Preparation of Cellulose Triacetate Pervaporation Membrane by Ammonia Plasma Treatment

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ABSTRACT: Homogeneous cellulose triacetate membranes were prepared by the solution-casting method. The surface of this membrane was modified with gaseous plasma of a 10-W discharge power in the presence of ammonia gas at 0.15 Torr pressure. The percentage of weight loss of the CTA membranes was found to be 0.7 for 20 min of treatment time in the ammonia plasma. The contact angle measurement indicated that hydrophilicity of the surface increases. ATR-FTIR spectral analysis showed that the hydrophilicity is mainly derived from the amino groups on the modified surface. SEM studies indicate that no considerable change of surface morphology occurred up to 5 min of treatment time, but a considerable change of surface morphology resulted for treatment of 10 and 20 min. The modified membranes were used for pervaporation studies for separation of an isopropanol–aqueous mixture. These membranes showed excellent selectivity for water. The water flux increases with an increase in treatment time for all concentrations of isopropanol in the feed. The isopropanol flux decreases for initial treatment time (2 and 5 min), but showed an increasing trend for a higher treatment time (10 and 20 min). © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 258–265, 2000

Key words: ammonia plasma; hydrophilicity; morphology; plasma etching; pervaporation; selectivity; flux

INTRODUCTION

Low temperature plasma is a soft radiation source. Its interaction even at long exposure times affects material only over a range of hundred to several thousand angstroms in depth. In dry gas, plasma surface interactions are generally free of secondary reactive species causing undesirable side reactions. Plasma surface treatment also offers the advantage of greater chemical flexibility. By choosing different reactive gases or mixture of gases, for generating reactive chemical species, different surfaces can be produced.[1,2] The plasmas of ammonia or a mixture of nitrogen and hydrogen gases were used to create amino groups that then attached to various polymer surfaces, without substantially altering the bulk properties of the polymers.[3] Such plasma treatment enhances the wettability of polymer surfaces, resulting in a more compatible interface with biological fluids.[4–7] Taking advantage of this fact, hydrophobic polymeric membranes have been modified such that one side of the membrane becomes hydrophilic while keeping the other side hydrophobic by protecting it from exposure to plasma.[8] A polymeric membrane thus obtained showed better biocompatibility found in applications in blood oxygen exchangers and biosensors. The plasma-treated membranes were also developed for reverse osmosis[9,10] and gas separation.[11–13]

The utilization of CTA as membrane material was recommended by Kesting.[14] CTA reverse-osmosis membranes were developed for desalination of sea water.[15,16] The development and ap-

plicability of CTA asymmetric membranes in the treatment of wastes from plating, fertilizers, and textile dye industry have been examined.[17] Homogeneous CTA membranes were used for separation of ethanol–water and isopropanol–water by pervaporation.[18,19]

In this article we report the modification of the CTA membrane in ammonia plasma, and its application in separation of an aqueous–isopropanol mixture by the pervaporation process. In separation processes, selectivity and flux are the major factors. If one tries to improve selectivity, its flux reduces, and vice versa. Here, we have shown that by ammonia plasma treatment, selectivity as well as flux both are increased. Further, the treated surfaces were analyzed by using scanning electron microscopy (SEM), Fourier transform infrared-attenuated total reflectance (FTIR-ATR) Spectroscopy, and contact angle measurements. The % wt change of the films with treatment time was also studied.

EXPERIMENTAL

Materials

Cellulose triacetate (acetyl content 43.2%) was obtained from M/S Mysore Acetate and Chemicals, India. Chloroform, methanol, and isopropanol were obtained from S. D. Fine Chemicals, India (AR Grade). These chemicals were used without further purification.

Membrane Preparation

Cellulose triacetate was dissolved in chloroform–methanol (9 : 1 vol %) mixture to form a 2% solution. Films were casted onto optically flat Petri dishes. The thickness of the films was controlled by the volume of polymer solution. Every time a 7-mL polymer solution was poured into each Petri dish, the dish was then heated in an oven at 40°C. Thin films were obtained after the complete evaporation of the solvent, which were used for further investigation after 24 h. The thickness of the film was measured at five randomly selected places with a thickness gauge within an accuracy of 1 μm, and its average was determined. The average thickness of the membranes was found to be 25 μm.

Plasma Treatment

The apparatus used for plasma polymerization is described elsewhere.[20] The system consists of a glass bell-jar type of reactor with two stainless steel electrodes. The electrodes were capacitively coupled and water cooled. The lower electrode consists of a magnetron, and is coupled with an RF power generator (13.56 MHz), through a proper matching network. The upper electrode is grounded. For surface modification, the CTA membrane was first placed on top of the lower electrode in the reactor. The flow of ammonia was controlled with the help of a precision needle valve. The chamber was first evacuated to a pressure of 0.001 Torr, and ammonia was purged into it. This procedure was repeated three times. Then the ammonia flow was adjusted to get a steady pressure of 0.15 Torr. A glow discharge was created with 10 W of power. The membranes were treated for various durations of time (2, 5, 10, or 20 min).

Etching

The % wt changes were calculated using the weight change occurring in the membranes for various time durations by the following formula:

$$\% \text{ weight change} = \frac{W - W_0}{W_0} \times 100$$

where W_0 is initial weight of substrate, and W is weight of substrate after treatment.

Surface Characterization of the Membrane

The attenuated total reflectance infrared (ATR-IR) spectra of the modified membranes was obtained by using a Paragon 500 Perkin–Elmer FTIR spectrometer. A KRS-5 crystal with an angle of incidence 45° was used for recording the ATR spectra. The microstructure of composite membranes was observed under a Philips 515 scanning electron microscope. The contact angle of membrane was measured with distilled, deionized water as the contacting liquid, by the sessile drop method. At least 10 readings were taken at different places, and an average was determined. The contact angle was calculated by the following equation

$$\text{Contact angle} = \sin^{-1}\left[\frac{2rh}{r^2 + h^2}\right]$$

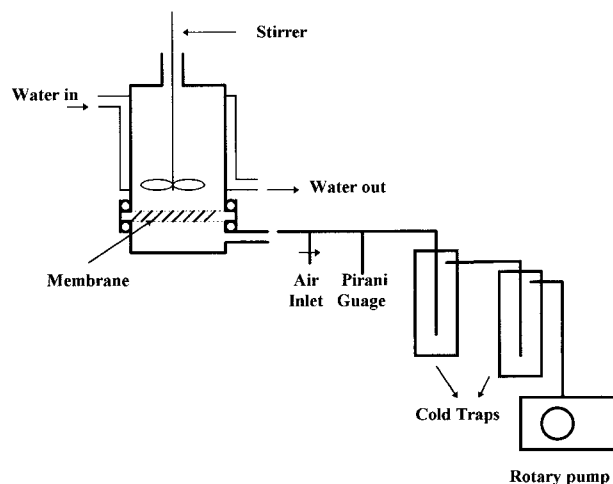where h is the height of spherical segment, and r is the radius of spherical segment.

Figure 1 Schematic diagram of setup used for pervaporation studies.

Pervaporation

Pervaporation performance was measured for isopropanol aqueous solution, by using the apparatus shown in Figure 1. The volume of feed solution was about 100 cm². The feed solution was well stirred to eliminate concentration polarization. The effective membrane area for pervaporation was 11.9 cm². The pressure at the downstream side was maintained at 1 Torr with a vacuum pump, while the upstream side was at atmospheric pressure. As a feed, isopropanol aqueous solutions with concentrations of 20, 40, 60, 80, and 90% were examined. Vapors permeated through membranes were condensed in a trap maintained at liquid nitrogen temperature. The amount of permeate was obtained by measuring the increase in the weight of the trap. The composition of the feed and the permeate was analyzed by using the method of refraction. Refractive index was measured with the help of Abbe Refractometer (Bausch and Lomb Co.) with an accuracy of 0.0005. The separation factor $\alpha_{H_2O/isoproH}$ was calculated from following equation,

$$\alpha_{H_2O/isoproH} = \frac{Y_{H_2O}/Y_{isoproH}}{X_{H_2O}/X_{isoproH}}$$

In pervaporation X_{H_2O}, $X_{isoproH}$, and Y_{H_2O}, $Y_{isoproH}$ are the weight fractions of water and isopropanol in the feed and permeate, respectively. The pervaporation experiment was carried out at temperature of 25°C.

RESULTS AND DISCUSSION

Etching

Figure 2 shows % wt loss of CTA films, when treated in ammonia plasma for various durations of time. It is seen from the figure that their is a rapid loss in the beginning, followed by a decreasing rate, with a maximum loss of about 0.7% for 20 min of treatment. The % wt loss after 2 min of treatment decreases mainly because of the reactions occurring at the surface. It is believed that the interaction of ions, electrons, and energetic species of neutral atoms cause the etching or rapid removal of low molecular weight contamination like additives, processing aids, and adsorbed species, which is also called plasma cleaning. After plasma cleaning, ablation of the polymer chain starts. The etching process is more predominant on the amorphous region of the surface than the crystalline regions. Therefore, it is possible that the initial rates of the etchings are more rapid. Once all the etchable amorphous materials on the surface have been removed, the remaining crystalline and tightly bound amorphous material cannot be removed easily, causing
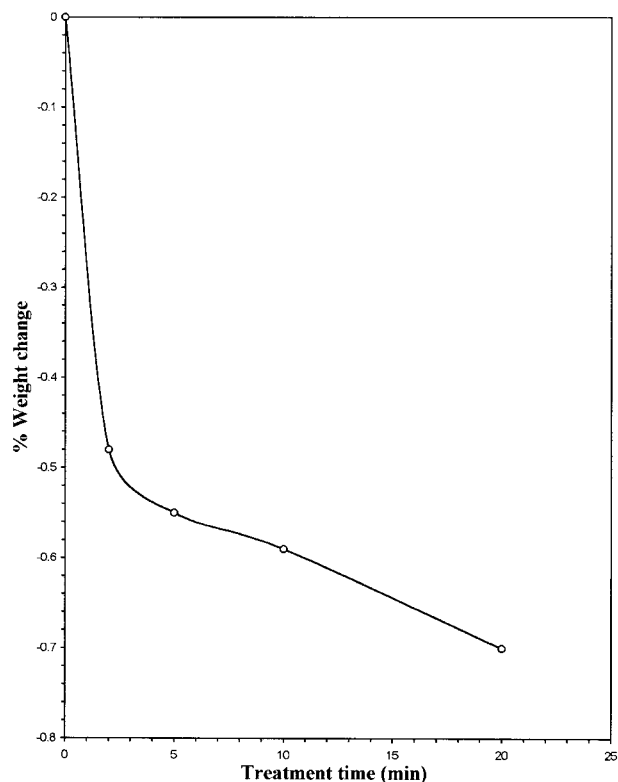

Figure 2 % weight change versus treatment time.

a decline in the etching rates. In Figure 2 it is observed that after 2 min of treatment the rates of etching decreases. The % wt loss then increases linearly.

The second reason for the decline in the etching rate could be the redeposition of sputtered fragments. Sputtered polymer fragments can be reactivated in plasma and redeposition takes place. There is enough evidence through surface studies and mass spectrometric analysis that fragmentation and redeposition of fragmentation takes place.[21,22]

FTIR-ATR Spectroscopy

Hollahan et al.[23] showed that the treatment of polymer films in radiofrequency ammonia plasma results in an attachment of amino groups on polymer surfaces. The plasma emission spectra of ammonia have been studied, and has revealed the presence of NH_3, NH_2, NH, N_2, H_2, and H spectral features, and various reactions have been postulated.[24] Due to the presence of these highly reactive species in plasma, the following bands are observed.

Figure 3 shows FTIR-ATR spectra of control and treated CTA membrane in ammonia plasma for 5 and 20 min. These spectra were recorded within 5 h of the plasma treatment. The absorption of band between 3200 and 3500 cm^{-1} has increased, which may be due to —OH and >NH stretching. The absorption of the band at 1738 cm^{-1} increased due to >C=O. The new absorption band that appeared at 1640 cm^{-1} can be attributed to >C=N stretching. The absorption band that appeared at 1545 cm^{-1} can be attributed to monosubstituated NH bending vibrations. All above-mentioned absorption bands strongly indicate the presence of amino groups.

Contact Angle

The change in surface energy can be determined by observing the extent of wetting of the surface by the solvent such as water. The angle of contact of the water gives a direct measure of the modification of polymeric surface, as wetting is a property that is governed by the top molecular layer of any surface. The contact angle measurement was usually carried out within 3–5 h of the plasma treatment. Until now, most of the contact angle measurements of membrane characterization have been made on hydrophobic membranes used for pervaporation or gas permeation,[25–28] and on
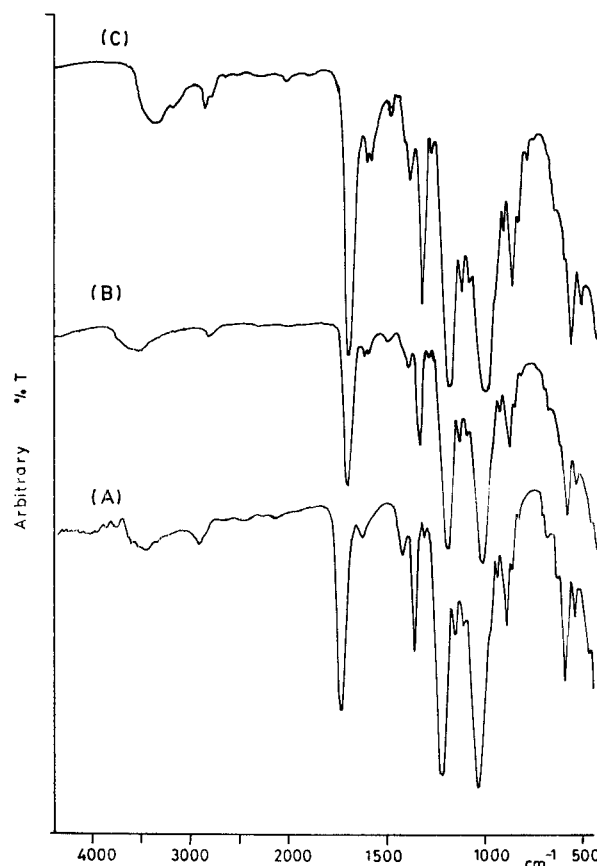

Figure 3 ATR-FTIR spectra of (A) control CTA film, (B) treated CTA film in ammonia plasma for 2 min, and (C) treated CTA film in ammonia plasma for 20 min.

porous hydrophilic or hydrophobic membrane used for Microfiltration (MF) or Ultrafiltration (UF).[29,30] Fane et al.[29] correlated flux decline with variation of membrane hydrophilicity, while Oldani and Schock[30] showed that hydrophilic membranes do have better flux recoveries.

The increase in wettability after treatment was evident from the results of contact angle measurement (Fig. 4). The contact angles of membranes decreased from 59 to 50 and 44 for 2 and 5 min plasma treatment. The contact angle method is sensitive to both the chemical nature of the surface and also the smoothness or roughness of the surface. It is evident from FTIR-ATR measurements that in ammonia plasma, attachment of amino groups onto polymer surfaces takes place; due to this, the wettability of the surfaces increased. For a longer plasma treatment the surface layers were degraded by surface etching, and cracks or defects were formed on the surface, which is also evident from surface morphology. Due to this roughening of the surface, the contact
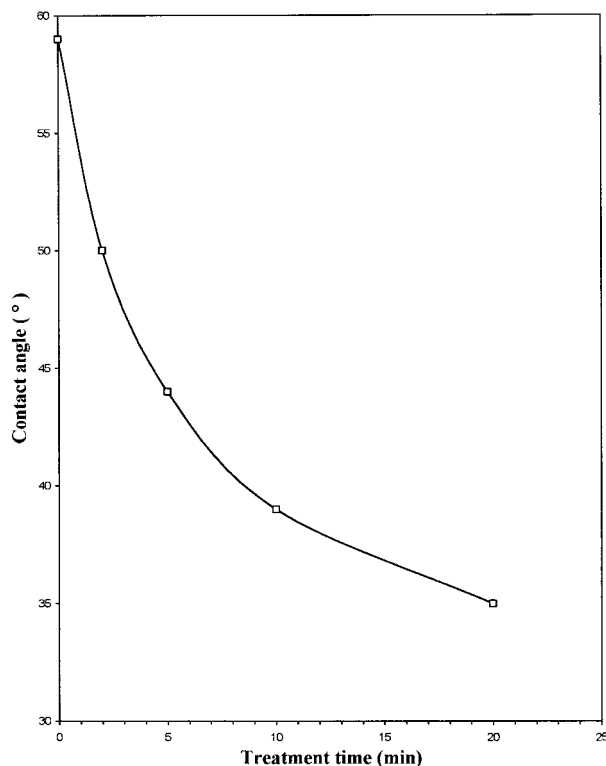
Figure 4 Contact angle versus treatment time.

Figure 6 SEM micrograph of CTA film treated in ammonia plasma for 5 min.

face morphology was observed up to 5 min of treatment time (Fig. 6). When the treatment was for a 10-min duration, the etching of the substrate was quite prominent (Fig. 7). When the etching was for 20 min, a wavy kind of morphology was seen (Fig. 8). Also, occasionally in some regions, redeposition of sputtered fragments could be seen.

angle still decreased. The contact angle is 39 and 35 for 10 and 20 min of plasma treatment.

Pervaporation

Isopropanol–water permseparation through the ammonia plasma-modified CTA membranes was investigated by pervaporation. Figure 9 shows the effect of ammonia plasma treatment of CTA membranes on water selectivity for different concentration (wt %) of isopropanol in the feed. The

Morphology

The SEM micrographs of control and treated membranes are given in Figures 5–8. Figure 5 depicts a smooth surface structure of the control CTA membrane. No considerable change in sur-
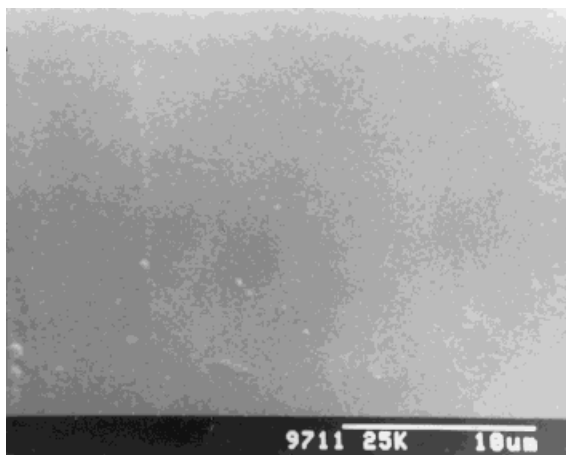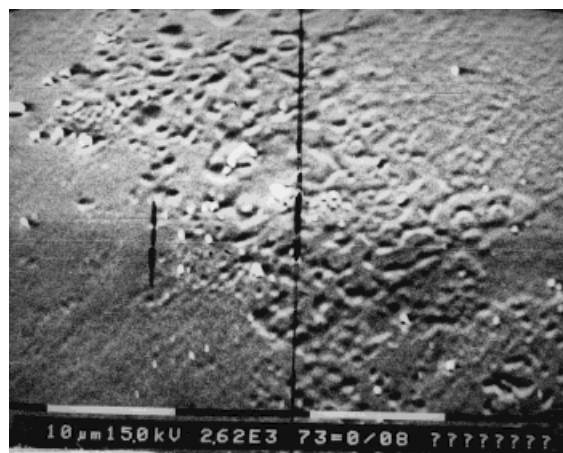

Figure 5 SEM micrograph of control CTA film.

Figure 7 SEM micrograph of CTA film treated in ammonia plasma for 10 min.
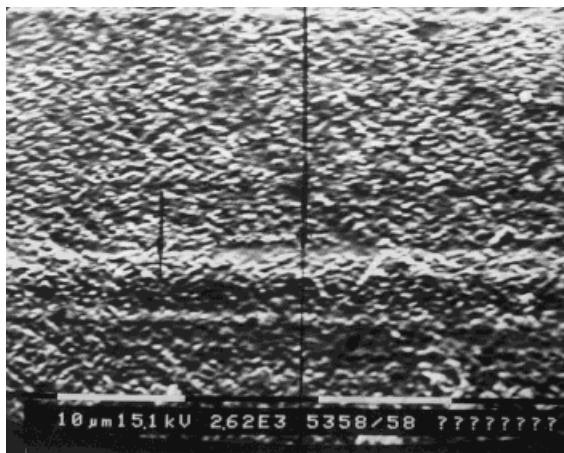
Figure 8 SEM micrograph of CTA film treated in ammonia plasma for 20 min.

variation of the permeation flux of water and isopropanol as a function of treatment time are shown in Figure 10 for different concentration (wt %) of isopropanol in the feed. For the initial treatment time (2 and 5 min) water selectivity increased enormously (Fig. 9). For 90% (wt %) concentration of isopropanol in the feed the water selectivity was 27 for the control CTA membrane, 36 for the 2-min–treated membrane, and 57 for the 5-min–treated CTA membrane. For these treatment time (2 and 5 min) the water flux increased, but isopropanol flux decreased. The main factors that contribute to improvement in water selectivity and water flux are (i) incorporation of hydrophilic groups into membrane surfaces causes an increase in surface hydrophilicity remarkably (as is revealed by ATR-FTIR spectroscopic studies and contact angle measurements); (ii) no considerable etching is observed up to 5 min of treatment time, as revealed by SEM studies; and (iii) crosslinking within the CTA membranes upon exposure to plasma is possible.

The water selectivity of CTA membranes treated in the ammonia plasma for 10 and 20 min was reduced more than that for the 2- and 5-min–treated membranes for all concentrations (wt %) of isopropanol in the feed. For 90% (wt %) concentration of isopropanol in the feed the water selectivity was 44 and 34 for 10- and 20-min–treated membranes, respectively. For these membranes, both water flux [Fig. 10(A)], as well as isopropanol flux [Fig. 10(B)], both increased. SEM studies revealed that the skin layer of the surface is etched off, and some cracks have developed on the surface. Due to this etching and cracks on the surface

both water and isopropanol flux increased, and hence, the reduction in water selectivity took place.

Figure 11 shows the relation of total flux with the contact angle. The contact angle is sensitive to both the chemical nature of the surface and the smoothness or roughness of the surface. As the contact angle decreases, total flux increases for all concentrations of isopropanol in the feed. There was a sharp increase in the total flux observed for a contact angle of 34°, which corresponds to the 20-min–treated CTA membrane because more etching was observed for the 20-min–treated membrane.

On the basis of observation we find that the selectivity reaches highest value when the plasma treatment was for 5 min. In terms of structural changes, it is understood that the membrane can become more hydrophilic due to incorporation of nitrogen moieties. It is interesting to note that no substantial morphological changes are observed up to 5 min of treatment. It, therefore, means that the incorporation of the hydrophilic groups are responsible for the increased flux of the water and the decreased flux of the isopropanol, giving rise to a maximum value
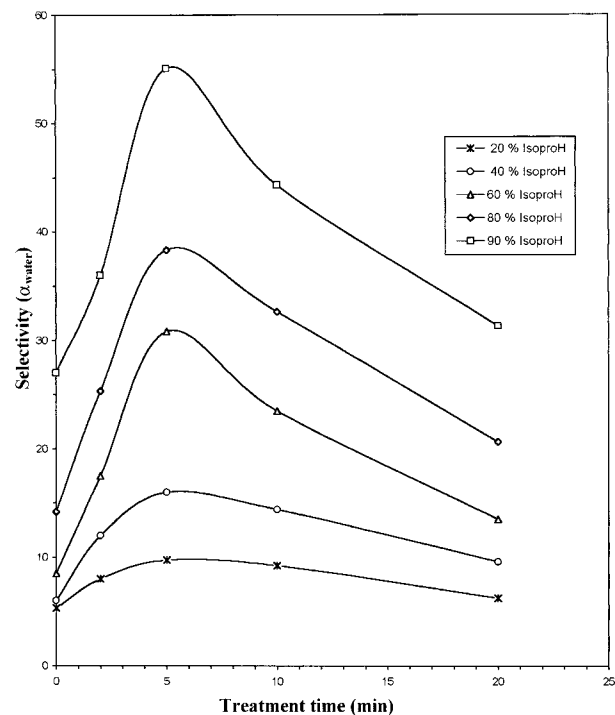

Figure 9 Water selectivity of CTA films treated in ammonia plasma for various periods of time, for different wt % of isopropanol in the feed.
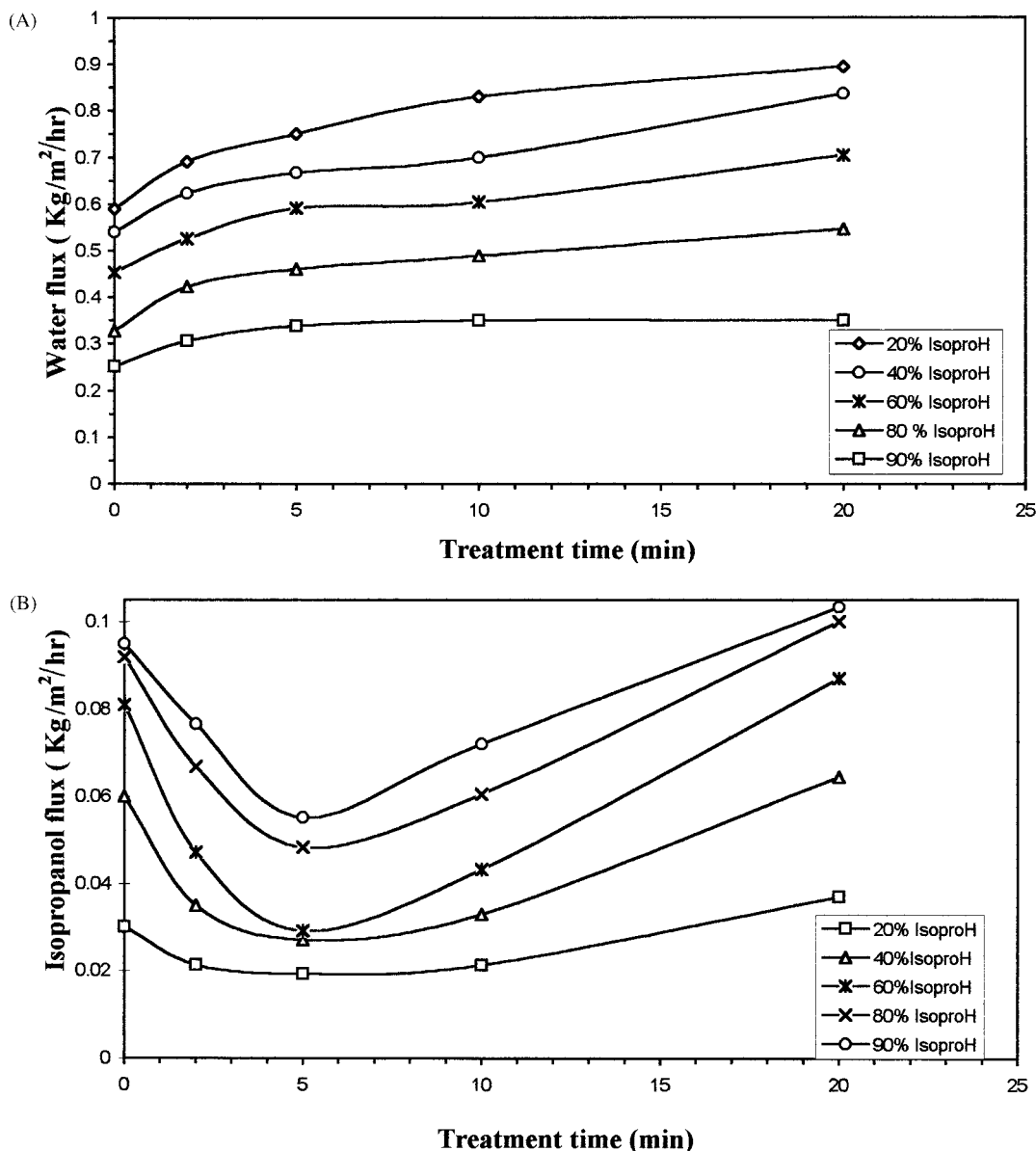
(A)

(B)

Figure 10   (A) Variation of water flux with treatment time of CTA films in ammonia plasma for different concentrations (wt %) of isopropanol in the feed. (B) Variation of isopropanol flux with treatment time of CTA films in ammonia plasma for different concentrations (wt %) of isopropanol in the feed.

of selectivity. However, continuation of plasma treatment for higher times (for 10 and 20 min) results in substantial etching of the surface (as supported by SEM, weight loss studies) which give rise to a higher total flux without additional advantage of selectivity.

CONCLUSION

The % wt loss of CTA membranes was found to be 0.7% for 20 min of treatment time when treated in

ammonia plasma. It was found that this treatment makes the surface more hydrophilic. Due to incorporation of amino groups into the polymer matrix, hydrophilicity increases. The study of morphology revealed that up to 5 min of treatment time no considerable etching occurred. When treated for a longer time (10 min and 20 min), heavy etching was observed, with the development of a wavy structure. These membranes showed excellent selectivity for water in up to 5 min of treatment time. The water flux increases
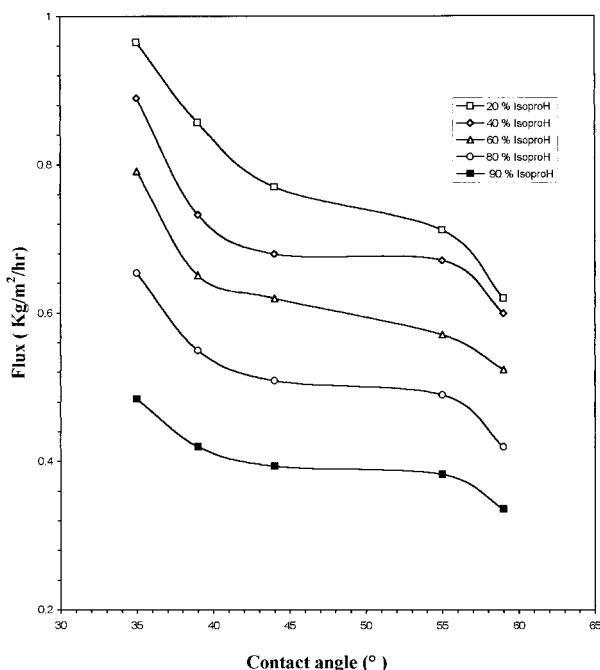
Figure 11 Total flux vs. contact angle of CTA films treated in ammonia plasma, for various periods of time, for different concentrations (wt %) of isopropanol in the feed.

with an increase in treatment time for all concentrations of isopropanol in the feed. The isopropanol flux decreases for an initial treatment time (2 min and 5 min), but showed an increasing trend for a higher treatment time (10 min and 20 min), resulting in decreased water selectivity for a higher treatment time.

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