

Preparation of Composite Reverse Osmosis Membranes by Plasma Polymerization of Organic Compounds. IV. Influence of Plasma-Polymer (Substrate) Interaction

H. YASUDA, H. C. MARSH, *Camille Dreyfus Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709*, and E. S. BRANDT, and C. N. REILLEY, *Chemistry Department, University of North Carolina, Chapel Hill, North Carolina*

Synopsis

Preparation of composite membranes by plasma polymerization is affected not only by the type of monomer and the mode of discharge but also by the interaction of plasma-polymer substrate. Consequently, the reverse osmosis characteristics of composite membranes are dependent on the combination of substrate and monomer(s). The interactions of plasma and polymer are investigated using porous polysulfone film and cellulose nitrate-cellulose acetate (CNCA) porous film as the substrates, and acetylene/H₂O/N₂ and acetylene/H₂O/CO as the monomer systems. The effects of plasma pretreatment of the substrates on the chlorine resistance of the membranes are also investigated.

INTRODUCTION

In the first paper of this series of studies,¹ it is pointed out that physical and chemical natures of the substrate on which plasma polymer is deposited have significant influence on the preparation of the composite membranes. However, the main emphasis in the subsequent parts (i.e., parts II and III) of this series is placed on the polymerization of various monomers in the efforts to find monomers which yield good reverse osmosis characteristics.

In recent studies with acetylene/H₂O/N₂ and acetylene/H₂O/CO as monomer systems and porous polysulfone film and porous film of cellulose nitrate-cellulose acetate (CNCA) as the substrates, sufficient data have been accumulated to review the influence of some factors which are dependent on the combination of monomer or plasma and substrate materials. Although they may not be conclusive, they seem to be valuable for better understanding of rather complicated phenomena involved in the process of preparing composite membranes by plasma polymerization. Therefore, some results and tentative interpretations are presented in this paper.

EXPERIMENTAL

The equipment and method used are identical to those reported previously.^{2,3} The plasma pretreatment of the substrate is carried out after the substrate is well degassed and the line pressure reaches below 0.5 $\mu\text{m Hg}$. Approximately 40 $\mu\text{m Hg}$ of gas (N_2 or Ar) pressure is maintained before plasma is initiated.

All polymerizations and plasma treatments are carried out at 30 watts (reflected power is less than 5%). The pressure change during the plasma treatment or plasma polymerization is recorded using a pressure transducer (Baratron Pressure Meter). Reverse osmosis tests are carried out with 3.5% NaCl solution at applied pressures of 1500 psi.

RESULTS AND DISCUSSION

Plasma created by glow discharge is considered to contain not only ions (i.e., the classical definition of plasma is the ionized gas) but also many other energetic species such as electrons, free radicals, excited molecules, and photons. It has been generally observed that nearly all polymers lose weight when they are exposed to plasma of Ar, He, and N_2 , indicating some decomposition of polymers under the influence of plasma. The decomposition of the polymer is considerably less if the plasma contains organic vapor(s) which deposits polymer on the substrate. However, it is found that the deposition of new polymer is not always sufficient to shield the substrate from the effect of plasma, depending on the conditions of the discharge.

A recent study of plasma polymers by electron spin resonance (ESR) spectroscopy⁴ indicates that the damaging effect of plasma is closely related to the UV emission of the plasma. The irradiation effect of UV, particularly short-wave length UV which seems to play an important role in the radiation damage by plasma, has much deeper penetration than electrons and ions in the plasma. Consequently, the UV irradiation by plasma should be considered to occur simultaneously in the process of plasma polymerization; i.e., the effect will be on the substrate polymer as well as on the polymer formed by the plasma polymerization. Therefore, the UV emission of polymer-forming plasma and the UV susceptibility of the substrate polymers play important interrelated roles in the preparation of composite reverse osmosis membranes by plasma polymerization.

Effects of Plasma on Substrate Membranes

In order to investigate the interaction of the plasma on substrate membranes, ESCA (Electron Spectroscopy for Chemical Analysis) has been employed to observe the effects of nonpolymer-forming plasma on different substrate materials, e.g., CNCA (porous film of cellulose acetate-cellulose nitrate), porous and nonporous polysulfone, and cellulose acetate. The instrument used is a Du Pont Model 650 ESCA equipped with a multichannel analyzer and data reduction system.

Figure 1 is a collection of scans taken in various binding energy regions (C 1s, O 1s, N 1s, S $2p_{1/2,3/2}$), for porous and for nonporous polysulfone. The S

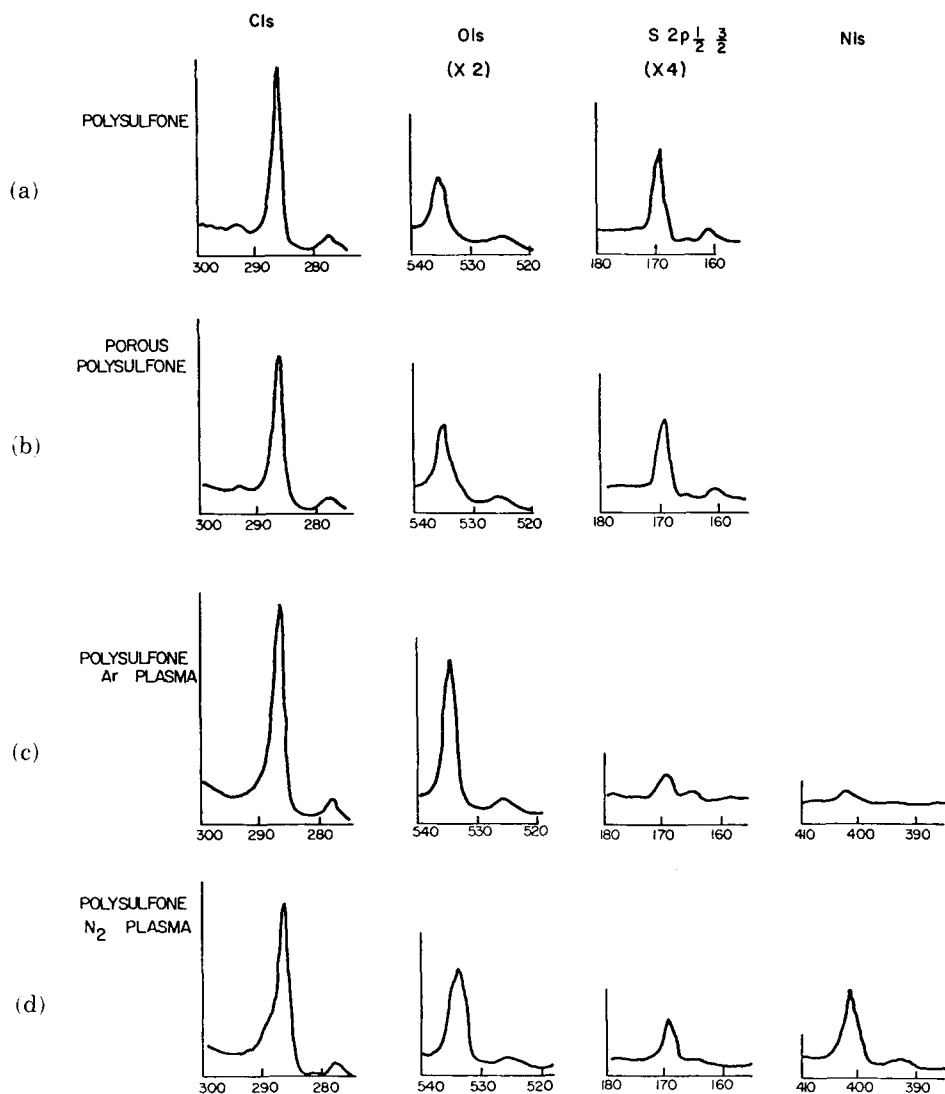


Fig. 1. ESCA spectrum of polysulfone films.

$2p_{1/2,3/2}$ is an unresolved doublet which occurs between 165 and 164 eV (B.E. for elemental sulfur). Since only comparisons are made with no attempt at this point to distinguish the precise functional groups on the basis of absolute shifts, the peaks were recorded as observed with no correction for charging effects. In any case the differences due to charging should be relatively small as all C 1s peaks fall within ± 0.2 eV of 286.2 eV.

Figure 1a is an ESCA spectrum of an untreated nonporous polysulfone film, while Figure 1b is an ESCA spectrum of a porous polysulfone. No large differences were found to exist between the two types in respect to elemental ratios or binding energy shifts. In both, as expected, no nitrogen 1s peak is observed. The O 1s regions of both porous and nonporous polysulfones are of composite character, indicating at least two kinds of oxygen functionality.

This is expected in terms of the substrate structure. The relative intensity differences between the O 1s peaks of the two physically dissimilar substrates may be due to surface ordering within the polymer which allows the oxygen of certain functional groups to be more surface oriented in the porous polysulfone.

Figure 1c is of nonporous polysulfone which has been treated with Ar plasma. The small peak in the N 1s region is thought to arise from contamination either within the argon introduction system or within the plasma reaction tube itself. This small peak tends to appear whenever nitrogen incorporation into a given substrate seems particularly facile when treated with N₂ plasma.

Figure 1d is of nonporous polysulfone which has been treated with N₂ plasma. A strong N 1s signal (ca. 401.5 eV) provides direct evidence of nitrogen attachment to the polysulfone surface. The smaller peak at 392.6 eV is attributable to the $K\alpha_{3,4}$ satellite from our nonmonochromatic source. The O 1s peak intensity for either plasma-treated membrane is greater than that for the untreated sample (by ~ 2.5 in the case of argon and ~ 2 in the case of nitrogen plasma). The O 1s peak for both plasma-treated substrates has characteristics indicative of a single type of functional oxygen group. In addition the S $2p_{1/2,3/2}$ intensities are decreased upon either type of plasma treatment.

These observations indicate that the sulfone group is attacked and removed by the plasma process. The increase in the O 1s intensity can be attributed to oxygen contamination within the plasma reaction system, similar to the case outlined above for nitrogen in the Ar plasma-treated substrate. The possibility also exists that this increase is a result of reaction of atmospheric oxygen with free radicals on the substrate left over from the plasma treatment.

Figure 2 is the ESCA spectra for CNCA and CA substrates. Figure 2a clearly shows the N 1s signal arising from the nitrate group (ca. 409.8 eV). The treatment of CNCA with nitrogen plasma shows two features in the N 1s region (Fig. 2b): first, a new peak arising at 402.5 eV which is attributable to the same form of nitrogen being incorporated into the substrate surface from the plasma treatment; and second, a large decrease of N 1s peak intensity at 409.8 eV relative to that found in the untreated substrate material.

A similar result is obtained with Ar plasma. The new peak at 402.5 eV is much too large for the $K\alpha_{3,4}$ satellite peak and occurs at approximately the same binding energy as that observed for the nitrogen incorporated in the polysulfone substrate. If corrections are made to account for charging effects, the binding energy for this peak occurs within the regions normally associated with nitrile (~ 398 – 399 eV), amide (~ 398 – 399.5 eV), or amine (~ 399 – 402 eV) type nitrogen, which are chemically reasonable groups to associate with the random free-radical-type reaction environment of the plasma treatment. Examination of the C 1s region also reveals changes associated with surface structural modification by the plasma. In the untreated substrate, peaks at 286.8 eV and at 284.5 eV are evident. Both N₂ and Ar plasma-treated substrates show a major peak at ~ 288.3 eV, with evidence for two unresolved shoulders at ~ 291 eV and 286 eV.

The implication is that not only does nitrogen not attach to the surface, but apparently the existing nitrate-type nitrogen is removed. Therefore, we

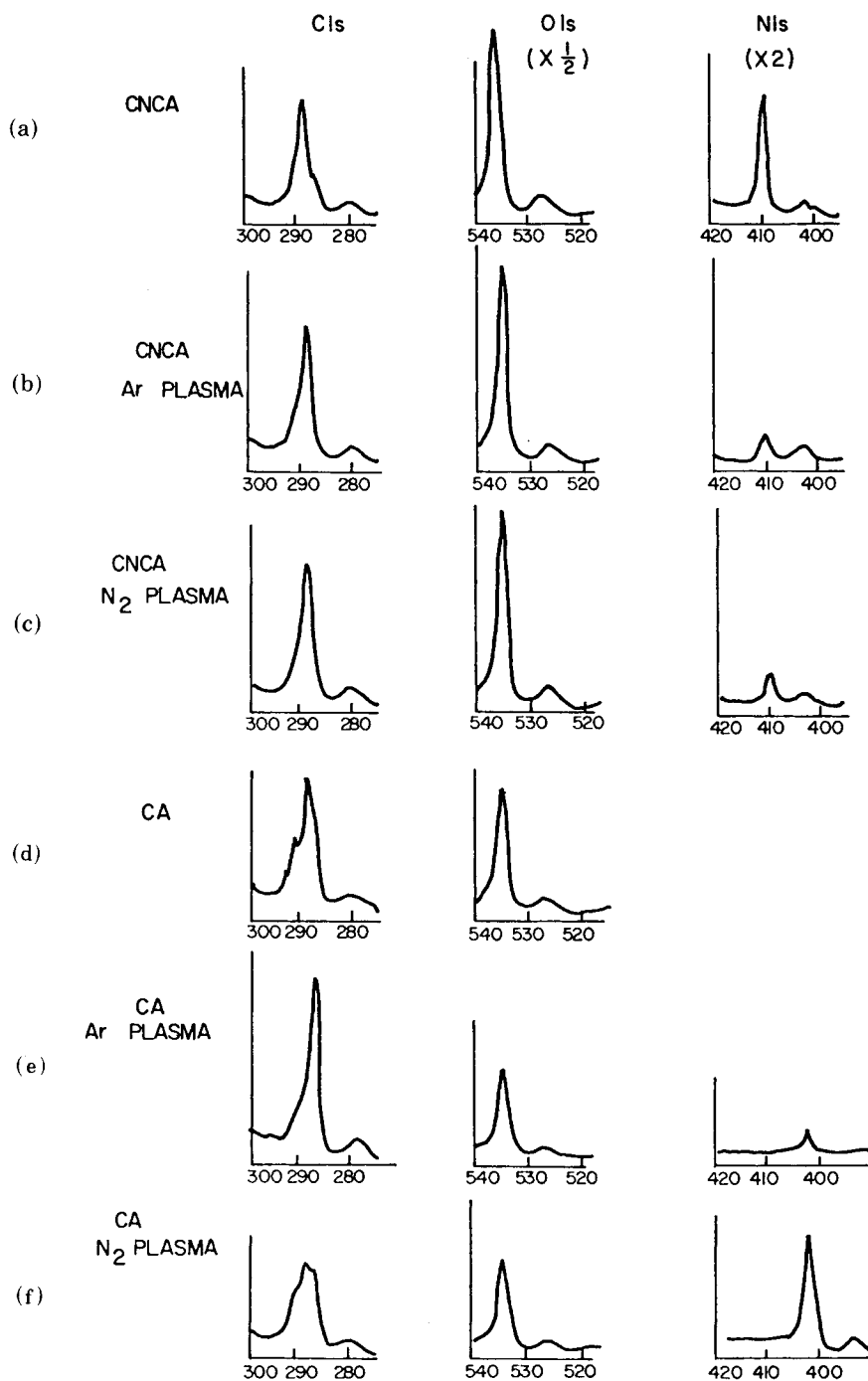


Fig. 2. ESCA spectrum of porous film of cellulose nitrate-cellulose acetate (CNCA) and cellulose acetate film (CA).

conclude that cellulose acetate-cellulose nitrate is susceptible to plasma degradation. However, an interesting contradiction is observed in the corresponding ESCA spectra of cellulose acetate (Figs. 2d, 2e, 2f). Argon plasma, as mentioned above, results in a very weak N 1s signal. Nitrogen plasma, however, produces a strong N 1s signal, again indicative of nitrogen attachment to the cellulose acetate surface. An immediate conclusion is that the susceptibility of the CNCA to the degradative effects of the plasma treatment is more or less specific to the nitrate groups. This being the case, one would suspect that the cellulose acetate portion of the CNCA should have attached nitrogen groups and show a fairly strong N 1s signal. As evidenced in Figure 2c, this is not the case.

It is possible that the cellulose acetate portion of the CNCA film is selectively excluded from the top (small pore) surface of the asymmetric membrane during casting, since certain casting conditions may not result in a completely homogeneous physical structure. Obviously, the carbon-nitrate bond is particularly susceptible to rupture in the high-energy plasma conditions and the $-\text{NO}_3$ group itself when split off does not tend to reform a surface species under these conditions. However, this does not explain why the oxygen intensities of all three samples are approximately the same. The oxygen could be picked up from a postplasma reaction with atmospheric oxygen, thus replacing that "lost" with the nitrate group. A difference is observed in the O 1s binding energy between the untreated substrate (536.2 eV) and the Ar and N_2 plasma-treated substrates (535.5 eV), indicating a change in the oxygen functionality on the surface. Since the binding energy shifts of oxygen in various functional groups are not large (ca. 1–3 eV), we cannot at this time specify the structure of this oxygen group.

The measurements of pressure of a flow system in which a sheet of substrate membrane is exposed to plasma also show the same phenomena; i.e., (1) incorporation of N onto the polysulfone surface by N_2 plasma; (2) a relatively small change by Ar plasma; and (3) considerable degradation of CNCA by both N_2 and Ar plasma. The pressure changes observed with these substrates are shown in Figures 3 and 4 for porous polysulfone and CNCA substrate, respectively.

The characteristic difference in plasma susceptibility of these two substrates is also seen in the pressure changes observed during the plasma polymerization of acetylene/ $\text{N}_2/\text{H}_2\text{O}$ system as shown in Figure 5. With a porous polysulfone substrate, which is quite stable in plasma, considerable pressure decrease is observed; whereas, with CNCA, a marked increase of pressure is observed in the polymerization of the same monomer system. In both cases, however, there seem to be indications of simultaneous processes of the pressure decrease due to the plasma polymerization of monomers, and of the pressure increase due to the decomposition of the substrates. In the case of porous polysulfone, the quick decrease of pressure due to polymerization is counterbalanced by degradation of the substrate which results in the gradual creeping-up of the pressure. In the case of CNCA, the quick increase of pressure due to degradation of the substrate is followed by gradual but appreciable decrease of the pressure due to the plasma polymerization. When the polymerization of the same monomer system is carried out in a glass tube in absence of the substrate, the pressure decreases to a new steady-state value and no minimum or maximum is observed.³ This indicates that even in the case

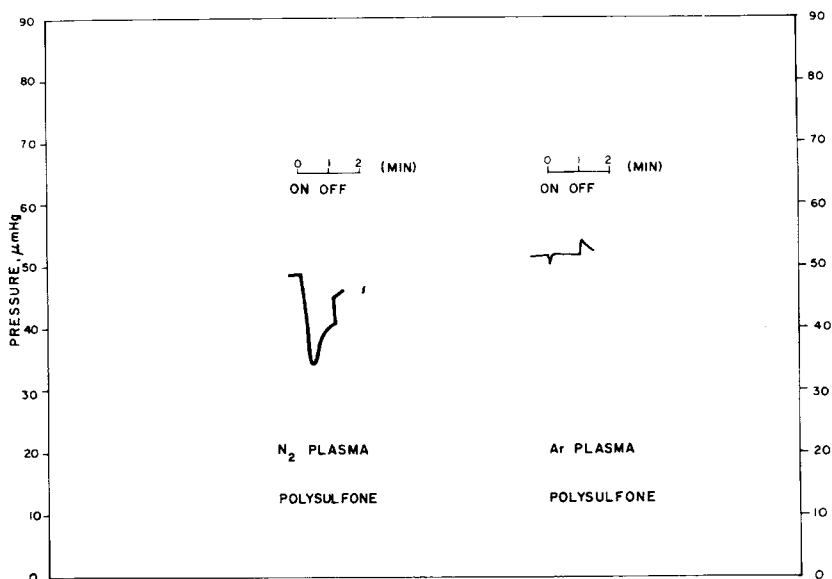


Fig. 3. Pressure changes observed with porous polysulfone substrate exposed to plasma.

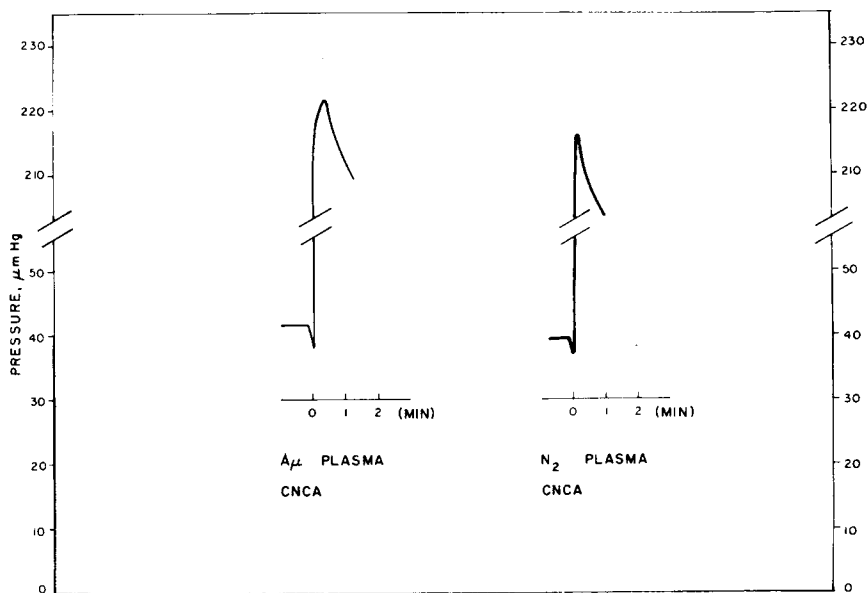


Fig. 4. Pressure changes observed with CNCA substrate exposed to plasma.

of porous polysulfone, the polymer substrate interacts with the polymer-forming plasma and is not completely inert to the plasma.

These observations indicate that there is interaction of plasma and substrate polymer, and also that the extent is dependent on the chemical nature of the substrate polymers. However, they do not tell how the interaction will affect the properties of the composite membranes formed by plasma polymerization. Some insight in this question can be gained by the following experiments.

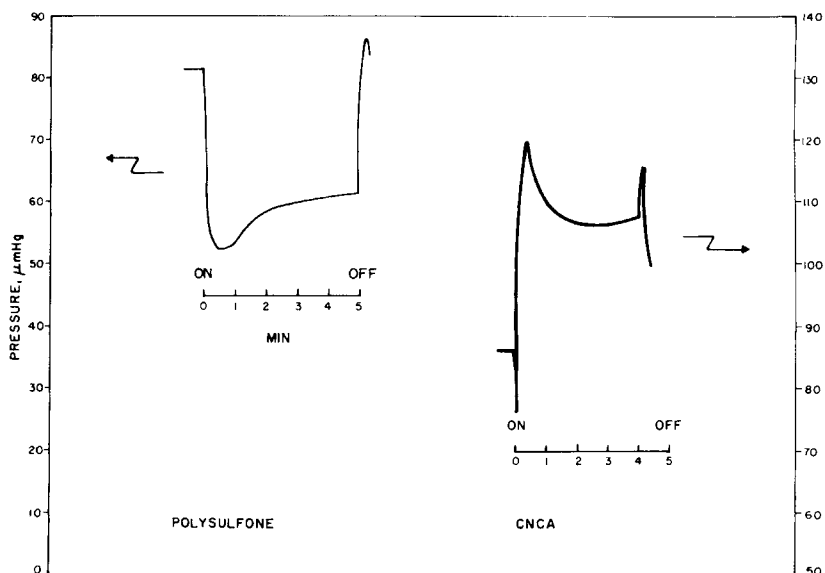


Fig. 5. Pressure change observed during the polymerization of acetylene/ N_2 / H_2O with substrate.

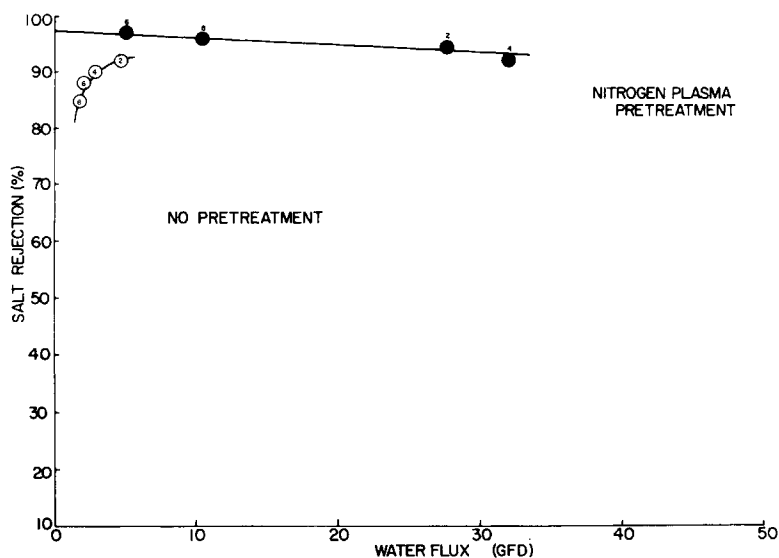


Fig. 6. Effect of nitrogen plasma pretreatment of porous polysulfone substrate on the reverse osmosis characteristics of composite membranes of plasma polymer of acetylene/water/nitrogen. Numbers indicate the deposition time in minutes.

Effect of Plasma Pretreatment of the Substrates on Reverse Osmosis Characteristics

Acetylene/nitrogen/water (40/28/13; μm Hg) glow discharge polymers are deposited, during various deposition times, onto both porous polysulfone and CNCA porous substrates. Another group of membranes are prepared by first

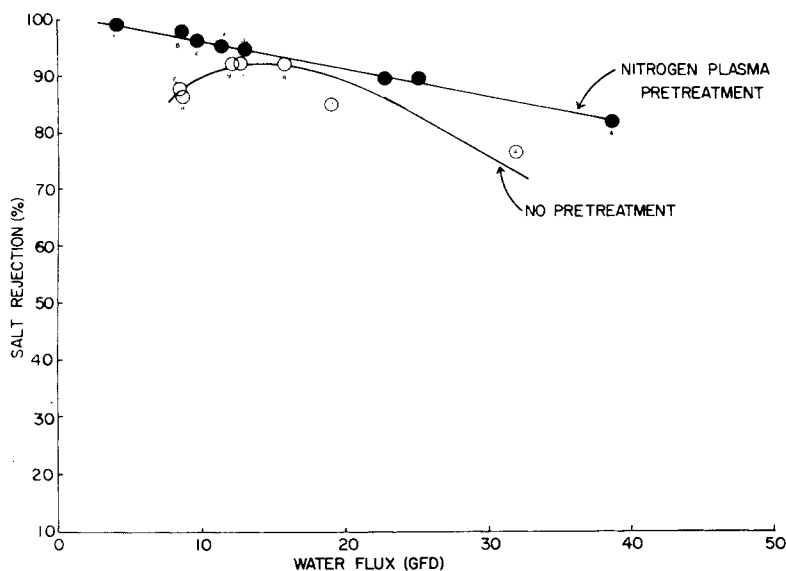


Fig. 7. Effect of nitrogen plasma pretreatment of CNCA porous substrate on the reverse osmosis characteristics of composite membranes of plasma polymer of acetylene/water/nitrogen. Numbers indicate the deposition time in minutes.

treating the substrates with nitrogen plasma (40–50 $\mu\text{m Hg}$, 30 watts, 1 min) and then depositing the same polymer as before. Figures 6 and 7 show the effect of nitrogen plasma treatment of porous polysulfone and CNCA substrate, respectively, on the reverse osmosis characteristics of the composite membranes.

As it is clearly seen in Figure 6, the nitrogen plasma pretreatment of porous polysulfone substrate results in higher salt rejections at much higher water flux at the same deposition time. With membranes prepared from a CNCA substrate, the effect of N_2 plasma pretreatment is much less pronounced.

The polysulfone groups without nitrogen plasma pretreatment produce consistently low water fluxes (less than 5 gfd), while the CNCA counterparts produce water fluxes over a range similar to the nitrogen plasma-pretreated group (5–40 gfd). The difference is clearly reflecting the results of ESCA spectra which indicate that the nitrogen plasma affects the substrates in a different manner.

Further insight into the role of nitrogen pretreatment of porous polysulfone substrate is found in the studies of chlorine resistance of the composite membranes. Results are shown in Table I, which reveal the following trends:

1. Although the nitrogen plasma pretreatment of porous polysulfone substrate increases the reverse osmosis characteristics of composite membrane (of acetylene/ $\text{N}_2/\text{H}_2\text{O}$), the nitrogen plasma pretreatment renders the membrane much more susceptible to the deteriorating effects of chlorine.

2. Pretreatment with argon plasma produces membranes which react to chlorine in a manner more similar to unpretreated substrate than to the pretreatment with nitrogen plasma.

The severity of the chlorine treatment should be noted. In practice, reverse osmosis membranes encounter chlorine concentrations on the order of

parts per million. The tests described here, however, subjected membranes to concentrations around $\frac{1}{2}$ of 1% chlorine for $\frac{1}{2}$ -hr duration (except where noted). The higher concentrations were chosen to accentuate the effects, while the extended exposure times of actual working membranes were kept in mind.

The same tests were run on NS1 membranes (North Star Research Institute) obtained from the Gulf Environmental System. Because of the high water flux, two separate samples were tested to check the possibility of inadvertent leaks or pinholes. The results have been included as a point of reference as to the relative effects of chlorine.

NS1 membrane is essentially a crosslinked (with nitrogen-containing crosslinker) membrane of polyethylenimine, which shows an excellent reverse osmosis characteristic with feed solutions which contain no chlorine. Many reverse osmosis membranes which are made of nitrogen-containing polymers (including NS1 membrane) seem to deteriorate their reverse osmosis characteristics severely by the action of a very small amount of chlorine in the feed solution. Although membranes used in this study contain nitrogen, plasma-polymer membranes seem to be much less labile to the action of chlorine.

After chlorine treatment, reverse osmosis membranes lacking nitrogen plasma pretreatment appeared somewhat lighter in color, although they are otherwise unchanged. More drastic changes in physical appearance were observed for the nitrogen plasma-pretreated membrane. The deposited polymer coat appeared to slough off in large pieces, suggesting that bonding between the substrate and deposited polymer was preferentially attacked by the chlorine.

Scanning electron micrographs corroborate these observations. Figure 8 shows the surface of membrane prepared without N_2 plasma pretreatment of the substrate after chlorine action. (The horizontal parallel lines are believed to be due to low-temperature cracking, since fracture surfaces were initially desired.) Figure 9 shows the nitrogen plasma-pretreated membrane surface after chlorine action. Two distinct and separate layers are quickly

TABLE I
Effect of Plasma Pretreatment of Substrate on the Chlorine Resistance of Composite Membranes Prepared by Plasma Polymerization of Acetylene/ H_2O/N_2 with Porous Polysulfone Film as the Substrate

Plasma pretreatment time, min	$C_2H_2/H_2O/N_2$ plasma time, min	Membrane treatment	Salt rejection, %	Water flux, gfd
0	5	None	94.8	1.2
0	5	50 ppm NaOCl	93.7	7.3
0	5	0.5% NaOCl	86.4	10.2
1, Ar	5	None	95.3	7.0
1, Ar	5	0.5% NaOCl	80.3	6.2
1, N_2	5	None	92.1	19.1
1, N_2	5	0.5% NaOCl	13.9	163.0
(North Star, NS-1)		None	99.1	26.1
(North Star, NS-1)		0.5% NaOCl	2.9	400.0
		0.5% NaOCl	2.9	418.0

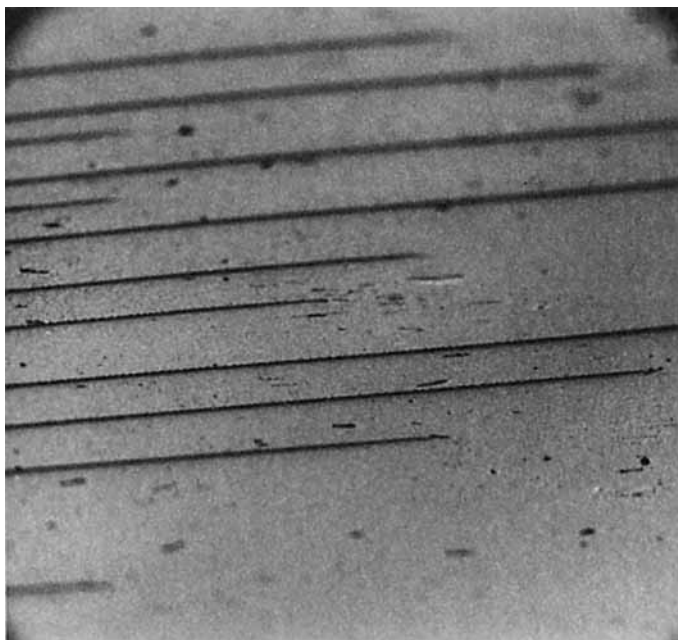


Fig. 8. Effects of chlorine—no pretreatment with nitrogen plasma.

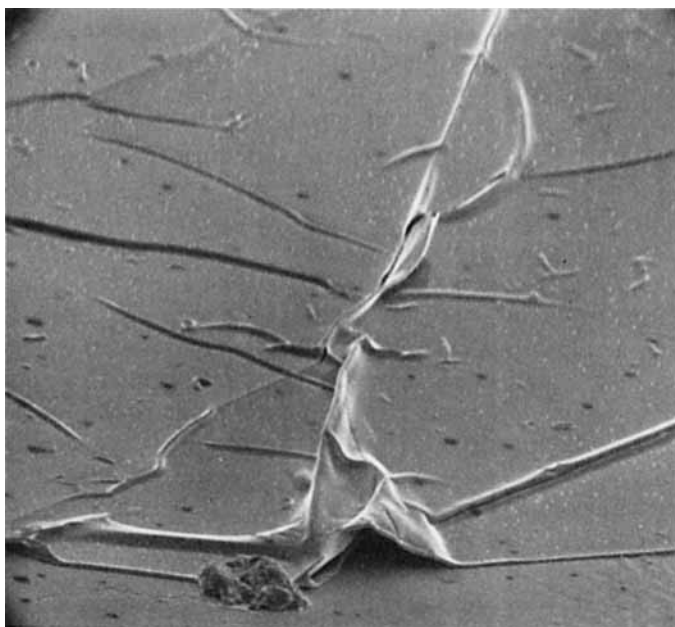


Fig. 9. Effects of chlorine—pretreatment with nitrogen plasma.

discernible, and the wrinkled nature of the upper layer indicates a lack of strong, uniform bonding between the layers.

Evidence indicates that bonding between the substrate and the deposited polymer was preferentially attacked by chlorine. This suggests an interme-

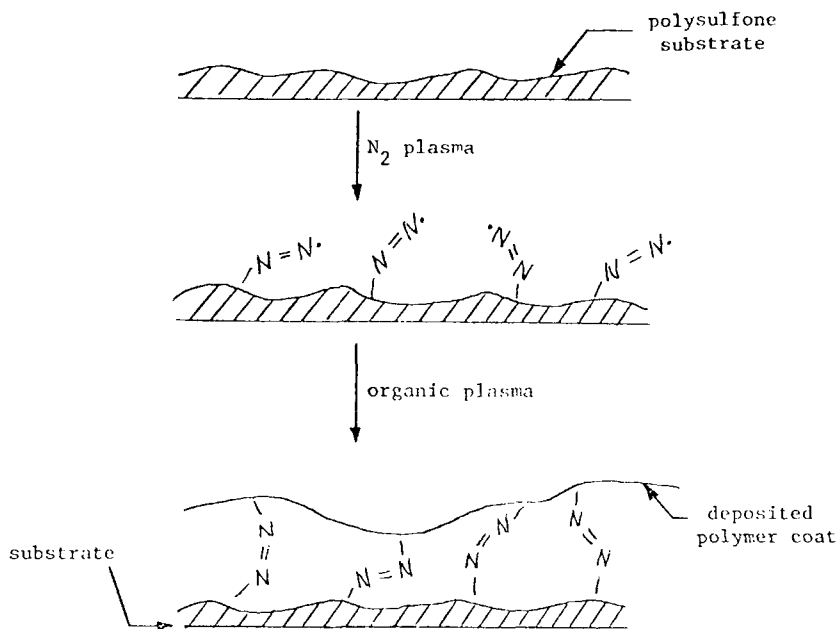


Fig. 10. Representative scheme for N_2 and organic plasmas.

diate layer of some form of nitrogen incorporated as a result of pretreatment with nitrogen plasma.

Since, in these studies, the deposited polymer layer also contained nitrogen, it, too, was susceptible to chlorine attack. The results of such attack, however, are much less severe. The effects of chlorine are less pronounced because (1) the chlorine-labile nitrogen-containing functions have a lower density when incorporated with the organic monomer, and (2) the polymer is highly branched so that cleavage at nitrogen functions liberates only small segments of the polymer chains.

The effects of nitrogen plasma pretreatment are quite dramatic. Nitrogen plasma can no longer be considered a cleaning or preparatory process but rather a step significantly affecting the chemical, and possibly structural, nature of the substrate. Although evidence is still not conclusive, a representative scheme for nitrogen plasma pretreatment may be proposed (see Fig. 10). In Figure 10, the chemically weak nitrogen-containing layer is schematically represented by $-N=N\cdot$ and $-N=N-$; however, no evidence of such chemical bond has been confirmed.

It seems that the aspects of cleaning of the surface by plasma pretreatment and of the formation of free radicals on the surface, which might improve bonding between the substrate and the deposited layer, have relatively small effects on the properties of the composite membranes, as evidenced by the effect of nonreacting argon plasma pretreatment. The question of why those effects are relatively small may be answered by the fact that some polymer-forming plasmas produce so many free radicals on the substrate⁴ that the additional effort to form free radicals on the surface becomes less important. Another factor to be considered is that the major portion of free radicals are formed by UV radiation emitted by the plasma. Consequently, the popula-

tion of free radicals created by the pretreatment is not concentrated on the surface, and thus only small portions of them can be utilized for the better bonding.

CONCLUSIONS

It may be concluded that the interaction of plasma and the substrate polymer plays an important role in determining the reverse osmosis characteristics of the composite membranes. Nitrogen plasma is highly reactive with many organic polymers, and the pretreatment of the substrate with N_2 plasma can be utilized to improve the membranes which are intended to be used in certain applications where the action of chlorine is absent.

The importance of the interaction may be more dramatically seen in a certain combination of the substrate and the polymer-forming plasma. For instance, plasmas of acetylene/ CO/H_2O yields good reverse osmosis membranes when they are deposited onto CNCA substrate; however, the application of similar conditions onto a porous polysulfone substrate fails to yield similar results. In view of the fact that the plasma of acetylene/ N_2/H_2O produces equivalent membranes with both CNCA and porous polysulfone substrates, the difference may be best attributed to the different interaction of plasma and the substrate. As is clear from this example, the importance of the interaction is dependent on the combination of plasma and substrate, and also on other factors of glow discharge. Nevertheless, this is an important factor which must be taken into consideration for the proper application of plasma polymerization.

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