMs

NH_3 plasma treatment time (min)	0	0.5	1	2	4	8
Reduction from pure water flux (%)	49.3	39.4	51.2	50.0	47.0	47.0
Flux ratio after fouling	1.00	1.06	1.39	1.03	1.10	0.87
Flux recovery after water cleaning (%)	58.2	75.8	109.3	78.9	90.4	67.1
Flux recovery after caustic cleaning (%)	60.2	80.6	120.9	78.9	90.4	69.4

plasma treatment time is shorter than 1 min, the membrane pores are severely blocked when the plasma treatment time is longer than 1 min. Moreover, the water contact angle decreases quickly with the increase of plasma treatment time up to 1 min, then it remains nearly unchanged with the further increase of plasma treatment time. Similar results have been obtained in our previous work [23].

Typical results for the permeation fluxes of BSA dispersion through the original and plasma-modified PPMMs are depicted in Table 3. The dynamic protein dispersion permeation process, which chose BSA as model protein to examine the antifouling properties of PPMMs, shows a similar trend to that of the relative pure water flux discussed above. The lowest reduction from pure water flux belongs to the membrane with a plasma treatment time of 1 min. Moreover, water flux recoveries after water and caustic cleaning of this membrane also are the maximal.

In the permeation process, pore size and hydrophilicity are the two parameters, which affect water flux most [33]. Hence, before 1 min plasma treatment time, the surface hydrophilicity is the dominant factor, accordingly, the water flux increases with the increase of plasma treatment time despite pore blocking. However, pore blocking becomes the leading factor after 1 min plasma treatment time and causes the decline of the water flux. It can be seen that the surface-modified membranes show better regeneration performance, i.e. higher flux recoveries after water and caustic cleaning than those of the nascent PPMM. After the filtration of BSA, flux recoveries after water and caustic cleaning for the NH_3 plasma treated PPMM for 1 min were 51.1 and 60.7%, respectively higher than those of the virgin membrane. Flux recoveries after water and caustic cleaning for NH_3 plasma treated PPMM even are higher than 100% (initial water flux before surface modified). It was substantiated that surface modification by NH_3 plasma treatment could improve the filtration performance and make fouling less troublesome and membrane regeneration more efficient. However, reduction from pure water flux for the modified PPMMs are also very low, despite the lower water contact angle and higher pore size and porosity. This can be attributed to the fact that hydrophilic surface decreases the overall resistance, causing an increase in flow rate, resulting in significant cake formation and compaction. Cake formation and compaction on the membrane surface increases (porosity decreases) causing the resistance increase, which results in a decrease of the flow rate. This result confirms that if the membrane surface is more hydrophilic, the cake thickness increases and thus cake resistance increases, causing the decrease in the flow rate [34].

Protein adsorption is one of the most important phenomena determining the fouling characteristics of materials [30,35–38]. Fig. 8 shows the results of BSA adsorption on the unmodified and plasma modified membranes for 2, 4 and 8 min, respectively. It can be found that the amount of BSA adsorbed on the modified membranes decreases with the increase of plasma treatment time and increases with the increase of BSA concentration. During the BSA adsorption measurement, samples were immersed in aqueous medium. As was confirmed by Huang [39] that, in the aqueous environment, the relative high level of free water fraction on the membrane surface can effectively suppress protein adsorption. The lower the water contact angle, the higher level of free water fraction on the membrane surface, as a result, BSA adsorption amount on the membrane surface decreases with the decrease of water contact angle.

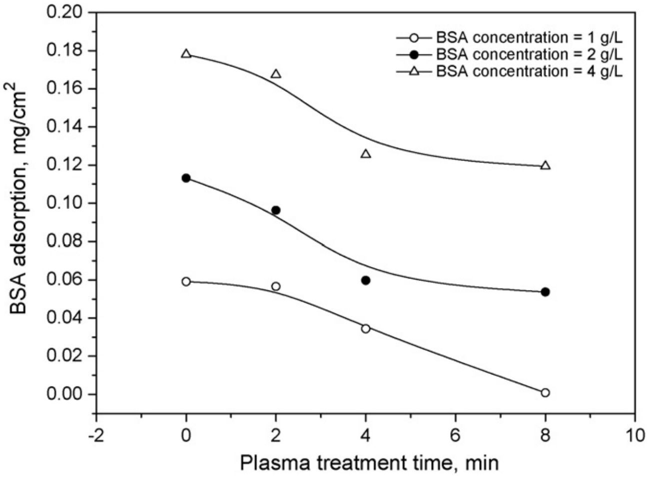

Fig. 8. BSA adsorption on the unmodified and plasma modified membranes for 2, 4 and 8 min, respectively.

4. Conclusions

Hydrophobic polypropylene microfiltration membranes were surface modified by low temperature NH_3 plasma treatment. The wetting properties measured by goniometer showed that the hydrophilicity of the NH_3 plasma treated membranes increased with the increase of plasma treatment time and decreased with the increase of storage time. The relative pure water flux of the modified membranes increased with the increase of the plasma treatment time up to 1 min, then it decreased gradually. The membrane fouling by bovine serum albumin on the modified membranes was suppressed significantly. Flux recoveries after water and caustic cleaning for the NH_3 plasma treated PPMMs for 1 min were 51.1 and 60.7% higher than those of the virgin membrane. The adsorption of bovine serum albumin on the modified membranes was lower than that on the unmodified membrane surface. However, the mechanical properties decreased after plasma treatment. Taken the antifouling properties and the mechanical properties into consideration, the optimal conditions for membrane modification is plasma treatment time of 1 min.

Acknowledgements

Financial supports from the Science and Technological Fund of Anhui Province for Outstanding Youth (No. 04046065), the National Natural Science Foundation (No. 20871003) and the Education Department (No. 2006 KJ 006 TD) of Anhui province are gratefully acknowledged.

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