Perfluoropropene Plasma 처리에 의한 Polyethylene Pipe의 보호성 차단특성

서 은 덕 · H. Yasuda*

경남대학교 공과대학 화학공학과·*University of Missori-Rolla

(1989년 1월 23일 접수)

The Protective Barrier Characteristics of Polyethylene Pipe by Perfluoropropene Plasma Treatment

Eundeock Seo and H. Yasuda*

Department of Chemical Engineering, Kyungnam University, Masan 630-260, Korea
**Department of Chemical Engineering and University of Missori-Rolla, MO 65401*
(Received January 23, 1989)

요 약 : 여러가지 기체, 증기 및 액체에 대한 고분자물질의 보호성차단특성은 실용면에서 대단히 중요하다. 본 연구에서는 polyethylene pipe의 차단특성을 향상시키기 위한 목적으로 perfluoropropene 플라즈마 중합박막을 polyethylene pipe 내부에 코팅하였다. 출력에 따른 박막의 화학적구조를 ESCA에 의해 조사하여 차단특성과 화학적 구조와의 관련성을 연구하였다. 차단특성은 산소투과계수로서 얻어졌고 최고 31%의 향상을 보였다. 방전출력을 증가시키면 플라즈마 중합박막의 CF_2와 CF_3성분이 증가하면서 가교결합이 감소하고 차단특성도 감소하였다.

Abstract : To enhance the protective barrier property, the inner surface of polyethylene pipe was modified by the thin film coating of perfluoropropene plasma polymer. The chemical structures of the ultra thin plasma coatings, treated at different discharge powers, were characterized by ESCA. The protective barrier properties were interrelated to its chemical structures which depended on the discharge power. To estimate the protective barrier characteristics, oxygen permeability coefficients were measured. The permeabilities of plasma treated pipes were reduced, compared with untreated sample, up to 31%. It was observed that increasing the discharge power gave rise to increase in the contents of CF_2 and CF_3 groups and decrease in the degree of crosslinking and protective barrier characteristics. The best result of the barrier characteristic was obtained from the coating treated at 20W discharge power(350-500Å in thickness).

INTRODUCTION

The barrier properties of plastic materials against various gases, vapors and liquids are of great importance for many applications. Ashley[1] pointed out that in order to be a good all around barrier material the polymer should possess the following properties. It should have some polarity, high chain stiffness, inertness to permeants, some bonding, close packing ability and a high glass transition temperature. In this sense, plasma treatment is an attractive method for modifying the surface properties of a polymer without affecting the bulk properties of the materials since the film produced by this process is usually insoluble in solvent, pinhole free and highly crosslinked[2] and hence its properties are closely related to those of the above mentioned.

In the present work, polyethylene pipe was treated in plasma state to make a protective barrier coatings. The polyethylene pipe is intended for applications mainly with hot water under pressure. When the pipe is subjected to be in contact with hot water, two main type of degradation occur: a chemical and mechenical.[3] The chemical degradation is probably due to the oxidation at elevated temperature. The oxidation can be proceeded by oxygan permeated from outside to inside of the pipe, which is accelerated by leaching of stabilizer compounded in the pipe to retard the rate of oxidation. The mechanical degradation is caused by stress applied to the pipe. In such a circumstance, surface cracks are developed and consequently results in the burst of pipes. In this sense, the surface treatment by plasma coatings has several practical advantages against a conventional coating methods since the ultra thin films produced by plasma coating technique has unusual chemical and thermal stability and highly protective barrier characteristics which are appropriate to cut off the leaching of stabilizer and to reduce the oxygen permeability and to fill up the cracks of the pipes. To estimate the protective barrier characteristics, the oxygen permeabilities of polyethylene pipes which were modified by plasma coating were measured and

the results were related to the chemical structure of plasma polymerized coatings. For this purpose, surface fluorination was carried out at several discharge powers.

EXPERIMENTAL

Plasma Polymerization System

The glow discharge reactor was made of Pyrex grass cylinder 148cm long and 3.2cm in inner diameter, and its vacuum line was connected with 0 ring joint to avoid contamination by grease.

The polyethylene pipe used as substrate was 3cm in outer diameter, 60cm long and 0.3cm thick, which was supplied by Studsvik Energite knik Ab. Three pieces of the pipe(one 60cm and two 30cm long) were inserted into the reactor to isolate direct contact of plasma with Pyrex glass wall except the two end-tips of reactor as shown in Fig. 1. A band electrode made of thin copper which was fixed 3.6cm apart on wheelbase can be movable back and forth. Surface fluorination was carried out by moving it to original position. The time required for a round trip of 60cm long polyethylene pipe was 3min.. Plasma was excited by a Tegal Corporation 13.56MHz radio frequency generator capable of delivering a power output up to 300W. The generator was matched to the external inductively coupled an L-C matching network and the input power was monitored by Daiwa power meter.

The pressure was monitored by Baratron ABS gauge. Perfluoropropene monomer gas was supplied by PCR Incorporated and used without further purification.

Gas flow rate and the pressure of reactor was maintained at 0.36 cm(STP) / min and 60 mtorr by needle valve, respectively. The plasma treated surfaces were characterized by ESCA spectra
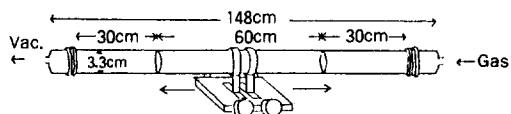

Fig. 1. The tubular reactor in moving electrode system.

which were obtained by Physical Electronics (Model 548) using Mgka photon source. Carbon 1s spectra were deconvoluted into six component peaks using a nonlinear least square curve fitting program :

CF_3	294.0eV
CF_2	291.9 ± 0.1
$CF-CFn$	289.8 ± 0.1
CF	288.3 ± 0.2
$C-CFn$	286.5 ± 0.2
$=C=$	285.0 ± 0.02

For the assignment of ESCA spectra, previously published works by several authors were referenced. [4~6] In doing the deconvolution. the binding energies of carbon 1s peaks were corrected to compensate the sample charge effect. This was done by assuming that the component peak with highest binding energy be the one due to the CF_3 structure which was assigned to be at 294.0eV.

Permeability measurement apparatus is dipicted in Fig. 2. A polyethylene pipe 10cm long and 3mm thick was inserted in permeability measuring chamber as a permeability measuring sample. The equations used to calculate the surface area and permeability coefficient of the pipe were $A = 2\pi L(r_o / r_i) / Ln(r_o / r_i)$ and $P = V(dp / dt) (273 / T)(1 / 76)(L / A)(1 / \triangle p)$, respectively. where r_o, r_i, L, P, V, T, A, dp / dt and $\triangle p$ are outer and inner radius, length, permeability, volume, temperature, area, pressure increment per unit time of permeability measuring chamber and pressure difference, respectively.

The equation used to calculate the permeabilities of plasma coatings is $Pc = lc / ls(1 / Po - 1 / Ps)$, where Pc, Ps, Po, lc and ls are permeabilities of plasma coating, polyethylene itself, plasma coated polythylene, thickness of plasma coating and thickness of polyethylene itself, respectively.[1] The evacuation time of pipes were entire 3 days, which condition was obtained by preliminary experiment, to get rid of dissolved gases in pipe completely. After 3 days of evacuation, oxygen was introduced to permeability measuring chamber and then it took about 3 days to get steady flow of oxygen permeated through the pipe wall, viz, constant value of dp / dt. Accordingly, it took 6 or 7 days for one sample. The thickness of the plasma polymer coating was estimated using Inficon XTM thickness monitor. The film thickness of the coatings was controled by manipulation of plasma treating time.

RESULTS AND DISCUSSION

The specifications of pipes used in this work are summarized in Table 1 along with its permeability data. As shown in Table 1, all of values of permeabilities of samples modified with plasma coating (Po) were decreased compared with the untreated one(Ps), and its values are different with each other depending upon thickness and discharge power. Above all, the permeabilities of coating film itself (Pc) are considerably lower than that of polyethylene pipe itself, viz, 10000 fold range decrease.

This is a direct evidence that plasma treantment is a powerful method to improve the protective barrier characteristics, and that the lowerings of permeabilities of plasma-treated samples solely came from ultraprotective barrier characteristics of plasma coating itself. Those results are shown in Fig. 3 and 4. It can be observable that the the permeabilities of coating film are a function of film thickness and discharge power, and that there is a certain optimum coating thickness
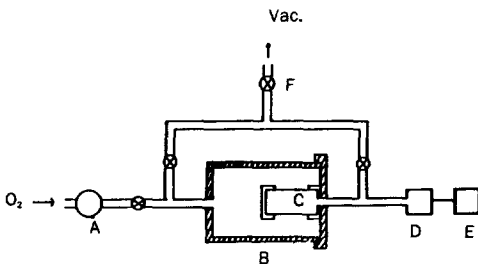

Fig. 2. The block diagram for permeability measuring apparatus : A)O_2 pressure measuring gauge, B)Permeability measuring chamber, C)Polyethylene pipe, D)Absolute pressure monitoring transducer, E)Recorder, F)Cock.

Table 1. The Data for Permeabilities of Plasma treated Polyethylene Pipes and Plasma Coating

Sample	Power(W)	P_o	P_c	Film Thickness (Å)	Treating Time (Min.)
Pure-PE		8.76(Ps)			
C_3F_6-PE-11	10	8.00(Po)	6.30	205	3
″ 12	″	7.42	5.98	370	6
″ 13	″	7.58	9.66	515	9
″ 14	″	7.78	13.79	595	12
″ 21	20	7.03	2.13	180	3
″ 22	″	6.08	2.45	370	6
″ 23	″	6.15	3.57	520	9
″ 24	″	7.43	11.26	690	12
″ 51	50	6.64	2.10	230	3
″ 52	″	6.35	2.62	340	6
″ 53	″	8.10	20.96	585	9
″ 54	″	8.14	24.53	640	12
″ 101	100	7.95	5.30	185	3
″ 102	″	7.93	9.76	350	6
″ 103	″	8.32	27.33	495	9

The units of Po, Ps and Pc are cm^2sec^{-1} $(cmHg)^{-1}$ $\times 10^{-11}$ and cm^2 sec^{-1} $(cmHg)^{-1}$ $\times 10^{-15}$, respectively. The range of error for measuring film thickness is 5Å.
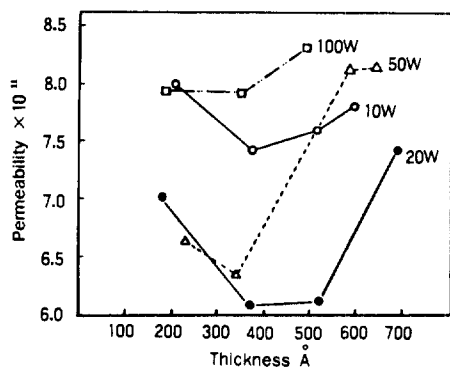

Fig. 3. The relationships between permeabilities and coating thickness of plasma treated polyethy lene pipes at various discharge powers.
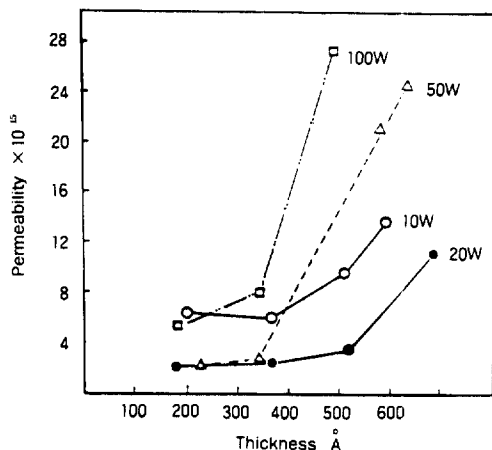

Fig. 4. The relationships between permeabilitis and coating thickness of plasma coating itself.

and discharge power for obtaining good barrier coating. To explain these results, we investigated chemical structures of plasma polymer coatings by ESCA.

In Fig. 5, ESCA spectra which were obtained at various discharge powers are presented. The results were analized and are listed in Table

2, and shown in Fig. 6. With increasing discharge power, the intensities of CF_2 and CF_3 groups increased in contrast to the marked decrease of =C= and C−CFn groups whereas CF-CFn and CF groups did'nt show a prominent change like foregoing groups.
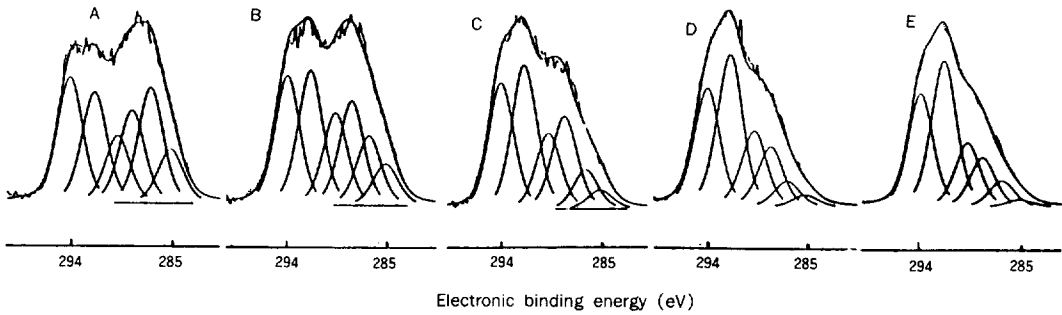
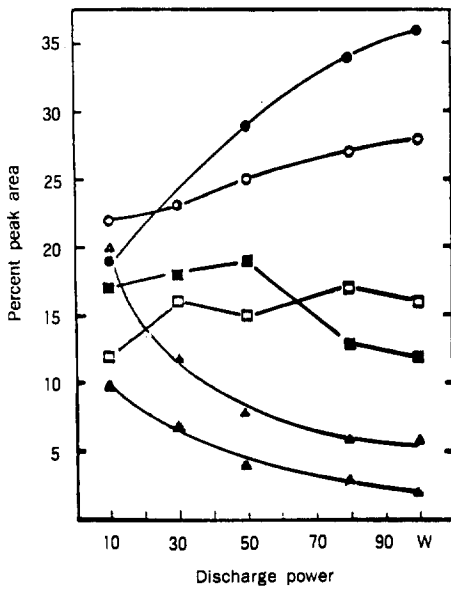Fig. 5. The ESCA spectra of carbon ls at various discharge powers : A)10W, B)30W, C)50W, D)80W, E)100W.

Fig. 6. The variations of components of carbon ls spectra : CF_3:○, CF_2:●, CF-CFn:□, CF: ■, C-CFn:△, =C=:▲.

Table 2. Percentage contribution of Each Carbon Group at Various Discharge Power

Peak	Percentage Peak Area				
	10W	30W	50W	80W	100W
CF_3	22%	23%	25%	27%	28%
CF_2	19	23	29	34	36
CF-CFn	12	16	15	17	16
CF	17	18	19	13	12
C-CFn	20	12	8	6	6
=C=	10	7	4	3	2

Our results are in disaccord with that of early works of several authors.[4,7,8] It is considered that the discrepancy arises from different system parameters, eg, sustrate, discharge power, monomer and reactor itself.

However, the changes in permeability are closely related with variation of these groups since the permeability is dependent on chemical composition of plasma film.[9] In that sense, it is supposed that the increase of CF_2 and CF_3 groups and decrease of =C= and C-CFn groups give rise to an increased permeability, and vice versa. This viewpoint can be justified by considering that carbons of =C= and C-CFn groups are tetravalent and trivalent, respectively, which are responsible for crosslinking of plasma coating, and that carbons of CF_2 and CF_3 groups are divalent and monovalent which are responsible for reducing crosslinkage. Especially CF_3 group play an important role in increasing the bulkness of plasma coating because CF_3 groups are pendent groups which decrease the tightness of plasma coatings. This opinion can be supported with the work reported by Ashley[1] who mentioned the effect of bulky side group on permeability. He pointed out that when a hydrogen of polyethylene was replaced with methyl and isobutyl group, its permeability was increased ca 1.4 and 36.4 times, respectively. Another example of the effect of bulky groups is from the work by Muruganadam et al.[10] They observed that a threefold to fourfold increase in permeability was caused by the substitution of hydrogen with tetramethyl group

in polycarbonates. Consequently. the decrease of tightness by decrease of$=$C$=$ and C-CFn groups or the increase of bulkness by increase of CF_3 group result in the enhancement of the permeabilities of the coatings. However, it seems that there is some disadvantage of the phenomenon. It is well known that excess crosslinking gives rise to increase internal stress which might be liable to crack or separation of plasma coating from the substrate.[11~13] Probably, the abnormal behavior of the permeability of samples treated at 10W might come from this fact.

REFERENCES

1. R. J. Ashley, in Polymer Permeability, J. Comyn, Eds., Elsevier Applied Science Publishers, London and New York, 1985.

2. H. Yasuda, Plasma Polymerization, Academic Press, Orlando, Florida, 1985.

3. M. Ifwarson, from Studsvik report, NESTE 4531 / 4650, 1987.

4. D. T. Clark and D. Shuttleworth, *J. Polym. Sci., Polym. Chem. Ed.,* **18**, 27(1980).

5. D. T. Clark and D. R. Hutton, *J. Polym. Sci., Polym. Chem. Ed.,* **25**, 2643(1987).

6. M. S. Munro and C. Till, *J. Polym. Sci. Polym. Chem. Ed.,* **22**, 3933(1981).

7. H. Yasuda, *J. Polym. Sci., Macromol. Rev.,* **16**, 1999(1981).

8. A. T. Bell, et al, ACS Symposium Series, No 108, Chap. 9, American Chemical Society, Washington D. C. 1979.

9. N. Inagaki and Ohkubo, *J. Membrane Sci.,* **27**, 63(1986).

10. N. Muruganadam, W. J. Koros, and D. R. Paul, *J. Appl. Polym. Sci.,* **25**, 1999(1987).

11. H. Yasuda, T. Irotsu, and H. G. Olf, *J. Appl. Polym. Sci.,* **21**, 3179(1977).

12. A. Morinaka and Y. Asana, *J. Appl. Polym. Sci.,* **27**, 2139(1982).

13. M. Kawakami, Y. Yamashita, M. Iwamoto, and S. Kagawa, *J. Membrane Sci.,* **19**, 249 (1982).