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Plasma modification of polyacrylonitrile ultrafiltration membrane

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Abstract

Polyacrylonitrile (PAN) ultrafiltration (UF) membranes were modified by plasma treatments and plasma polymerization. Influences of plasma modifications on membrane characteristics were investigated. The obtained results indicated that plasma treatments using non-polymer-forming plasma gases such as Ar, He and O_2 led to the increase of membrane surface hydrophilicity and membrane permeability. By using O_2 plasma treatment, UF property of PAN membranes could be improved with the enhancement of membrane flux meanwhile its albumin rejection was almost maintained. The experimental results also showed that plasma polymerization using acrylic acid vapor as monomer and PAN UF membrane as a substrate led to the formation of reverse osmosis membrane due to the deposition of plasma polymer layer onto substrate membrane surfaces. Plasma techniques can control membrane pore size and have a potential to improve the membrane characteristics by using their advantages.

Keywords: Plasma modification; Polyacrylonitrile membrane; Ultrafiltration; Reverse osmosis

1. Introduction

Plasma modification is useful and effective method to prepare high performance separation membranes [1–5] such as ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and gas separation membranes. Generally, plasma processes to modify membranes can be divided into plasma treatment and plasma polymerization depending on the type of gases, which were used in plasma.

Plasma treatment is non-polymer-forming plasma process; it can be chemically non-reactive or chemically reactive plasma. Plasma treatment is a convenient technique for improving of membrane surface hydrophilicity. Also, permeability of plasma treated membranes is often higher than that of untreated membranes [6–8].

Plasma polymerization is polymer-forming plasma process; it can lead to form polymeric solid films deposited onto the substrate membrane surfaces. The formation of an ultrathin, defect-free barrier layer by plasma deposition of a polymeric material upon the surface of microporous substrate membranes has been promising prospect to prepare composite separation membranes [9–11].

The capability of plasma to alter the physical and chemical properties of polymeric surfaces without affecting the bulk properties of the base material is advantageous for the design and development of surface-modified polymer membranes [12].

In this study, we have chosen polyacrylonitrile (PAN) membrane as a substrate material for plasma modifications because it is widely used commercially as UF membranes. This material has a good thermal stability (up to 130 °C) and has a good resistance to many chemicals. Therefore, it is very useful to use in UF, NF and RO processes. However, NF and RO membranes could not be prepared from PAN by conventional casting method [13] because these membranes have rather large skin pore size. Some investigations of plasma to modify PAN membrane have been reported. T. Shimomura et al. [14] reported that plasma treatments using non-polymer-forming plasma gases such as helium, hydrogen and etc. could be applied to prepare PAN RO membrane. Zhao et al. [15] prepared NF membrane from PAN UF membrane by grafting of monomer in gas onto membrane surface. Tsutsui et al. [16] prepared the PAN based RO composite membranes via plasma polymerization using allylamine as monomer. In this work, PAN UF membranes were modified by plasma treatment using

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argon, helium, oxygen gases to improve their flux and plasma polymerization using acrylic acid vapor as monomer to prepare RO membranes for desalination. Influences of plasma effects on membrane characteristics such as hydrophilicity, permeability and separation performance including UF and RO properties of modified PAN membranes have been investigated.

2. Experimental

2.1. Preparation of substrate membranes

Polyacrylonitrile ultrafiltration membranes were prepared by the conventional casting method [17]. Membranes were casted by using polymer solutions of 22 wt.% PAN (molecular weight M_n ca. 30000 g/mol) in *N*,*N*-Dimethylformamide onto glass plate. The membranes were annealed for 10 min at 90 °C and dried at room temperature. Fig. 1 shows cross-section scanning electron microscope (SEM) images of substrate PAN UF membrane. The cross-section picture indicated that PAN UF membrane has an asymmetric structure, which consists of the very thin, flat and dense skin top layer and finger-like structure, which occupies the greater part of cross-section under the top layer. Although a part of the top layer can be seen in Fig. 1, pores in the top-layer of membrane surface could not be detected clearly and consequently they were estimated to be less than 0.01 μm in diameter.

2.2. Plasma modifications

A schematic diagram of plasma modification system used in this study is shown in Fig. 2. It consists a tubular type reactor (i.d = 3 cm, length = 40 cm) with two external electrodes (1 cm wide, 8 cm apart), a rotary vacuum pump, a radio-frequency (13.56 MHz) power generator and matching network. PAN substrate membrane was placed in reactor between two electrodes. Before plasma initiation, reactor tube was evacuated by rotary vacuum pump until the vacuum degree inside the reactor was reached at least 5 mTorr, then plasma gas was introduced into reactor by adjusting mass-flow meter and metering valve to control gas flow rates. In this study, we had two kinds of processing to PAN UF membrane. One was the surface modification due to plasma treatments using argon, helium and oxygen gases at flow rate of 18 sccm with discharge power of 10 W. And another was the plasma polymerization using acrylic acid monomer vapor at flow rate of 2 sccm and discharge power of 10 W. It is commonly known that modification by low-temperature plasma is usually confined to the top several tens of nanometers without effecting of the bulk polymer properties [18]. Therefore, plasma modification will affect on outermost layer of substrate membrane surface.

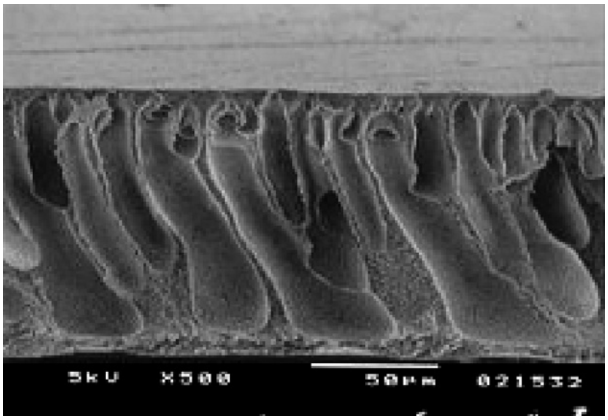

Fig. 1. PAN UF membrane cross-section.

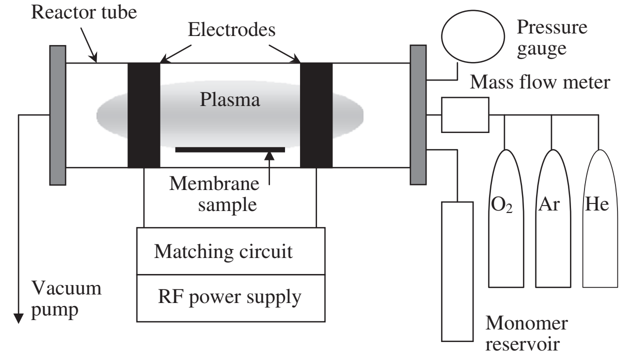

Fig. 2. Experimental setup.

2.3. Membrane characteristics

Plasma modifications can cause the degradation of substrate polymer or the deposition of plasma polymer layer from monomer vapor onto membrane surfaces and these effects lead to the changes of membrane weights. The loss/gain ratio of membrane weight was examined by comparison the weight of unmodified and modified membranes.

Hydrophilicity of PAN membrane surfaces was examined by the contact angle measurements using water/air system. In order to obtain more detailed information about the structural changes of membrane surface after plasma modifications, FTIR spectra were recorded using the ATR technique.

Permeability of membranes was determined by measurement of pure water flux permeated through membrane surface at the certain pressure. Separation performance of membranes was evaluated through UF and RO experiments in which membrane rejection (R) and water flux (J) were calculated by formulae: $R = \{[(C_0 - C)/C_0] \times 100\}[\%]$ and $J = V/(S \cdot t)$ [l/m^{2}h], where C_0 and C are concentrations of albumin (in UF experiment) or sodium chloride (in RO experiment) in the feed solution and filtrate, respectively; V, S and t are filtrate volume, membrane area and separation time, respectively.

In this study, the skin pore size of PAN membranes is so small that they could not be detected clearly by SEM images. Therefore, pore size of unmodified and modified membrane surfaces could not be compared based on SEM images. However, the skin pore size influences much on membrane rejection and membrane flux, so the changes of membrane skin pore size would be identified by the changes in membrane rejection (R) and membrane flux (permeability or water flux J).

3. Results and discussion

3.1. Plasma treatments

3.1.1. Membrane weight decrease

Polyacrylonitrile substrate membranes were treated by argon, helium and oxygen plasma. The experimental results showed that with plasma treatment time of 150 s, about 3% of membrane weight was lost by oxygen plasma, but in the cases of argon and helium plasma, only about 0.5% of membrane weight decreased after plasma treatments. In argon and helium plasmas, ablation effects occur by the momentum-exchange process (physical sputtering). In oxygen plasma, this effect could occur not only by physical sputtering but also by chemical etching processes [19].

3.1.2. Contact angle measurements

Fig. 3 shows the changes in contact angles of PAN membrane surface due to oxygen and helium plasma treatments. The results indicated that the wettability of plasma treated PAN membranes is higher than that of untreated membrane. Moreover, the obtained results showed that under the same of plasma treatment conditions, the initial rates of hydrophilicity change were almost same, but the final hydrophilicity treated with O_2 plasma was significantly enhanced due to the chemical reaction which could lead to the formation of C=O, O–CO–O and C–O–C functionalities on membrane surface.

3.1.3. Permeability

Fig. 4 shows the influence of oxygen and helium plasma treatments on permeability (pure water flux at 1.0 MPa) of PAN membranes. The obtained results indicated that under the same of plasma treatment conditions, permeability of oxygen plasma treated PAN membranes increased more significantly than that of helium plasma treated membranes. The increase of permeability could be explained by enlargement of membrane skin pore size and/or the increase of pore density after plasma treatments. Apart from that, the increase of membrane surface hydrophilicity plays an important role for the enhancement of membrane permeability.

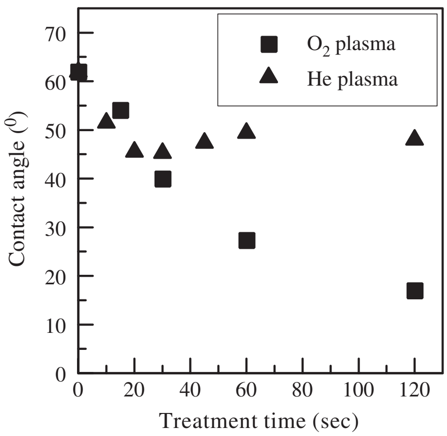

Fig. 3. Contact angles of plasma treated PAN membrane surfaces.

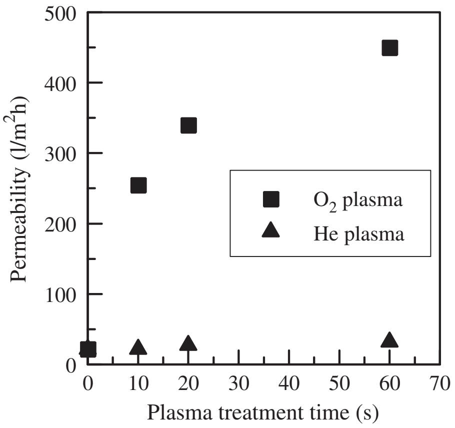

Fig. 4. Permeability of plasma treated PAN membranes.

3.1.4. Separation property

Separation property of plasma treated PAN membranes was determined through UF experiment using albumin 1 wt.% feed solution at 2.0 MPa. The experimental results (Fig. 5) indicated that with the short plasma treatment time, UF property of O_2 plasma treated membranes was improved with the enhancement of membrane flux (*J*); meanwhile its albumin rejection (*R*) was almost maintained. In the case of He plasma treatment, membrane flux increased slightly, although its rejection *R* was kept. Also, desalination experiment was carried out at 3.5 MPa with 2500 ppm sodium chloride feed solution. The experimental results showed that O_2 and He plasma treated membranes cannot reject salt ($R=0\%$) from sodium chloride feed solution, that means these membranes do not work as RO membranes. It has been known that membrane rejection depends much on membrane skin pore size, membrane flux relied not only on skin pore size but also on pore density. Ablation etching effects of plasma treatments can cause the increase of membrane skin pore density and the enlargement of membrane skin pore size [20]. In this work, original PAN membrane can reject albumin but cannot reject salt from feed solutions. After treatment within 100 s of oxygen or helium plasmas, membrane rejection was almost not changed, that means membrane skin pore size was nearly kept and the increasing of membrane flux here was mainly due to the

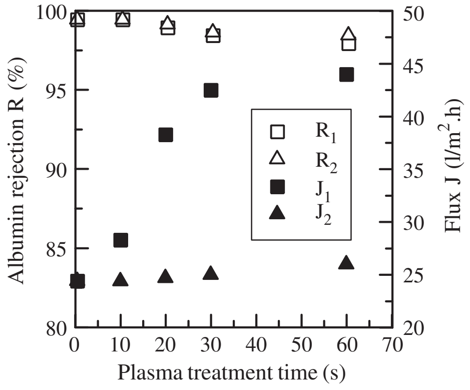

Fig. 5. UF property of plasma treated PAN membranes. R_1, R_2: albumin rejection of O_2 and He plasma treated membranes, respectively. J_1, J_2: the flux of O_2 and He plasma treated membranes, respectively.

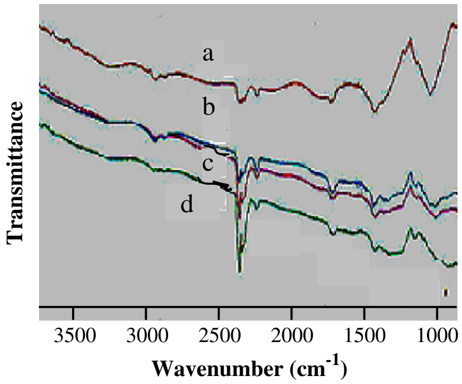

Fig. 6. FTIR-ATR spectra of (a) unmodified, (b) 30 s, (c) 120 s and (d) 600 s plasma modified membrane surfaces.

increasing of membrane skin pore density and hydrophilicity. In addition, under the same of plasma treatment conditions, membrane flux of oxygen plasma treated membranes is higher than that of helium plasma treated ones.

3.2. Plasma polymerization

3.2.1. Membrane weight increase

In this work, plasma polymerization experiments were carried out with acrylic acid monomer vapor at flow rate of 2 sccm and discharge power of 10 W. The experimental results indicated that membrane weight increased lineally up to 1.4% with the increasing of plasma polymerization time within 60 min. This could be due to the deposition of plasma polymer layer onto substrate membrane surface and thickness of this deposition layer may increase proportionally with plasma polymerization time. In fact, there are two opposing processes: polymer formation, which leads to the deposition of plasma polymer layer, and ablation, which leads to the removal of substrate material. The balance between polymerization and ablation depends on plasma conditions. In this experiment, the deposition was dominant process; therefore, membrane weight increased after plasma polymerization.

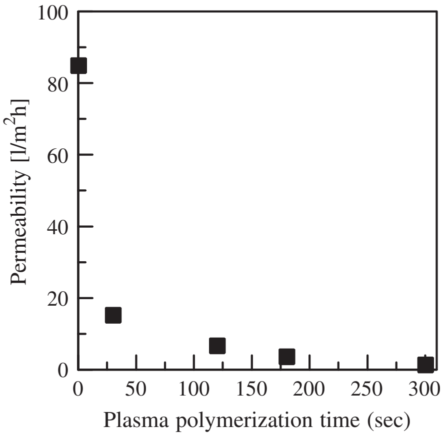

Fig. 7. Permeability of plasma modified PAN membranes.

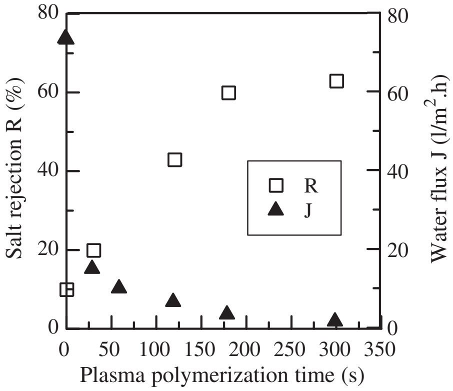

Fig. 8. RO property of plasma modified PAN membranes.

3.2.2. FTIR-ATR spectra

Hydrophilicity of membrane surface increased slightly after plasma polymerization. The change of membrane surface hydrophilicity could be due to the changes of membrane surface composition. In plasma, acrylic acid monomers may polymerize by opening of the double bond or by formation of reactive species through fragmentation. Opening of a C=C bond requires less energy than dissociation of a C–C bond. In this work, polymerization was carried out at low discharge power (10 W), therefore, polymerization mainly proceeded by opening of double bonds of acrylic acid molecules. The qualitative information about chemical composition of the outermost surface layer was obtained by FTIR/ATR spectra (Fig. 6). The results indicated that C≡N bonds (2300 cm^{-1}) of original PAN membranes were not broken during plasma irradiation. With the increasing of plasma polymerization time, spectra exhibited increased absorbance around 1250 and 1720 cm^{-1} due to C(O)OH hydrophilic groups which were introduced into PAN membrane surface by plasma polymerization of acrylic acid monomer vapor.

3.2.3. Permeability

Fig. 7 showed that permeability (pure water flux at 3.5 MPa) of modified PAN membranes decreased with the increasing of plasma polymerization time. This can be considered to be caused by the increase of plasma polymer layer thickness

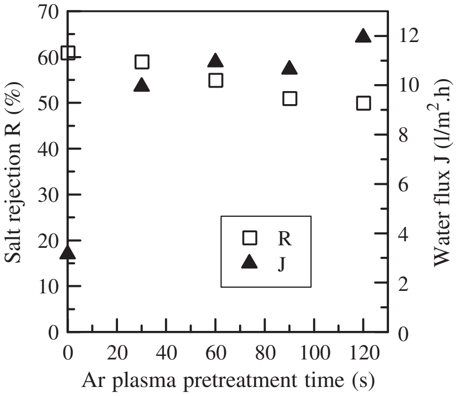

Fig. 9. RO property of Ar plasma pretreated modified PAN membranes.

deposited on substrate membrane surface and/or the decrease of membrane skin pore sizes because of this polymer layer.

3.2.4. Separation property

The experimental results indicated that plasma polymerization changes membrane separation property significantly. At first, separation property of PAN membrane was tested by ultrafiltration experiment using albumin 1 wt.% as feed solution at 2.0 MPa. The obtained results demonstrated that membrane flux J is too small to work as UF membrane any longer, although membrane can reject albumin completely ($R=100\%$). Next, modified PAN membrane was tested with desalination experiments using NaCl 2500 ppm feed solution at 3.5 MPa. The obtained results showed that plasma modified membrane can reject salt as RO membrane. Salt rejection increased and water flux decreased gradually with the increasing of plasma polymerization time (Fig. 8). These results confirm again the decrease of membrane skin pore size due to the deposition of plasma polymerized acrylic acid layers onto substrate membrane surface.

In order to improve water flux of RO modified membranes, plasma pretreatment using non-polymer-forming plasma gas could be done shortly before plasma polymerization. In this study, Ar plasma pretreatment was carried out at discharge power of 10 W with Ar flow rate of 18 sccm and plasma polymerization of acrylic acid vapor was executed subsequently for 3 min at discharge power of 10 W and monomer flow rate of 2 sccm. Fig. 9 shows the influence of Ar plasma pre-treatment time on RO property of modified PAN membranes. The results indicated that by using Ar plasma pretreatment, water flux of RO modified PAN membranes may increase significantly. In this experiment, within 60 s of Ar plasma pretreatment, water flux of these membranes increased clearly in comparison with non-pretreated modified membrane meanwhile its salt rejection was almost retained. The increase of water flux here could be due to the increasing of pore density on membrane surface by non-polymer-forming plasma effects. Moreover, Ar plasma pretreatment can create free-radical sites [1] on substrate membrane surface, which are active positions for subsequent polymerization, so the amount of hydrophilicity groups introduced into substrate PAN membrane surface by plasma polymerization could be increased, therefore, water flux of RO modified membranes was improved.

4. Conclusions

Plasma treatments using non-polymer-forming plasma gases lead to the increasing of membrane surface hydrophilicity and membrane permeability due to mainly ablation-etching effects. By using oxygen plasma treatment, ultrafiltration property of PAN membranes could be improved with the enhancement of membrane flux meanwhile its albumin rejection was almost maintained.

Plasma polymerization using acrylic acid vapor as a monomer and PAN UF membrane as a substrate material leads to the formation of RO membrane due to the deposition of plasma polymer layer onto substrate membrane surface. Membrane skin pore size reduced and the rejection of RO modified membranes increased gradually with the increasing of plasma polymerization time.

Plasma techniques can control membrane skin pore sizes and have a potential to improve the membrane separation performance by applying of pretreatment membrane surface using non-polymer-forming plasma and subsequent plasma polymerization.

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