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Characterization of Plasma-Polymerized Thiophene onto Cellulose Acetate Membrane and Its Application to Pervaporation

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ABSTRACT

Surface modification of cellulose acetate (CTA) membranes was achieved by subjecting them to magnetron-enhanced plasma. Plasma polymerization and deposition of thiophene were achieved on these membranes in a nitrogen atmosphere. Such modified membranes were characterized by determining the rate of deposition, angle of contact with water, and IR spectroscopy. The morphology of deposition was studied by SEM, and it was found that the globular particles grow with time to give a honeycomb or platelet structure. The water vapor transmission rates were measured and were found to decrease with an increase in the time of deposition. The pervaporation process of such modified CTA films for the separation of an isopropanol–water mixture was investigated. The water selectivity of the modified membranes was found to be increased.

INTRODUCTION

Plasma polymerization is a process for the preparation of ultrathin coatings by the influence of plasma on monomer gas or vapor and subsequent deposition and polymerization of excited species on the surface of a substrate. One of the primary advantage of plasma polymerization is the ability to deposit

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films with thicknesses in the range from several tens of angstrom to several thousands of angstrom (1). The plasma polymerization technique has been investigated by many authors, and the films have been used for various purposes such as insulating films (2), protection coatings (3), and separation membranes in medicines and industry (4). Plasma polymerized composite membranes have been applied to reverse osmosis (5, 6), gas separation (7–9), and pervaporation (10–12).

Pervaporation is a well-known technique used for the separation of liquid mixtures. This technique differs from other separation processes such as reverse osmosis and gas separation because of the phase change of the permeate. A set of transport equations for pervaporation based on the pore flow mechanism was developed by Sourirajan et al. (13, 14). The pore flow mechanism consists of three consecutive steps: 1) liquid transport from the pore inlet to the liquid–vapor boundary, 2) evaporation at the phase boundary, and 3) vapor transport to the pore outlet. In this transport mechanism it was assumed that the separation of the liquid mixture occurs primarily at the phase boundary and through the vapor transport. Therefore the depth of liquid permeation in the membrane should exert a strong effect on the selectivity of a membrane, i.e., if the liquid–vapor boundary is shifted toward the feed side, selectivity should increase. Using this concept, Deng et al. (15) studied separation of the acetic acid/water mixture by pervaporation using laminated hydrophobic and hydrophilic membranes. They laminated a polydimethylsiloxane (hydrophobic) membrane on the top of an aromatic polyamide (hydrophilic) membrane. The hydrophobic membrane was in contact with the feed mixture. In their study they observed that the hydrophobic membrane effectively prevented penetration of the liquid–vapor boundary into the asymmetric aromatic polyamide membrane, and hence the water selectivity increased.

For the present study we thought it interesting to use the same concept to improve the water selectivity of cellulose acetate (CTA) membranes. Instead of laminating two different membranes, we used the plasma polymerization technique for the purpose. An ultrathin coating of plasma polymer (hydrophobic) was deposited onto a CTA membrane (hydrophilic). One of the primary advantage of this technique is that we can deposit a hydrophobic film of plasma polymer on a CTA membrane with thicknesses in the range from several tens of angstroms to several thousand of angstroms.

Thiophene was used as the monomer for plasma polymerization with the intention that even though the plasma polymer is hydrophobic, the presence of sulfur may influence water selectivity. These composite membranes were further characterized by deposition rate, contact angle, water vapor transmission rate measurements, and ATR-FTIR spectroscopy. The morphology was studied by SEM.



EXPERIMENTAL

Material

Cellulose triacetate (acetyl content 43.2%) was obtained from M/S Mysore Acetate and Chemicals, India. It was dissolved in a chloroform–methanol (9:1 vol%) mixture to form a 2% solution, 6 mL of which was poured in different Petri dishes. These films were cast in an oven at 40°C. The thicknesses of the films were controlled by the volume of polymer solution. The thickness of each film was measured at 10 randomly selected places with a thickness gauge within an accuracy of 1 μm and its mean was found. The average thickness of the films was 24 μm . Chloroform, methanol, and isopropanol were obtained from S. D. Fine Chemicals, India (AR Grade). Thiophene was obtained from Aldrich Chemicals. These chemicals were used without further purification.

Plasma Reactor

The apparatus used for plasma polymerization is described elsewhere (16). The system consists of a glass bell-jar with two stainless steel electrodes. The electrodes are capacitively coupled and water cooled. The lower electrode consists of a magnetron and is coupled with a RF power generator (13.56 MHz) through a proper matching network. The upper electrode is grounded. The flow of monomer and nitrogen was controlled with the help of a precision needle valve. The chamber was first evacuated to a pressure of 0.001 torr and the nitrogen flow was adjusted to set a pressure of 0.07 torr. Monomer was introduced till the pressure stabilized at 0.15 torr, and the polymerization was carried out for various time durations.

Deposition

The percentage weight changes were calculated by using the weight change occurring in the substrate for various time durations:

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

where W_0 is the initial weight of substrate and W is the weight of substrate after deposition.

The deposition was calculated by the weight gain of the substrate per square centimeter and expressed as $\mu\text{g}/\text{cm}^2$.

Infrared Spectra

Infrared spectral analysis of untreated CTA film, treated CTA films in thiophene plasma, and plasma polymer film on a NaCl crystal were carried out using a Paragon 500 Perkin-Elmer FTIR spectrometer equipped with an ATR



accessory. A KRS-5 crystal with an angle of incidence of 45° was used for recording ATR spectra.

Contact Angle

The angle of contact of water was measured by the sessile drop method. Water used for measurements was double distilled. At least 10 readings were taken at different places and the average was determined. The contact angle was calculated by

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

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

Morphology

The microstructure of composite membranes was observed under a Philips 515 scanning electron microscope. The samples were coated with gold by a sputter coater to a thickness of about 200 Å.

Water Vapor Transmission Rates

The water vapor transmission rates were determined using a ASTM setup (17). Calcium chloride was used as a desiccant. The films were sealed on aluminum cups which contained the desiccant. The effective surface area of the film was 43 cm² for water vapor transmission. The cups were placed in an environment with 85% relative humidity as controlled by a saturated KCl solution. The cups were weighed at 12-hour intervals.

Pervaporation

Pervaporation performance was measured for an isopropanol aqueous solution by using the apparatus shown in Fig. 8. The volume of feed solution was about 100 cm³. The feed solution was well stirred to eliminate the effect of 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 the feed, isopropanol–aqueous solution with concentrations of 20, 40, 60, 80, and 90% were examined. Vapors permeated through the 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 compositions of the feed and the permeate were analyzed by using the refraction method. The refractive index was measured with an Abbe Refractometer (Bausch and Lomb Co.) with an accuracy of 0.0005. The separation



factor $\alpha_{H_2O/isoproH}$ was calculated from

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

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 a temperature of 25°C.

RESULTS AND DISCUSSION

Deposition

The rates of deposition on a substrate depends on several parameters: diffusion, kinetic energies, molecular weight, etc. During deposition, etching of the substrate also takes place due to bombardment of ions, electrons, and activated species on the surface. The rate of deposition and etching depends on the types of monomer and substrate, respectively. It has been observed that there is competitive ablation and polymerization when plasma is struck in the presence of monomer vapor. Since deposition and etching are opposite processes, it is very difficult to determine the actual deposition rate on a polymer substrate. However, in the present investigation an attempt was made to determine the actual deposition rate of plasma-polymerized thiophene (PPTh) on CTA films by taking deposition on glass plates as a standard. Since plasma polymerization of thiophene is carried out in a nitrogen atmosphere, etching of CTA films in nitrogen plasma was also studied. Curve B of Fig. 1 shows

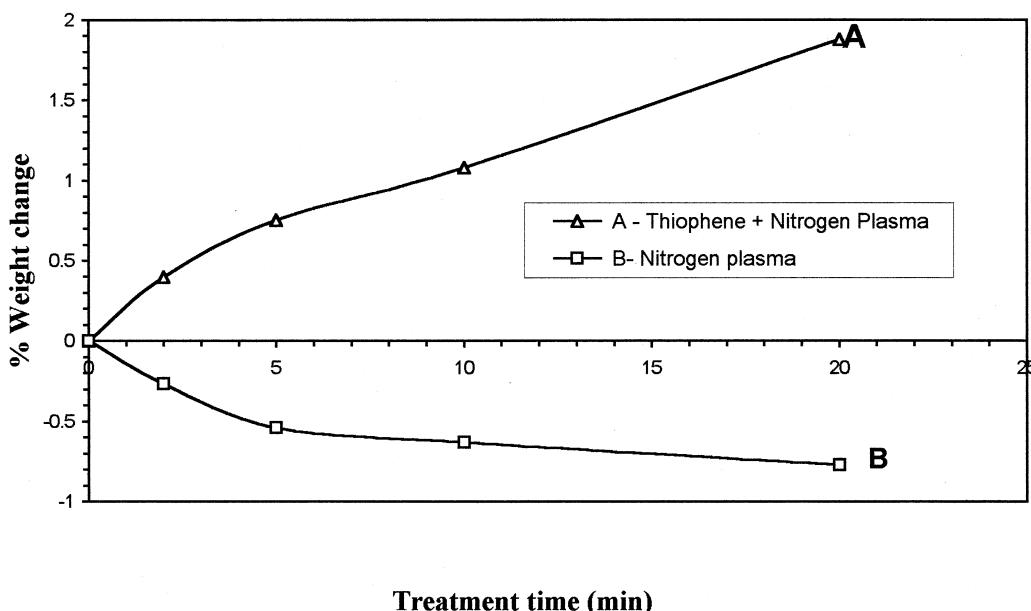


FIG. 1 Percent weight change vs treatment time in (A) thiophene + nitrogen plasma and (B) nitrogen plasma.

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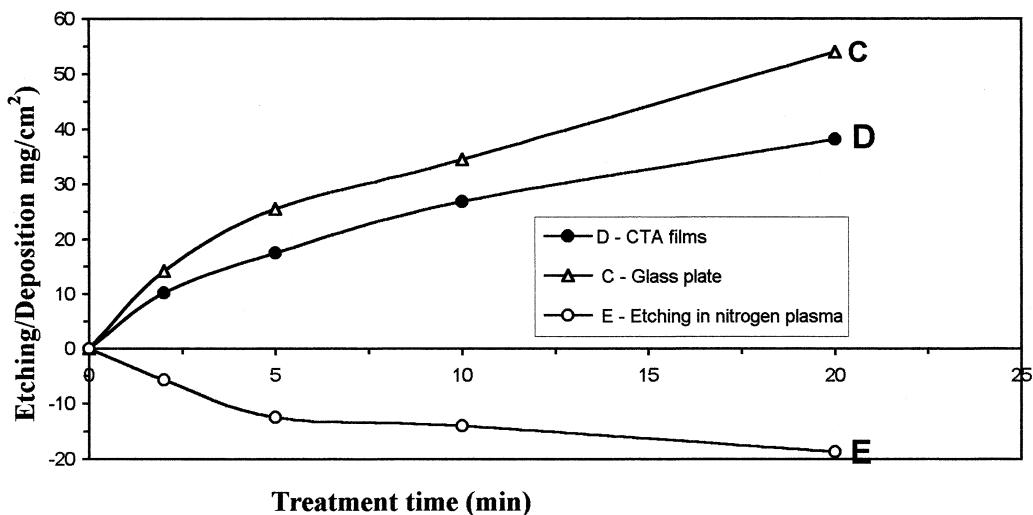


FIG. 2 Plasma polymerization and deposition of thiophene on (C) glass plates, (D) CTA films, and (E) etching of CTA in N_2 plasma.

that there is about 1% loss of weight on etching up to 20 minutes. It is clear from the curve that for the initial time of treatment the etching rate is high, then decreases, and attains a stable value after about 10 minutes of treatment. The initial high rate may be due to fast etching of low molecular weight volatile products. The deposition of thiophene plasma on CTA films and glass plates was investigated. It can be seen from Curve A of Fig. 1 that the deposition of polythiophene on CTA film increases as indicated by the % gain in weight. It is of interest to express the data in terms of total deposition as $\mu g/cm^2$. Figure 2 depicts this deposition or etching with respect to time. It can be seen that the deposition is quite high initially, then decreases, and finally tends to a steady rate. The high rate of deposition in the initial stage can be understood as due to the adsorbed layer of monomer on the substrate. This causes an increased concentration of monomer at the inception of glow discharge, so that the deposition rate is high in the initial stage. Figure 2 also shows the deposition observed on a glass plate (Curve C) and on CTA films (Curve D).

Infrared Spectroscopy

In general it is observed that the absorption bands of IR spectra are broadened for plasma polymers. This can be explained as due to the typical molecular structure of plasma polymers. During the plasma process, numerous different fragments, radicals, ions, etc. are generated. These form plasma polymer. They build up an amorphous structure with a large number of different and nonuniform chemical bonding states. Each molecular structure is



embedded in a different molecular surrounding, and a high degree of crosslinking is typical. Therefore, IR bands are shifted compared with their initial spectral positions in conventional polymers and broadened asymmetrically.

Figure 3(A) shows IR spectrum of plasma-polymerized thiophene. The peak at 700 cm^{-1} can be assigned to the C—H deformation vibrations of the

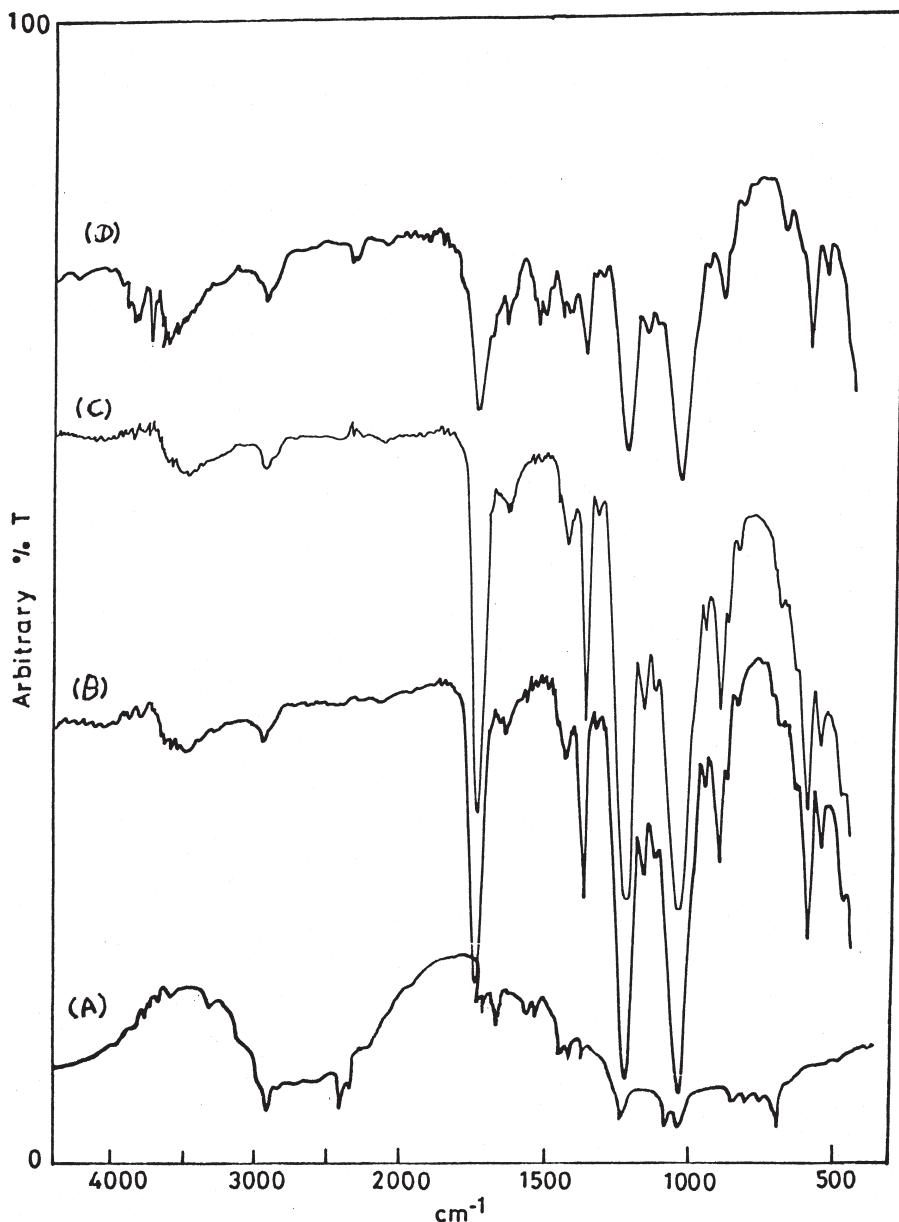


FIG. 3 (A) Infrared spectrum of plasma-polymerized thiophene on NaCl crystal, (B) ATR-FTIR spectra of control CTA film, (C) CTA film treated in thiophene plasma for 2 minutes, and (D) CTA film treated in thiophene plasma for 20 minutes.



2,5-disubstituted thiophene ring (18). The absorption at 1036 and 1438 cm^{-1} can be assigned to the $\alpha-\alpha'$ linkage of the polymer characteristic of poly-2,5-thiophene (19). The peak at 1221 cm^{-1} can be assigned to the ring vibration of 2,5-disubstituted thiophene (18). The plasma polymerization is carried out in a nitrogen atmosphere, and therefore some nitrogen moieties are likely to be incorporated in the polymer matrix. This incorporation in plasma is plasma copolymerization and not the trapping of nitrogen molecules in plasma polymer. The peaks at 1521 and 1580 cm^{-1} are a strong indication of the presence of secondary amides. The band at 1672 cm^{-1} is assigned to C—O bond stretching which is due to the low postplasma reaction of trapped free radicals with atmospheric oxygen. CTA is a transparent film, but after treatment with thiophene plasma its color changes to a yellowish-orange. This is a visible indication of the deposition of polythiophene. The UV/Visible spectra also indicate the deposition of polythiophene on CTA film. Spectra B, C, and D in Fig. 3 are ATR-FTIR spectra of the control CTA film and of CTA films treated in thiophene plasma for 2 and 20 minutes, respectively. CTA has strong absorption bands which overlap with polythiophene except the peaks at 700 and 1438 cm^{-1} which are characteristic peaks of polythiophene. The peak at 700 cm^{-1} is not clearly visible for 2 minutes plasma treatment, but as treatment time increases it becomes visible with an increase in its peak height. The peak heights of the absorption bands at 1529, 1571, and 1672 cm^{-1} also increase with time of treatment.

Contact Angle

The contact angle for water was measured for all films treated in monomer plasma for various periods of time. The decrease in wettability after plasma treatment was evident. The angle of contact versus deposition time is plotted in Fig. 4. It can be seen from the plot that in the initial time of treatment the contact angle increases rapidly. The contact angles for films deposited for 2 and 5 minutes were 84° and 86°, respectively. This may be due to the fact that during plasma deposition the surface becomes highly crosslinked. Better uniformity of the surface was achieved during the initial deposition and may be attributed to the surface property of the deposited polythiophene. The initial roughness of the CTA surface will decrease as crevices/rugosites become filled by the initial deposition. All the above-mentioned factors may lead to a decrease in hydrophilicity of the surface. On the other hand, contact angles for films treated for longer times (10 and 20 minutes) show a slight decrease in the angle. The contact angles of films deposited for 10 and 20 minutes were 83 and 81°, respectively. This decrement with increased time of treatment was somewhat surprising. It may occur either due to the CAP process or is a property of polythiophene. In order to decide which one of the causes is important,



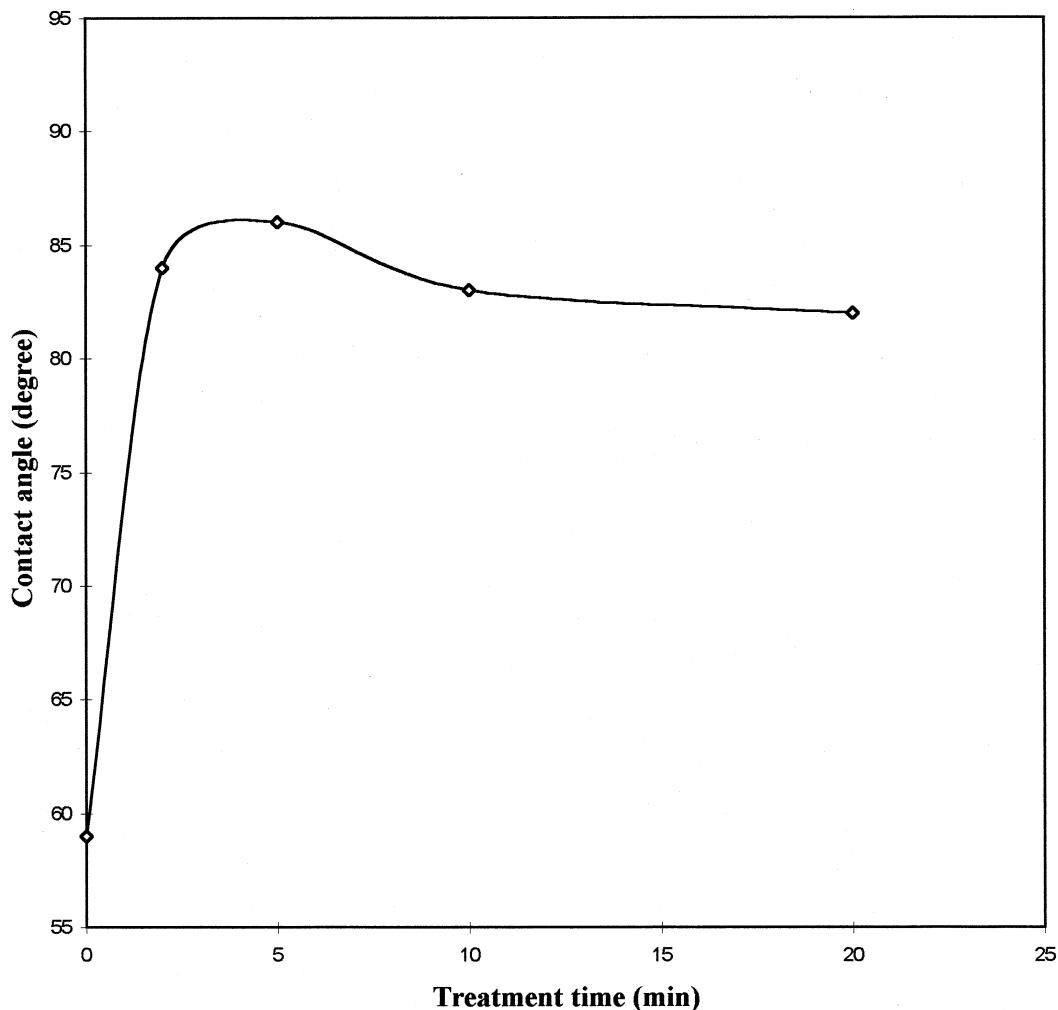


FIG. 4 Contact angle of water with CTA films treated in thiophene plasma for various time periods.

we measured the contact angle of a thick polythiophene film deposited on the neutral surface of a glass plate. The contact angle was found to be 78° . Thus, the decreasing trend observed for samples of CTA treated for increasing times indicates that the surface of CTA films is indeed uniformly coated with thiophene. This conclusion is supported by morphological observation of films by SEM.

Morphology

The morphological features of polythiophene deposited on CTA films were observed using SEM. The electron micrograph of control CTA film given in



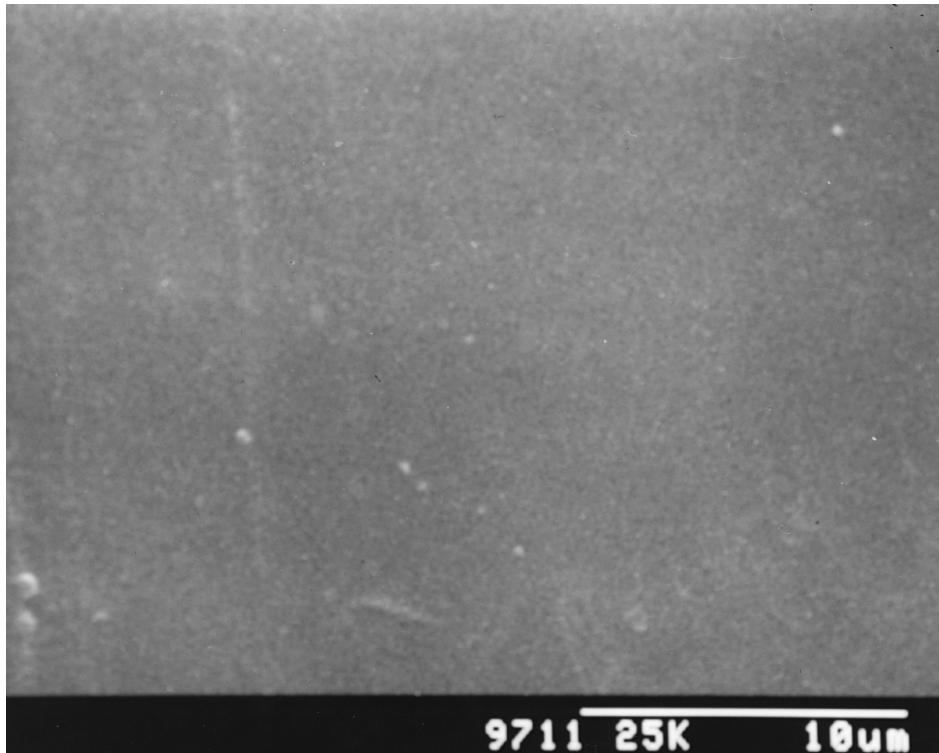


FIG. 5 Electron micrograph of control CTA film.

Fig. 5 shows a very smooth surface. An illustrative micrograph for a deposition of 2 minutes is given in Fig. 6. It can be seen that there are small globular particles, the minimum size of which is about 0.3 μm . Some large particles seen in the same photograph are obviously due to the coalescence of three or more individual globules (like droplets). When the time of deposition was increased to 5 minutes and then further to 10 minutes, the minimum size observed for the globules was still about 0.3 μm , which is more or less the same as that for the short time deposition. However, when the time of deposition was increased to 20 minutes, a very large area of the substrate became covered with the deposition. The morphology of growth indicates that two or more particles become fused to give a fibril-like appearance (Fig. 7). The process continues to give a honeycomb-like structure. However, it was found that they occasionally give rise to a platelet-like structure.

Water Vapor Transmission Rate

The water vapor transmission rates (WVTR) of modified CTA films are shown in Table 1. It can be clearly seen that the WVTR of CTA film is reduced by 50% for 2 minutes of deposition. However, a further increase in treatment



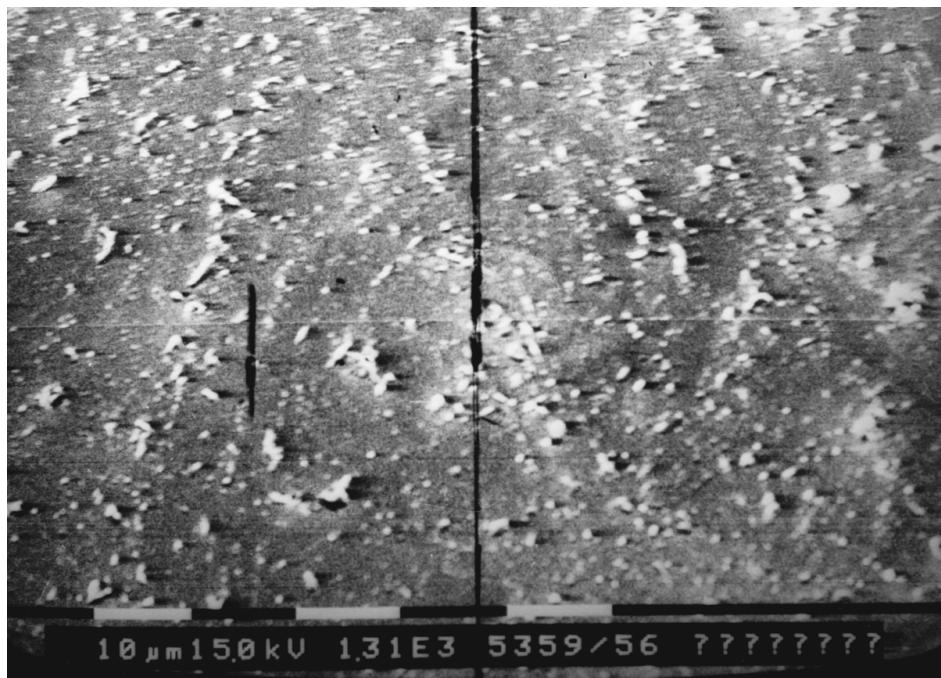


FIG. 6 Electron micrograph of CTA film treated in thiophene plasma for 2 minutes.

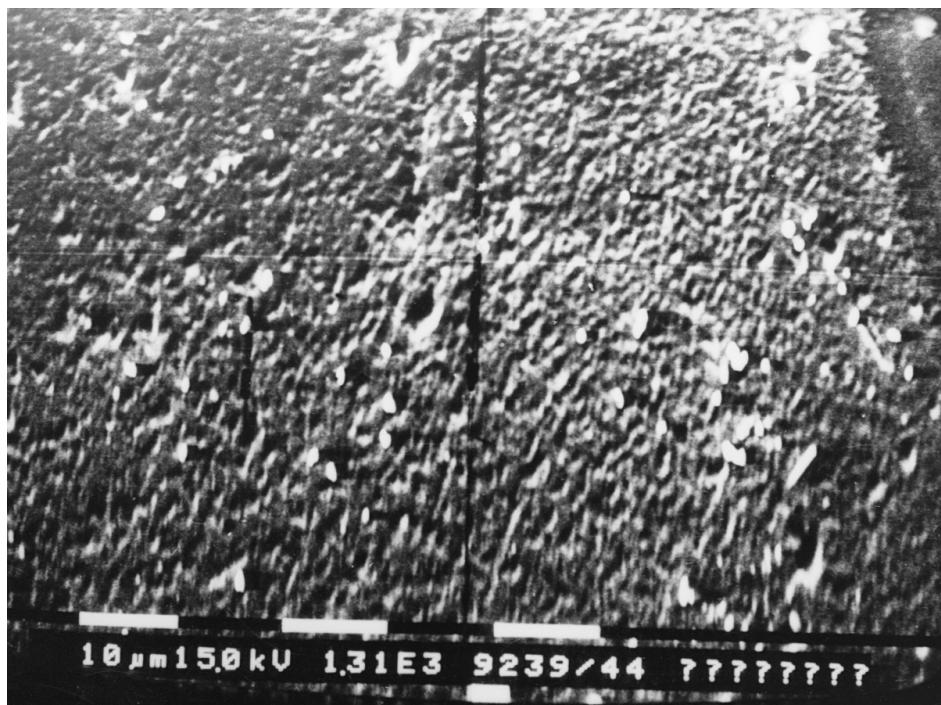


FIG. 7 Electron micrograph of CTA film treated in thiophene plasma for 20 minutes.



TABLE 1
Water Vapor Transmission Rate of CTA
Films Treated in Thiophene Plasma

Treatment time (minutes)	WVTR (mg/cm ² /h)
0	2.97 ± 0.12
2	1.594 ± 0.20
5	1.512 ± 0.2
10	1.381 ± 0.28
20	1.212 ± 0.25

does not lead to such a continuous fast decrease. The WVTR gradually decreases until it is reduced to 60% for 20 minutes of deposition. This may be due to the fact that the surface of the film is initially modified rapidly by the action of plasma as well as by the highly crosslinked layer of PPTh deposited on the surface. These results are to be expected on the basis of contact angle measurements where it was found that the surface became more hydrophobic.

Pervaporation

Pervaporation membranes are developed by plasma polymerization and plasma graft polymerization. Most authors have used porous membranes as substrates. In the present investigation we found it interesting to use a dense membrane as the substrate and to deposit a layer on it by plasma polymerization to form a composite membrane, one side of which became hydrophobic while the other side remained hydrophilic. In the present work the hydrophobic side of the membrane was facing the feed solution (Fig. 8). Permeation occurred in such a membrane through the deposited plasma polymer and then through the dense CTA membrane.

A plot of selectivity versus deposition time is given in Fig. 9, and a plot of flux versus deposition time is shown in Fig. 10. It can be seen that for the controlled CTA membrane the separation factor increases and the permeation rate decreases as the concentration of isopropanol in the feed increases. These results show a reverse relationship between selectivity of water and flux. This phenomenon can be explained in terms of a plasticizing effect. As the water concentration in the feed mixture is higher, the amorphous regions of the membrane swell and polymer chains become more flexible, thus lowering the ability of the membrane for selective transport (20).

Appreciable changes in the selectivity and flux to PPTh-deposited CTA membranes were noted. It is clearly seen from the plot that when PPTh is deposited on CTA film, water selectivity increases enormously. For all concen-



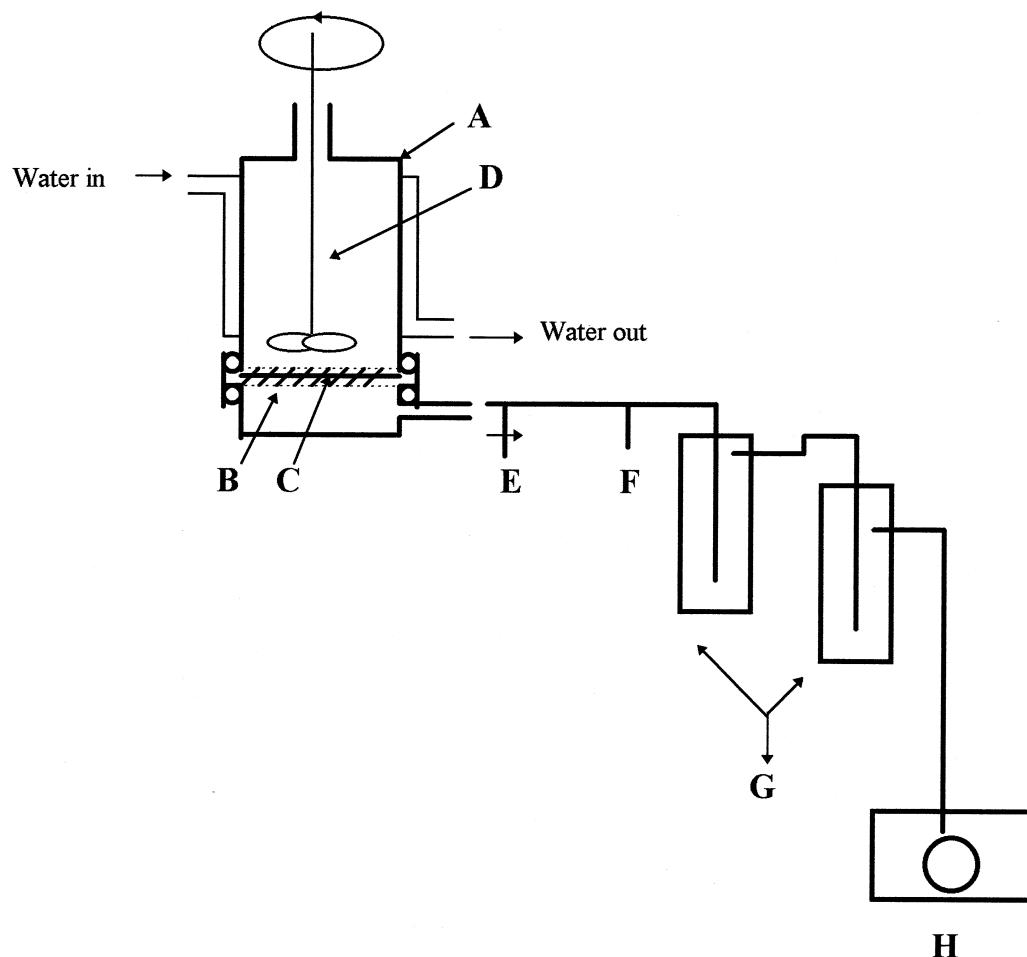


FIG. 8 Pervaporation test apparatus: (A) feed solution vessel, (B) porous stainless disk, (C) pervaporation membrane, (D) stirrer, (E) air inlet, (F) pirani gauge, (G) cold traps, (H) vacuum pump.

trations of isopropanol in the feedwater, selectivities are much higher than that for unmodified CTA membrane. For a 90% isopropanol concentration in the feed, the selectivity was 27 for the control CTA film and 57 and 63 for 2 and 5 minutes of deposition of plasma-polymerized thiophene on CTA films, respectively. It is seen from the Fig. 10 that there is a slight reduction in flux for both 2 and 5 minutes of deposited films as compared to unmodified CTA membrane. This increase in selectivity and slight reduction in flux can be explained as due to filling up of pinholes in the initial stages of the deposition. Therefore the inherent property of CTA as a water-selective membrane increases. The selectivity is also enhanced because of crosslinking within the CTA film on exposure to plasma. Another reason for increasing selectivity could be the presence of sulfur in plasma-polymerized thiophene and incor-



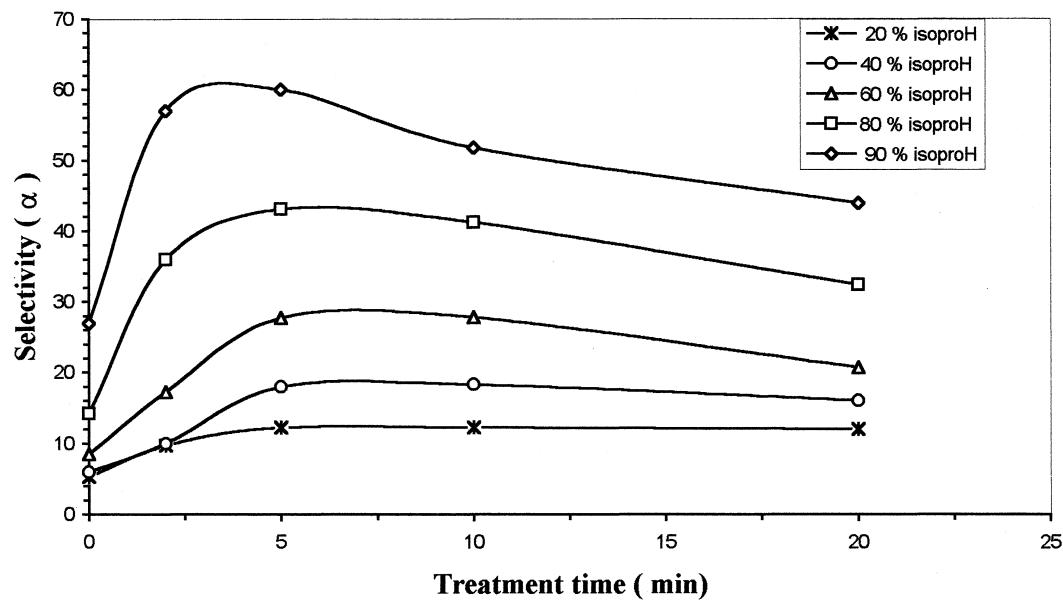


FIG. 9 Selectivity versus deposition time for various concentrations of isopropanol in the feed.

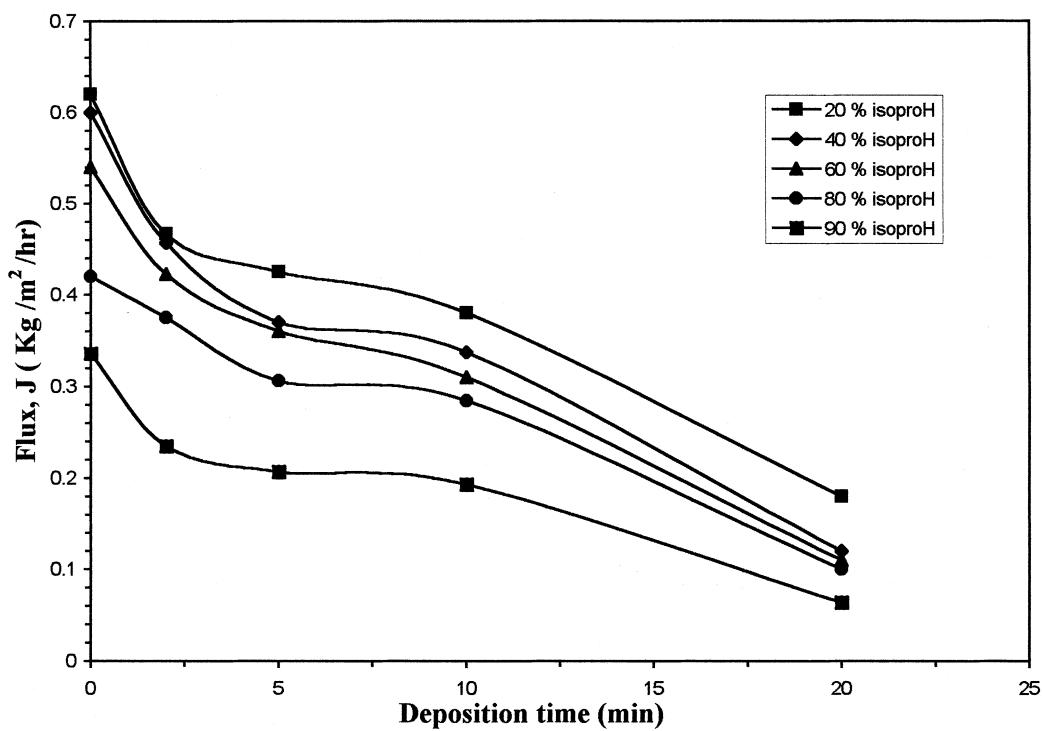


FIG. 10 Flux versus deposition time for various concentrations of isopropanol in the feed.



poration of nitrogen moieties during polymerization, which will have strong interactions with water molecules. All these factors contribute more or less for selectivity improvement. More study is required to find out exactly which factor plays a dominant role in improving selectivity.

For 10 and 20 minutes of deposition time, CTA films are seen to be totally covered by plasma polymer. This is further evidenced from SEM micrographs. The selectivity of these films was much higher than that of the control CTA film but slightly less than that of 2 and 5 minute deposited films. These results can be interpreted on the basis of a pore flow model which shows that if the liquid penetration depth in the membrane is reduced, the selectivity can be increased. Due to coverage of CTA films by plasma polymer which is highly crosslinked and pinhole-free, penetration by the liquid phase may be considerably reduced in the top PPT layer so that vapor permeation alone is occurring in the CTA film. The presence of sulfur and nitrogen might increase selectivity. The permeation rate was decreased significantly by deposition of a PPT layer.

CONCLUSION

Plasma-polymerized thiophene (PPT) deposited on CTA films showed that deposited side became hydrophobic due to a highly crosslinked layer of plasma polymer. The growth morphology was in terms of globules, the minimum size of which was 0.3 μm . Longer times of deposition resulted in these globules fusing into a fibril-like structure. The water vapor transmission rates of modified CTA films were drastically decreased. The modified CTA films showed an increasing trend of selectivity for the initial deposition time which then decreased slightly. However, the flux continuously decreased.

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