Preparation of CHF$_3$ Plasma Polymeric Composite Membrane and Characteristics of Surface Modification

Kyung-soo Kim, Bup-Ju Jeon and Il-hyun Jung[†]

Dept. of Chem. Eng., Dankook Univ., San 8, Hannam-dong, Yongsan-gu, Seoul 140-714, Korea
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Abstract–Low temperature rf-plasma was used to create a plasma-treated polymeric composite membrane made from CHF$_3$, a material that is very thermally and chemically stable. The chemical and physical properties of the CHF$_3$ plasma polymers were variously changed by plasma treatment on membrane surface. CHF$_3$ plasma polymers were efficiently deposited on an aluminum oxide substrate with a pore size of 0.02 μm at the plasma polymerization time 60 min, the rf-power 160 W, and the flow rate of the CHF$_3$ 16 sccm. It was found that O$_2$ plasma treatment had a much greater effect on the surface roughness of the CHF$_3$ plasma polymers than did Ar or N$_2$ plasma treatment. The attachment of functional groups to the CHF$_3$ plasma polymer surface as a result of plasma treatment increased the intensity of the oxygen functional group peak. It also increased the oxygen content and the O/C ratio. The plasma treatment also made to the surface that became to hydrophilic. The most effective hydrophilic surface modification occurred when the composite parameter ranged from 300-450 kJ·s/kg. It was confirmed that the gas permeability and selectivity changed as a result of crosslinking, chemical etching, and the importing of functional groups to the CHF$_3$ plasma polymeric membrane.

Key words: CHF$_3$ Plasma Polymer, Hydrophobic Film, Selectivity

INTRODUCTION

Plasma polymers are usually coated on the substrate surface in the form of a thin film having high crosslinkage and a fine structure. The crosslinking is not the simple molecular crosslinking generally found in polymers. Rather, it is crosslinking on an atomic level, which results in high chemical stability, heat resistance, and mechanical strength. Based on these characteristics, the polymers may have crystal structures similar to those of diamond or graphite. They adhere easily to substrates, cut off moisture and gas, and have surface passivation. As a result, they are currently receiving a great deal of attention for their uses in various metal materials, protective coatings of optical equipment, and insulated membranes [Wang and Chen, 1988].

Most polymeric materials tend to have poor adhesive properties when inked, painted, or bonded to another material using an adhesive. For paint or ink to adhere properly, the surface energy of the material must be high. Also, there must be the presence of functional groups that can create strong bonds such as chemical bonds with the solids in the paint or ink, hydrogen bonds, polar bonds, and acid-base interaction. However, most polymeric materials have rather low surface energy and tend not to react [Golander et al., 1993; Sakata and Yamamoto, 1988]. Plasma treatment can be used in hydrophilic surface modification that increases adhesion without changing the properties of the original material [Marchant et al., 1988]. Also, plasma polymerization can be used to selectively implement certain functional groups [Cho et al., 1990]. The increasing permeability of a separation membrane without decreasing its selectivity in microfiltration and ultrafil-tration is by increasing the membrane's solubility or wettability towards the substance. Permeability can be increased through modification by using plasma to create a hydrophilic surface. However, the study of surface modification using plasma has been limited to certain general polymeric materials [Golander et al., 1993; Sakata and Yamamoto, 1988].

With this in mind, research was conducted using polymeric materials having better physical properties than those used in the past. To observe the effects that surface modification had when it was applied to the polymers, CHF$_3$ was used as a monomer because of its excellent chemical stability even when it is polymerized. A CHF$_3$ plasma polymeric membrane was created using a rf-plasma reactor, and then the membrane's surface was modified. Physical and chemical properties such as surface morphology, bond structure, and atomic composition were examined in order to analyze the changes in surface wettability and gas permeability. This allowed us to reach conclusions about the potential industrial uses for modified plasma polymeric membranes.

EXPERIMENT

The rf-plasma reactor used in this experiment had a frequency of 13.56 MHz, and a maximum electrical output of 600 W. The reactor was a stainless steel one of the bell-jar type and it used a rotary pump to create a pressure of up to 10 mTorr. Its diameter was 29 cm and it stood 24 cm high. It was designed to keep the levels of reflective waves to under 5%, thus preventing reproducibility problems. A convection vacuum gauge was used to measure the pressure inside the plasma reactor and the gas flow was adjusted with a mass flow controller (MFC, Hitachi Co.).

The substrate used in the plasma polymerization was the widely used aluminum oxide membrane filter (pore diameter 0.02 μm,

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diameter 47 mm, Whatman Co.). The experiment was divided into two parts. The first part was concerned with plasma polymerization and the second part dealt with gas permeation. In the plasma polymerization experiment, the pressure of the reactor was lowered to 30 mTorr by using a rotary pump, and then the remaining gases and moisture were removed by using argon gas for about 5 min. Then, the monomer CHF_3 was injected through a ring near the plate and plasma was generated in the reactor at a pressure of 90 mTorr. CHF_3 plasma polymeric composite membranes were created at polymerization time 60 min, rf-power 120 W, flow rate of monomer 16 sccm. The surface treatment by using Ar, N_2, O_2 was progressed in rf-power 40-200 W, treatment time 2-30 min, gas flow rate 5-15 sccm, system pressure 70-150 mTorr.

The experimental wettability for the characteristics of the surface modification was executed by static contact angle meter, and the contact angle was calculated by average of value to be measured over 5th. The functional groups on surface and composition after plasma treatment were confirmed by FT-IR ATR (Attenuated Total Reflection, Shimadzu, 8501) using KRS-5 prism and XPS (x-ray photoelectron spectra EG Sci., EscaLab 220-IXL) analysis by AlKα. The relation between morphology and contact angle for variables of plasma was analyzed by AFM (atomic force microscopy, Dong-il Co., DAFM-6300) contact mode and SEM (scanning electron microscopy, Jeol, JSM-5800).

Gas was passed through a permeant section that maintained normal pressure. The variable volume method, which involves measuring the permeated gas by means of a flow meter that was set up on the permeant section, was used to measure the results. The permeated gases, pure oxygen and nitrogen, were sent from the gas cylinder using a pressure controller. The pressure was then fixed to a constant value by using a pressure gauge. Gas that entered from high-pressure regions passed through the membrane of the permeant cell and came out though the permeant section which maintained normal pressure. The amount of permeated gas was measured with a bubble flow meter.

A water bath was used to maintain a constant temperature within the cell, and permeability was calculated according to the following formula.

$$P/l = \frac{1}{p_2 - p_1} \times \left[\frac{q/t}{A} \right]$$

In the formula, P/l is the gas permeability, q/t is the flow rate of the permeated gas, l is the membrane thickness (cm), p_1 and p_2 are the pressures applied to the top and bottom of the permeant cell, respectively, and A is the actual permeant surface area which is represented by the effective membrane area. Selectivity was calculated by using the ideal separation factor (P_{O_2}/P_{N_2}), which is a ratio of the permeability coefficients of the two gases. The permeant experiment was conducted at room temperature, and measurement of the permeated gases was done after a sufficient amount of time had passed in order to get more accurate results. The permeant cell consisted of an inlet plate and an outlet plate, and a porous supporter was installed to prevent damage to the lower portion of the cell.

RESULTS AND DISCUSSION

The reaction of plasma polymerization is the process of growth

to polymer through consecutive activation-deactivation in plasma state. In the activation step, the growth reaction of plasma polymerization becomes plasma induced polymerization by the bond of reactive species as well as by chain reaction as such radical polymerization. Also, the sputtering and chemical etching reaction of various side reactions progressing in plasma play an role in ablating a part of thin film coating polymer. The plasma polymerization react to reactive species but reactive species do not keep up molecular bone and exist as atoms or fragmented molecules (atomic polymerization).

Fig. 1 and Fig. 2 show the SEM of both the surface and the inner structure of a plasma polymeric membrane (rf-power 120 W, polymerization time 60 min, CHF_3 flow rate 16 sccm) created on an aluminum oxide substrate with a pore size of 0.02 μm. Fig. 1 (a) shows that the aluminum oxide used as a substrate had uniform pores. In Fig. 1(b), the pores of the aluminum oxide used as a supporter were completely clogged off due to efficient depositing by plasma polymerization that created a fine structure on the surface. The surface of the membrane deposited with CHF_3 plasma polymers had hemispherical structures of various sizes. This was in harmony with results of research done by Huber and others [1997]. Also, Fig. 2(a) is an SEM of the cross-section of the aluminum oxide used in the plasma polymerization. Well-organized conical and straight pores can be observed. In Fig. 2(b), we
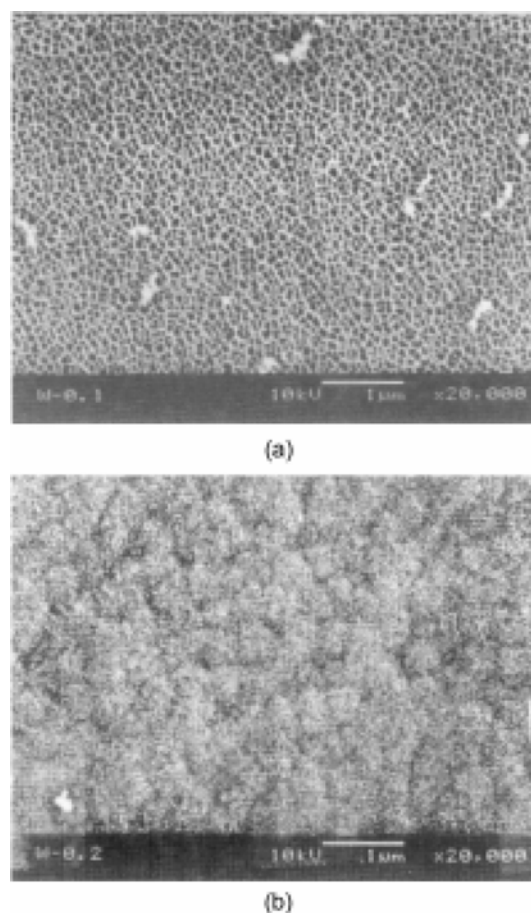

(a)

(b)

Fig. 1. SEM of the CHF_3 plasma polymer deposited on porous aluminum oxide membranes; (a) aluminum oxide surface (b) plasma polymerized surface.
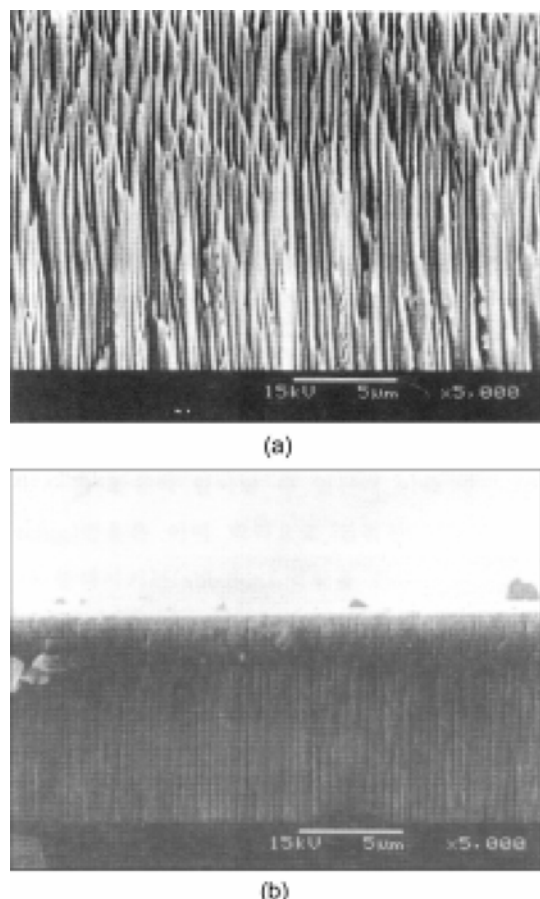
(a)

(b)

Fig. 2. SEM of the CHF₃ plasma polymer of deposited on porous aluminum oxide membranes; (a) aluminum oxide cross-section (b) plasma polymerized cross-section.

knew that the cross-section of the composite membrane formed by CHF₃ plasma polymerization was uniformly deposited on the barrier of the surface in a layer 0.9-1 μm thick.

CHF₃ plasma polymers created under set conditions (rf-power 120 W, polymerization time 60 min, flow rate 16 sccm) were treated by the plasma of Ar, O_2, N_2, etc. at an rf-power of 120 W, a treatment time of 5 min, and a gas flux of 10 sccm. In the AFM results, the untreated surface of the CHF₃ plasma polymers did not react and was simply activated when the surface of the polymer was treated by the inactive Ar plasma treated surface. The N_2 plasma treated surface directly attached functional groups to the polymeric surface. The O_2 plasma treated CHF₃ plasma polymer membrane saw an increase in the roughness of its surface.

Plasma treatment can result in a variety of reactions. Of these, sputtering and chemical etching remove or ablate polymers already coated on thin films [Yasuda, 1985]. Factors such as the gases used, the type of steam, the type and shape of the reactor, the position and temperature of the substrate, gas flux, gas pressure, and discharge output regulate this phenomenon. Therefore, the conducted research was able to show that the surface roughness changed following treatment of CHF₃ plasma polymers by plasma gas under set conditions.

Also, the R(S) value (surface roughness), which measured surface roughness through AFM analysis, was higher when treated

by O_2 (R(S)=8700) than when not treated (R(S)=1033) and when treated by other plasma gases Ar (R(S)=1477), N_2 (R(S)=3037). Generally, oxygen is considered to cause the greatest amount of surface etching. This agreed with the AFM results of the CHF₃ plasma polymeric membrane of the conducted research.

To examine the bond structure of CHF₃ plasma polymers, polymers were created under set conditions (rf-power 160 W, polymerization time 60 min, flux 16 sccm) and their FT-IR ATR absorption spectrum was analyzed. These results are shown in Fig. 4. We could confirm for the intensity of absorption band in the range of 1,150-1,250 cm^{-1} to indicate the CF_x absorption band in including CF_2 asymmetric stretching at near 1,220 cm^{-1}. Generally, polymers that were created with fluorine monomers have band broadening in the 950-1,250 cm^{-1} region and this means high crosslinking in the CF_x absorption band.

An increase in the amount of fluorine substituted by hydrogen in fluorine compounds leads to an increase in crosslinking [Doucoure et al., 1996]. Therefore, the CHF₃ plasma polymers created in this research had high crosslinking.

As the absorption band of LDPE using substrate for FT-IR ATR measurement when prepared CHF₃ plasma polymer, the 720 cm^{-1}, 1,460 cm^{-1}, and 2,600-2,800 cm^{-1} peaks were caused that FT-IR ATR measurements were done at a 45° collision angle.

Also, the peaks in the 1,690-1,750 cm^{-1} represent oxygen functional groups like those in C=O bonds. After the plasma was polymerized, high ionization energies created free radicals which caused active sites to form on the surface and bond with oxygen molecules in the atmosphere after the reaction had been completed. These bonds formed carboxyl, carbonyl, and aldehyde groups that are represented by the peaks [Marchant et al., 1988]. In plasma surface modification, the surface of the polymeric material is affected more by active sites formed after the reaction and by reacting with oxygen in the atmosphere than it is by the plasma gas in the plasma reactor [Occhiello et al., 1996].

Fig. 5 shows the FT-IR ATR absorption spectra for CHF₃ plasma polymers treated with Ar, N_2, and O_2 plasma. Plasma-treated polymers show spectra similar to those of untreated ones, but increases in carbonyl groups, carboxyl groups, and aldehyde groups led to higher absorption peaks. This is seen as being a result of the plasma treatment making the polymeric surface more active which, in turn, increased the number of free radicals that reacted with oxygen in the atmosphere. Therefore, plasma treatment caused modified characteristics by increasing the number of oxygen functional groups.

To examine the atomic composition of the CHF₃ plasma polymeric surface according to different variables in the experiment, the peak intensities of C_{1s}, N_{1s}, O_{1s}, and F_{1s} of the XPS broad scan spectrum were integrated. The results were recorded in Table 1.

The oxygen content of the surface of untreated CHF₃ plasma polymers (8.1%) increased when it was treated with O_2 (10.4%), N_2 (12.2%), and Ar (14.8%) plasma. N_2 plasma treatment led to nitrogen atoms (1.4%) being found on the surface. This was a result of the aforementioned creation of amines and other nitrogen functional groups after the reaction within the rf-plasma between N_2 plasma and the CHF₃ plasma polymeric surface.

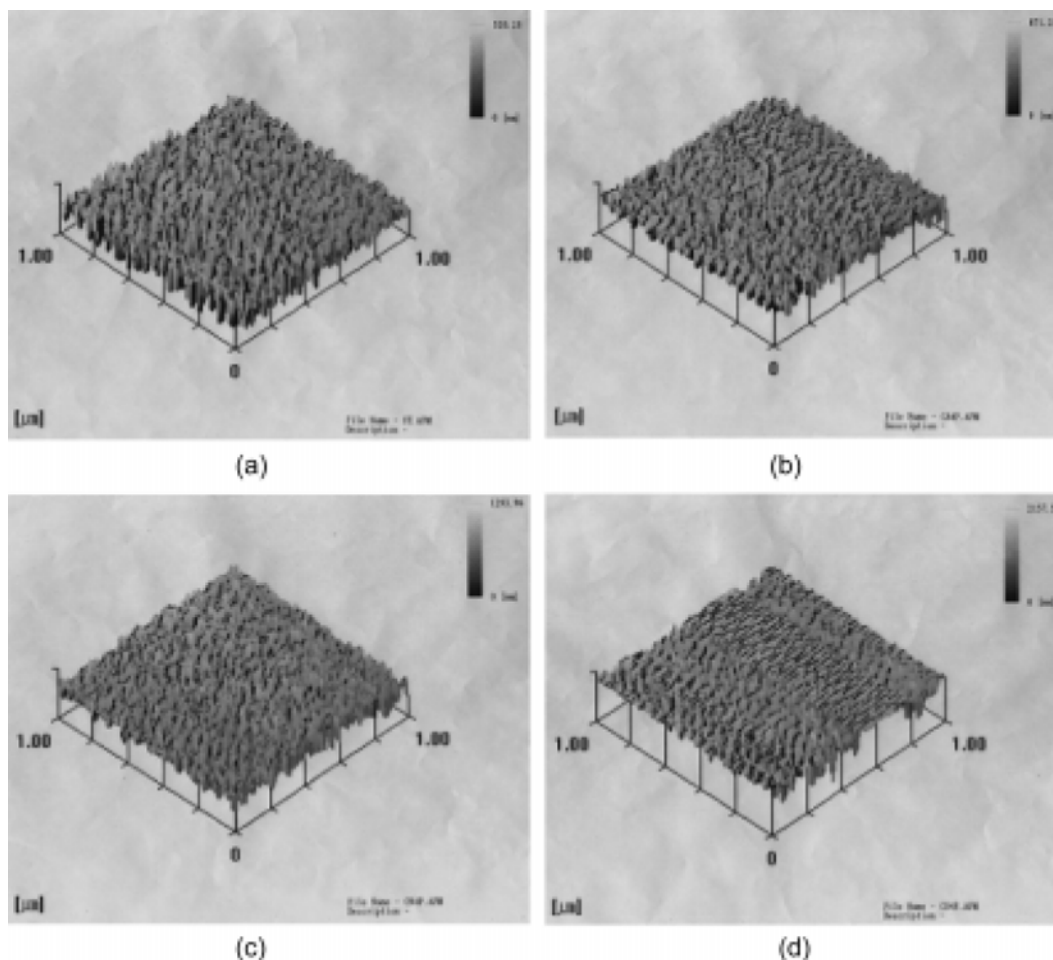Marchant and others [1988] found that the XPS atomic composition analysis of surface modification experiments conduct-

Fig. 3. AFM (scanning electron microscopy) of (a) untreatment, (b) Ar plasma, (c) N₂ plasma, and (d) O₂ plasma treatment for CHF₃ plasma polymer membrane.
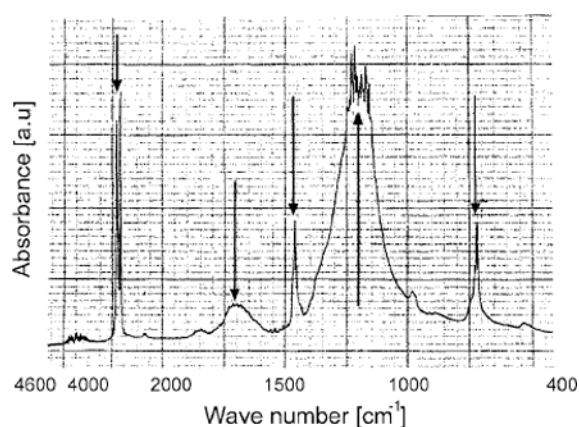

Fig. 4. Typical FT-IR ATR spectra of plasma polymerized CHF₃ on LDPE film (160 W, 60 min, 16 sccm).

Fig. 5. Typical FT-IR ATR 1,500-2,000 cm⁻¹ spectra of (a) untreatment, (b) Ar plasma, (c) N₂ plasma, and (d) O₂ plasma treatment for CHF₃ plasma polymer membrane.

ed on PP (polypropylene) film using N_2 plasma within a rf-plasma reactor showed that nitrogen atoms were found in a 7.5% ratio to the sample. They claimed that analysis of the XPS C1s spectra showed that the formed functional groups were amines. They reached this conclusion by comparing the binding energies shown in the spectra. Also, the ratio of oxygen to carbon (O/C) in the
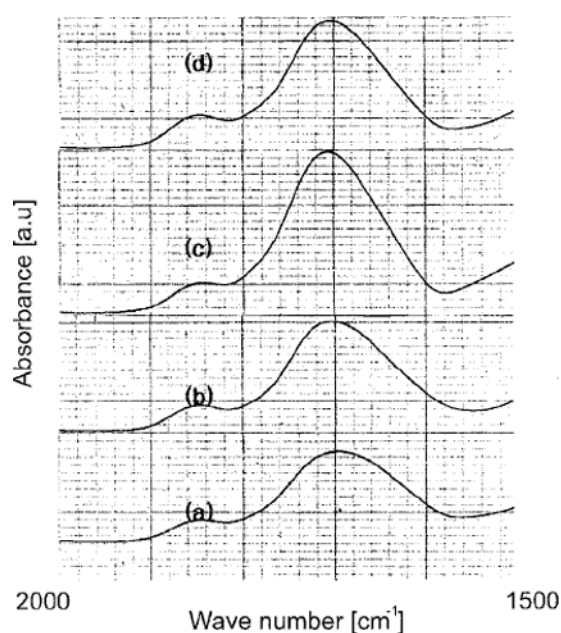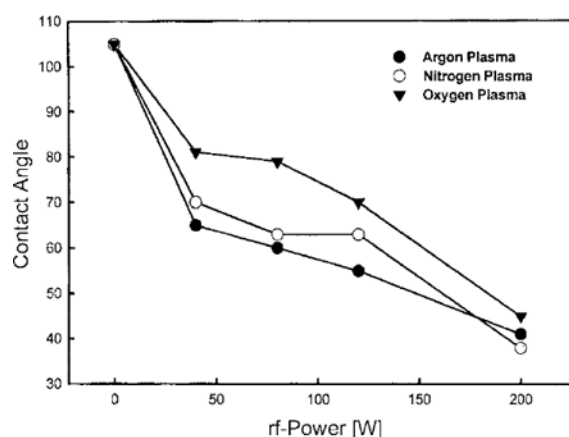
Table 1. Elemental composition of plasma polymer of CHF₃ at different plasma (120 W, 5 min, 10 sccm)

	Carbon (%)	Fluorine (%)	Oxygen (%)	Nitrogen (%)	O/C	Empirical formula
Untreatment	42.6	49.3	8.1	-	0.19	$CF_{1.16}O_{0.19}$
Ar	43.4	41.7	14.8	-	0.33	$CF_{0.96}O_{0.33}$
N₂	45.3	41.1	12.2	1.4	0.27	$CF_{0.91}O_{0.27}N_{0.03}$
O₂	39.0	50.6	10.4	-	0.28	$CF_{1.30}O_{0.28}$

Fig. 6. Dependence of rf-power for the contact angle on the CHF₃ plasma polymer (5 min, 10 sccm).

Fig. 7. Dependence of treatment time for the contact angle on the CHF₃ plasma polymer (120 W, 10 sccm).

CHF₃ plasma polymeric surface was higher in polymers treated with O₂ (0.28), N₂ (0.27), and Ar (0.33) plasma than in untreated polymers (0.19). This is seen as a result of inactive Ar plasma catalyzing bonds between the CHF₃ plasma polymeric surface and oxygen by inducing a chain reaction by simply activating the surface rather than as a result of active plasma that directly creates functional groups.

Fig. 6 shows the change in the static contact angle of distilled water when the rf-power was increased in CHF₃ plasma polymeric membranes created with gas flux 10 sccm and treatment time 5 min. The static contact angle tended to decrease as the rf-power increased, regardless of the type of plasma used. The percentage of change was largest when Ar plasma was used than when N₂ and O₂ plasma was used. It can be seen that the hydrophobic CHF₃ plasma polymers became hydrophilic as a result of surface modification using plasma treatment. The results of the different plasma gases agreed with the low-temperature plasma surface modification experiments of the fluorine compound PTFE (polytetrafluoroethylene) film conducted by Wakkida and others [1997] using O₂ and Ar plasma.
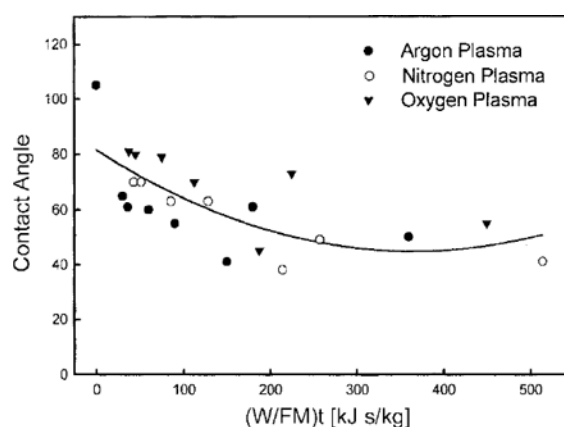
As mentioned earlier, Ar plasma is classified as an inactive plasma and unlike active plasma such as N₂ and O₂ plasma which directly create functional groups on the polymeric surface. It simply activates the surface, creates free radicals on it, or causes crosslinkage. From this, it can be said that the change in the static contact angle of the CHF₃ plasma polymers was affected more by increases in rf-power in Ar plasma caused by surface activation than by functional groups directly formed by N₂ and O₂ plasma such as carbonyl and carboxyl groups. Also, these results are in line with the XPS surface atomic structure results that concluded that

oxygen content was from lowest to highest : untreated CHF₃ plasma polymers, polymers treated with Ar, N₂, and O₂.

Fig. 7 shows the change in the static contact angle on the CHF₃ plasma polymeric surface (gas flux=10 sccm and rf-power=120 W) in relation to treatment time. When the treatment time was above ten minutes, the static contact angle of nitrogen plasma was smaller than that of Ar plasma. It is thought that two processes occur simultaneously during plasma surface modification. The first is the surface reaction and depositing that occurs when reactants inside the plasma react with the surface atoms of the sample. The second is the ablation or etching that makes volatile reaction products when oxygen atoms in the plasma react with carbon atoms in the substrate [Yasuda, 1985]. The balance between these two processes is regulated by the parameters of the experiment and they return to steady state after a time. Therefore, in this work, an increase of the treatment time caused active sites on the surface of the argon plasma-treated CHF₃ plasma polymers to become saturated, and N₂ plasma caused the decrease of the static contact angle decrease because of the continuous induction of functional groups.

Fig. 8 shows the overall percentage change of the static contact angle in relation to the composite parameter [(W/FM)t], which is the value of the total energy flux per mass unit of gas. W, F,

Fig. 8. Dependence of (W/FM)t for the contact angle on the CHF₃ plasma polymer.

M, and t represent rf-power, gas flux, molecular weight of the gas, and treatment time, respectively. When the composite parameter was increased, the static contact angle linearly declined and then increased with no regard to the type of plasma used. This shows that polymeric surface was modified when the plasma gas and CHF_3 plasma polymers reacted and consumed most of the input energy. In plasma surface modification, the surface was altered as result of a combination of reactions such as vapor decomposition, diffusion, and surface reactions. Therefore, the degree of modification relied upon the extent of these reactions. The composite parameter represented the total energy flux within the plasma. In low composite parameters, plasma surface treatment mainly results in surface reactions/depositing, while in high composite parameters desorption/etching occurs [Yasuda, 1985].

Therefore it was confirmed that in the surface modification experiment conducted, rf-plasma reactions increased the wettability of the CHF_3 plasma polymeric surface, and this caused the surface to become hydrophilic. The most effective CHF_3 plasma polymeric surface modification occurred when the composite parameter ranged from 300-450 (kJ·s/kg).

Fig. 9 shows the CHF_3 plasma polymeric membrane's (gas flux =10 sccm, treatment time=5 min) permeability and selectivity of oxygen over nitrogen in relation to increases in rf-power. There is no regular pattern. However, regardless of the plasma type the permeability of oxygen saw an overall decrease and selectivity saw a slight increase and then became constant as the rf-power increased. Generally, an increase of rf-power increased the electron energy and density within the plasma and highly active particles became even more active, which creates more active sites. This resulted in increasing the rate of surface modification.

In the experiment conducted, it was confirmed that an increase of rf-power increased the number of active sites, which
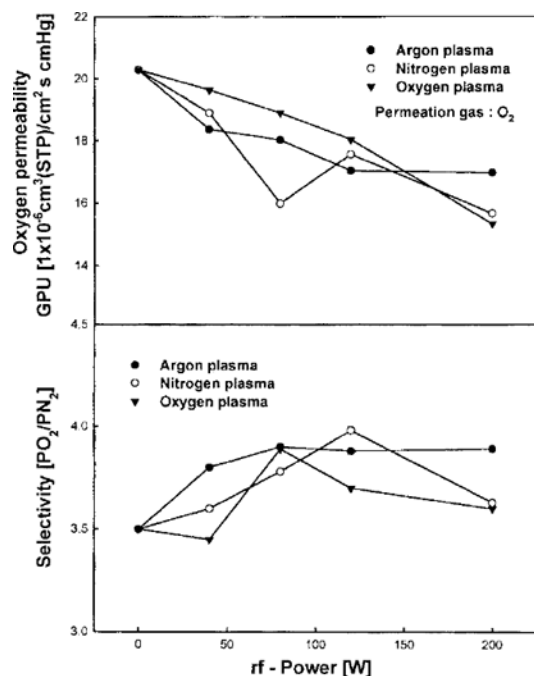

Fig. 9. Dependence of rf-power for the gas permeation of oxygen and nitrogen on composite membranes by the CHF₃ plasma polymer (5 min, 10 sccm).
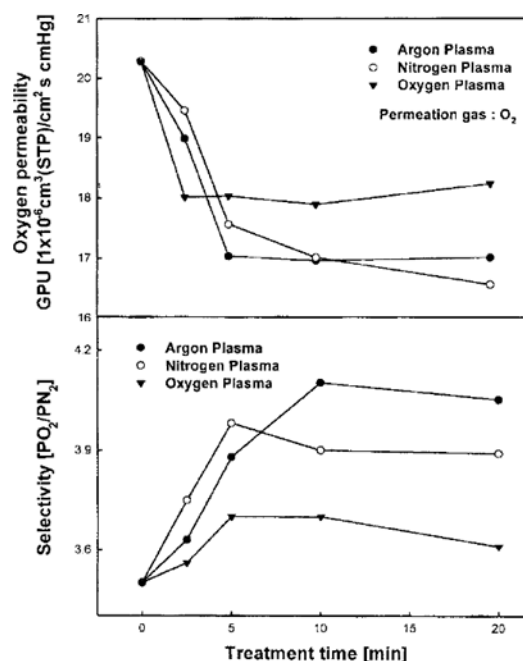
Fig. 10. Dependence of treatment time for the gas permeation of oxygen and nitrogen on composite membranes by the CHF₃ plasma polymer (120 W, 10 sccm).

caused surface modification to be more active. This led to functional groups becoming inducted and this changed the permeability of the plasma. Also, the use of inactive gases such as Ar crosslinked the polymeric surface and restricted the motion of the molecular chain. Large molecular chain gaps shrunk and prevented the diffusion of large molecules resulting in a large increase in selectivity but decreased in permeability. The CHF_3 plasma polymeric membrane also saw higher permeability when Ar plasma was used rather than N_2 plasma or O_2 plasma.

Fig. 10 shows the CHF_3 plasma polymeric membrane's (rf-power=120 W, gas flux=10 sccm) permeability of oxygen and selectivity of oxygen over nitrogen in relation to the treatment time. Up to five minutes, the permeability of oxygen decreased and then remained constant after five minutes, regardless of the type of plasma used. The reverse phenomenon occurred in terms of selectivity. This was seen as a result of the crosslinking that occurred at the beginning of the plasma treatment, and the chemical etching that occurred as more time elapsed. Similar to the trend of results in rf-power, Ar plasma increased the selectivity. Plasma treatment using active gases such as O_2, N_2, NH_3 inducted the functional groups directly to the surface. In addition, it caused ablation and crosslinking of the polymer chain.

Plasma treatment using inactive gases such as Ar and He created active radicals on the polymeric surface. These radicals recombined, crosslinked, bonded with nearby oxygen, or ablated the surface polymer chain which increases with time [Yasuda, 1985]. All these things created similar results even when different gases, substrates and plasma parameters were used. As a result, it was said that low levels permeability and high levels of selectivity were caused by the surface activation and crosslinking resulting from the Ar plasma treatment of the CHF_3 plasma polymeric membrane.
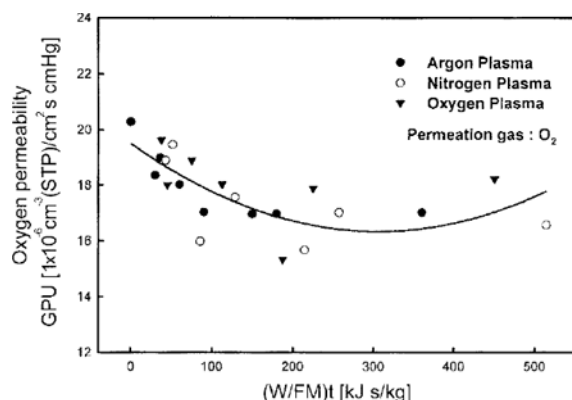
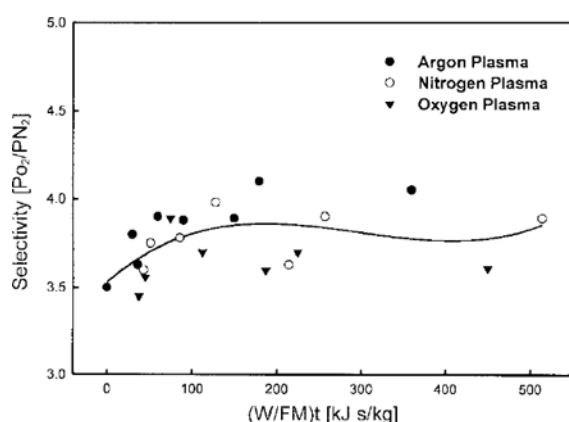**Fig. 11. Effect of (W/FM)t for the permeability of oxygen on composite membranes by the CHF$_3$ plasma polymer.**

Fig. 12. Effect of (W/FM)t for the selectivity of oxygen for a nitrogen on composite membranes by the CHF$_3$ plasma polymer.

The CHF$_3$ plasma polymeric membrane's permeability of oxygen and selectivity of oxygen over nitrogen in relation to the total amount of supplied energy are shown in Fig. 11 and Fig. 12. When the composite parameter [(W/FM)t] was increased, the permeability linearly decreased before increasing at the 320 (kJ·s/kg) region. Selectivity slightly increased and then remained constant when the composite parameter [(W/FM)t] was around 200 (kJ·s/kg). This was seen as being a result of the surface reactions that occurred on the CHF$_3$ plasma polymers when the composite parameter was a small value and also a result of the chemical etching that occurred when the composite parameter was a large value. In this work, it was confirmed that the CHF$_3$ plasma polymeric membrane had the best permeability properties when the composite parameter [(W/FM)t] was around 200 (kJ·s/kg), which was where selectivity and permeability were relatively high when the surface was modified. Similar to the change in static contact angles, change in permeability led to the surface modification of CHF$_3$ plasma polymeric membranes using plasma treatment.

CONCLUSION

A rf-plasma reactor was used to create a CHF$_3$ plasma polymeric membrane, and the changes in its physical and chemical properties were examined for surface modification conducted with different parameters. The following conclusions were reached.

1. CHF$_3$ plasma polymers were uniformly deposited on an aluminum oxide substrate with a pore size of 0.02 μm when the plasma polymerization time was 60 min, the rf-power was 160 W, and the CHF$_3$ flow rate was 16 sccm.

2. O$_2$ plasma treatment had the greatest effect on the surface roughness of the CHF$_3$ plasma polymeric membrane.

3. Oxygen in the atmosphere reacted with the activated surface of the CHF$_3$ plasma polymeric membrane to form oxygen functional groups such as carbonyl and carboxyl. These increased the oxygen content and O/C ratio of the surface. Treatment using Ar plasma, which is inactive, resulted in the largest oxygen content and O/C ratio.

4. It was confirmed that plasma treatment inducted polar functional groups and increased the wettability of the CHF$_3$ plasma polymeric surface. This caused the surface to become hydrophilic. As the oxygen content of the surface of the CHF$_3$ plasma polymeric membrane increased, the static contact angle linearly decreased. The most effective CHF$_3$ plasma polymeric surface modification occurred when the composite parameter ranged from 300-450 (kJ·s/kg).

5. Changes in selectivity and permeability of the CHF$_3$ plasma polymeric membrane were observed as resulting from crosslinking, induction of functional groups, chemical etching, etc. It was confirmed that the CHF$_3$ plasma polymeric membrane had the best permeability properties when the composite parameter [(W/FM)t] was near 200 (kJ·s/kg).

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