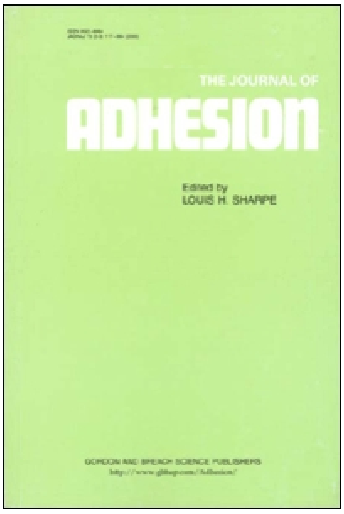

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Surface Modification of Some Fluorine Polymer Films by Glow Discharges

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Extensive study has been made of the effects of various types of glow discharge plasmas on the changes of the surface properties of some fluorine polymers. The properties were investigated as a function of such factors as the exposing period, aging after exposure, type of plasma, and so on.

It was found that the wettability and the critical surface tensions were changed considerably with plasma exposure and that periods of several tens of seconds are long enough to cause changes. The extents of change were not so prominent for fluorine polymers as for polyethylene, and this fact may show the important role of the fluorine atom in the surface properties even after the plasma treatments.

INTRODUCTION

Surface of polymers can be changed and modified by exposing them to plasmas produced with RF glow discharges.[1] One of the advantages is that only the surface properties can be changed without affecting the bulk properties. In addition, the surface properties, especially hydrophilicity and hydrophobicity, can be controlled by selecting the type of plasma.

Chemical and physical property changes resulting from plasma treatments of fluorine polymers has been investigated. Yasuda *et al.*,[2] have found in an ESCA study that polytetrafluoroethylene is comparatively susceptible to plasmas and a considerable amount of fluorine is detatched from just the surface layer. They also have reported that the N_{1s} peak is introduced by N_2-plasma and the O_{1s} peak by both Ar- and N_2-plasmas. Clark and Dilks[3] have applied ESCA to the investigation of the polymer surfaces modified by inert gas plasmas, and have determined the rates of the direct and the radiative energy transfer processes. Technical application of plasma treatments has also been made for the purpose of improving the adhesivity of polytetrafluoroethylene.[4]

In this study, the effects of plasma exposure on the changes of the surface properties of some fluorine polymers are investigated with respect to some experimental factors such as the type and time of plasma exposure. Plasma susceptibility is discussed on the basis of degradation rates, and the resulting surface properties are discussed on the basis of contact angles and the critical surface tensions.

EXPERIMENTAL

Materials

Gases used for plasma were helium, nitrogen and oxygen which were used as supplied.

Fluorine polymer films used in this study were of three different kinds as follows;

Polytetrafluoroethylene (PTFE), supplied from Nippon Asbestos Co. Ltd., Tokyo.

Tetrafluoroethylene-Ethylene copolymer (TFE–ET copolymer), supplied from Asahi Glass Co. Ltd., Tokyo.

Polyvinylidenefluoride (PVDF), supplied from Kureha Chemical Co. Ltd., Tokyo.

The films were cleaned by washing with soap and water, followed by rinsing with distilled water before the glow discharge exposure.

Plasma experiments

The glow discharge was generated with a radio frequency (RF) of 13.56 MHz, using inductive coupling. The apparatus for the plasma reaction is similar in design to the one previously reported by Yasuda and coworkers.[5] A film was set in the reaction chamber, 4.4 cm in diameter and 40 cm in length, and the system was evacuated. It was allowed to stand until the pressure reached 1.0×10^{-4} Torr. Successively, a gas for plasma was introduced into the chamber at 60×10^{-3} Torr, and the glow discharge was started. Discharge power of 50 watts was employed, and the plasma condition satisfied the reaction for carrying out the plasma surface modification.

Contact angle measurements

Contact angles on the polymers were measured with a Shadowgraph, Model H-14, Nikon Co. Ltd., Tokyo.

Critical surface tensions were obtained by the contact angle method using the following liquids:

Liquid	Surface energy, dyne/cm γ_L	γ_L^d	γ_L^p
Water	72.8	21.8	51.0
Glycerol	63.4	37.0	26.4
Formamide	58.2	39.5	18.7
Methylene iodide	50.8	48.5	2.3
Tricresyl phosphate	40.9	39.2	1.7
n-Hexadecane	27.6	27.6	0.0

Here, γ_L^d and γ_L^p respectively represent the dispersion and the polar terms in the critical surface energy of the liquid (L), and γ_L is equal to the sum of the two components, i.e., $\gamma_L = \gamma_L^d + \gamma_L^p$.

The details of the method in obtaining the energies can be found in the literature by Kaelble.[6]

RESULTS AND DISCUSSION

(a) Plasma degradation

It is known that the effect of a plasma on a polymer is confined just to the surface, and that the weight loss of a polymer in a plasma, which is often given as an indication of plasma susceptibility, is not dependent on the thickness of the polymer substrate.[7]

The degradation rates were obtained from the weight decrease after plasma exposure, and are presented in mg/(cm^2 × hour). The results are shown in Table I. Incidentally, much care must be paid in comparing the degradation rates. We have some other data reported previously in the literature, and some for PTFE and polyethylene (PE) are shown and compared in Table II. The rates are more or less different, and this difference may be due to the specific plasma conditions employed in the studies. Even if the experimental conditions, such as discharge power, vacuum pressure, or the type of plasma and substrates are the same, the efficiency could be different among the reaction systems. This is because the energy produced in the plasma is changed depending on the position in the apparatus, the geometry and the design of the reaction system. However, if the reaction is carried out in the

TABLE I

Degradation rate of fluorine polymers and polyethylene in plasmas from helium, nitrogen and oxygen

Polymer	Degradation rate × 10^2, mg/(cm^2 × hr)		
	Helium	Nitrogen	Oxygen
PTFE	2.0	7.3	56.0
TFE–ET copolymer	1.7	4.5	34.0
PVDF	8.3	9.1	106.0
PE	7.3	9.0	42.0

same system, the resulting degradation rates should represent the relative susceptibility determined by both the type of plasma and the polymer substrates.

If it were ideally considered that only H_2, F_2 and HF are dissociated respectively from the side chains of PE, PTFE and PVDF and TFE–ET copolymer, the ratio in the degradation rates should be 2:38:20 (= H_2:F_2:HF). However, the results show that the degradation rates are not so different as would be expected from the above. In fact, the results suggest that the rate of detachment of fluorine from the —CF_2— chain is smaller than that of hydrogen from the —CH_2— chain.

It is interesting to note the higher degradation rate of PVDF compared to that of the TFE–ET copolymer. Both contain the chains —CF_2— and —CH_2—, although the alternation is different in each. The difference in the degradation rates between the two polymers may be due to some kind of

TABLE II

Comparison of the data on the plasma degradation rates of PTFE and PE presented in the previous literature with those of this work

Polymer	Plasma from	Degradation rate × 10^2, mg/(cm^2 × hr)
PTFE	O_2	78.0[a]
	O_2	56.0[c]
PE	He	7.2[b]
	He	7.8[c]
	O_2	310.0[a]
	O_2	42.0[c]

[a] R. H. Hansen *et al.*, *J. Polym. Sci.* **A3**, 2205 (1963).
[b] H. Yasuda *et al.*, *J. Appl. Polym. Sci.* **17**, 137 (1973).
[c] This work.

physical parameters, such as crystallinity on the surface, although it is difficult or impossible to measure and to determine such parameters just on the surface.

(b) Change of surface characteristics by plasma

Wettability of the plasma treated films Contact angles of water on the plasma treated polymers were measured, and the change in wettability was investigated as an indication of the surface characteristics. Figure 1 shows the change of contact angles on the N_2-plasma treated PE's with the exposing period. The angles were taken immediately after the plasma treatments. As

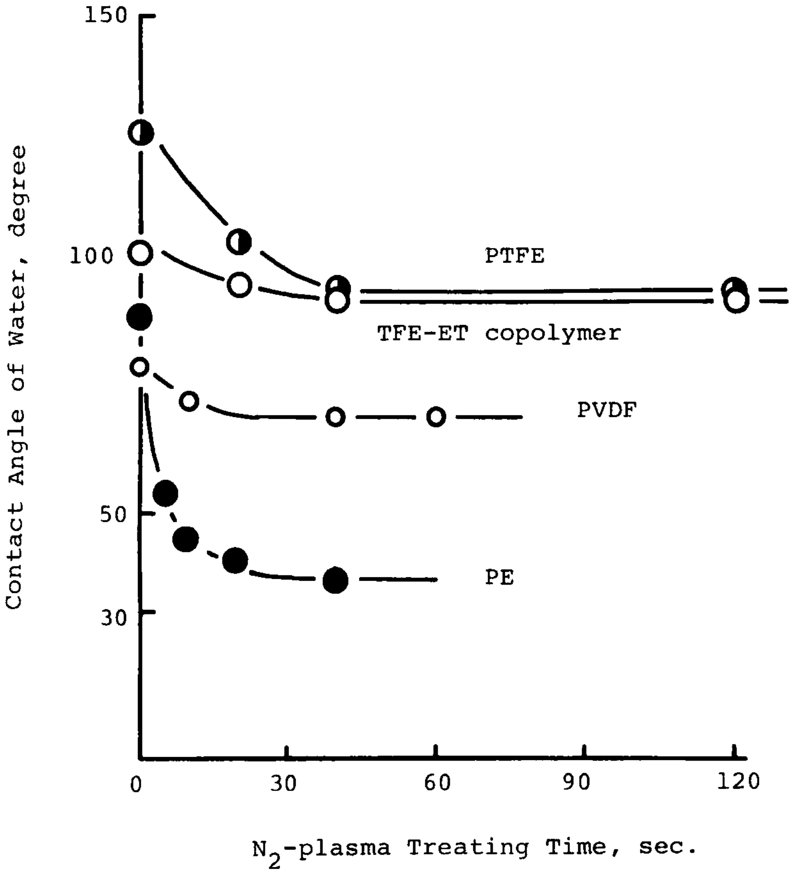

FIGURE 1 Effect of the N_2-plasma treating time on the contact angles of water on the polymers.

observed, the contact angles decrease gradually in the first 40 seconds of treatment and then reach a limiting value, different for each substrate.

It is interesting to note that the limiting values in contact angle are close between the TFE–ET copolymer and PTFE and, in contrast, PVDF has a lower value than the other two. One of the possible explanations may be that the plasma attacks more exclusively at the portion $—CH_2—CH_2—$, and that the $—CF_2—CF_2—$ portion on the surface acts as a kind of blocking layer against the plasma. As a result, the surface property of the TFE–ET copolymer becomes similar to PTFE rather than to PVDF after the plasma treatment. This assumption will be also related to the results described previously in the section on plasma degradation.

Next, the changes of contact angles of water which occur on aging after plasma exposure were investigated. The results are shown in Figure 2 for the He-plasma treated PE. The contact angle transients were plotted for the samples with exposure times of 5, 10, 20, 40 and 100 seconds. It was found that all the samples are the most hydrophilic when they are fresh, and

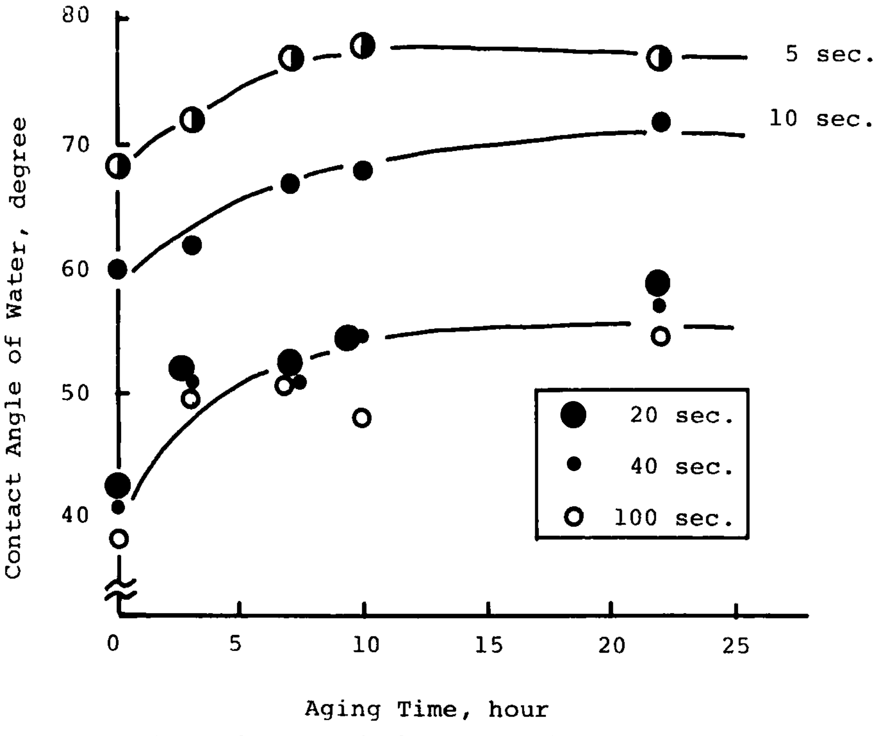

FIGURE 2 Changes of contact angle of water on He-plasma treated PE with aging after exposure.

TABLE III

Contact angle of water on plasma treated polymers

Polymer	Plasma from	Contact angle of water, degree (1)	(2)	(3)
PTFE	non	126	126	—
	He	110	111	+1
	N_2	105	95	−10
	O_2	100	100	0
TFE-ET copolymer	non	80	80	—
	He	74	68	−6
	N_2	72	76	+4
	O_2	72	70	−2
PVDF	non	102	102	—
	He	80	80	0
	N_2	82	82	0
	O_2	77	80	+3
PE	non	89	89	—
	He	41	56	+15
	N_2	49	65	+16
	O_2	40	58	+18

(1) Measured just after the plasma treatment.
(2) Measured 3 days after the plasma treatment.
(3) Change of contact angles in 3 days, i.e., (3) = (2) − (1).

that they become gradually less hydrophilic with age. They show more or less similar behavior with 20, 40 and 100 seconds exposure. The results therefore suggest that at least several tens of seconds of plasma exposure are long enough to cause changes in the surface properties.

The results for other polymers are summarized in Table III. They are for samples freshly prepared (1), and for samples measured 3 days later (2). Changes of the contact angles occurring in 3 days are shown in the third column (3), i.e. (3) = (2) − (1). The polymer samples were produced under the condition as described for 5 minutes, where the exposing time is long enough for the change in surface characteristics to be complete. It is found that the contact angles on the fluorine polymers do not change much even after 3 days.

Critical surface energies Surface characteristics of solids have been well explained by critical surface energy concepts. One of the popular methods is Kaelble's, which takes the dispersion and the polar contributions into consideration.

TABLE IV

Critical surface tensions, γ_S^d, γ_S^p and γ_S ($= \gamma_S^d + \gamma_S^p$), for the untreated fluorine polymers and PE

Polymer		Critical surface energy, dyne/cm		
		γ_S^d	γ_S^p	γ_S
PTFE	(a)	20.3	0.1	20.4
	(b)	14.54	1.0	15.56
TFE–ET copolymer	(a)	19.4	1.0	20.4
	(b)	22.42	2.19	24.62
PVDF	(a)	29.2	4.8	34.0
	(b)	26.19	6.08	32.28
PE	(a)	27.0	2.3	29.3
	(b)	31.39	1.10	32.39

(a) Data of this work.
(b) Data of D. H. Kaelble in *J. Adhesion* **2**, 66 (1970).

In the Table IV, the data on the energies of some untreated fluorine polymers are shown, and they are compared to the ones previously reported by Kaelble.[8] Here, γ_L^d and γ_L^p are respectively representing the dispersion and the polar terms, and the total energy, γ_s, is given in the summation of the two terms, i.e., $\gamma_s = \gamma_s^d + \gamma_S^p$. Although small differences can be observed in the two sets of data, the deviation will not be troublesome in discussing the surface characteristics. It is interesting that in the two polymers which

TABLE V

Critical surface tensions, γ_S^d, γ_S^p and γ_S of untreated and plasma treated PTFE

	Critical surface tension, dyne/cm		
	γ_S^d	γ_S^p	γ_S[a]
(1) Untreated	20.3	0.1	20.4
(2) He–p, fresh[b]	23.0	2.0	25.0
N_2–p,	16.8	1.2	18.0
O_2–p,	16.0	2.9	18.9
(3) He–p, 3 days later[c]	18.5	2.3	20.8
	19.4	1.4	20.8
	21.2	0.7	21.9

[a] $\gamma_S = \gamma_S^d + \gamma_S^p$.
[b] Obtained just after the plasma treatments.
[c] Obtained 3 days after the plasma treatments.

TABLE VI

Critical surface tensions, γ_S^d, γ_S^p and γ_S of untreated and plasma treated TFE–ET copolymers

	Critical surface tension, dyne/cm		
	γ_S^d	γ_S^p	γ_S[a]
(1) Untreated	19.4	1.0	20.4
(2) He–p, fresh[b]	32.5	4.4	36.9
N_2–p	26.0	6.3	32.3
O_2–p	25.0	8.4	33.4
(3) He–p, 3 days later[c]	27.0	6.8	33.8
N_2–p	22.1	6.3	28.4
O_2–p	26.0	6.8	32.8

[a] $\gamma_S = \gamma_S^d + \gamma_S^p$.
[b] Obtained just after the plasma treatments.
[c] Obtained 3 days after the plasma treatments.

contain both —CH_2— and —CF_2— groups, TFE–ET copolymer is much closer to PTFE, and PVDF to PE, with respect to the critical surface energies.

The critical surface energies for the plasma treated polymers were obtained for the two states, i.e. immediately after the plasma exposure and 3 days later. The energies change more or less with aging, and the period of 3 days is long enough for the energy to stabilize. The results are summarized in the Tables V–VIII. In addition, the polar contribution in the total energy is given in the form of γ_S^p/γ_S, and the results are shown in Table IX. Several

TABLE VII

Critical surface tensions, γ_S^d, γ_S^p and γ_S of untreated and plasma treated PVDF's

	Critical surface tensions, dyne/cm		
	γ_S^d	γ_S^p	γ_S[a]
(1) Untreated	29.2	4.8	34.0
(2) He–p, fresh[b]	29.2	10.2	39.4
N_2–p	29.2	10.2	39.4
O_2–p	29.2	10.2	39.4
(3) He–p, 3 days later[c]	28.1	11.6	39.7
N_2–p	31.4	5.8	37.2
O_2–p	32.5	9.0	41.5

[a] $\gamma_S = \gamma_S^d + \gamma_S^p$.
[b] Obtained just after the plasma treatments.
[c] Obtained 3 days after the plasma treatments.

TABLE VIII

Critical surface tensions, γ_S^d, γ_S^p and γ_S of untreated and plasma treated PE's

	Critical surface tension, dyne/cm		
	γ_S^d	γ_S^p	γ_S[a]
(1) Untreated	27.0	2.3	29.3
(2) He–p, fresh[b]	32.5	16.8	49.3
N_2–p	31.2	18.1	49.3
O_2–p	30.3	22.1	52.4
(3) He–p, 3 days later[c]	30.3	17.6	47.9
N_2–p	29.2	14.4	43.6
O_2–p	27.0	19.4	46.4

[a] $\gamma_S = \gamma_S^p + \gamma_S^p$.

[b] Obtained just after the plasma treatments.

[c] Obtained 3 days after the plasma treatments.

interesting points can be made from the Tables. In PTFE, γ_S^p increases markedly upon plasma exposure, but γ_S^d does not. However, the effect is much smaller than that given by the sodium treatments which has been reported by Cirlin and Kaelble.[8] Although the energies are largely different between the untreated TFE–ET copolymer and PVDF, they become closer to each other after the plasma treatments, especially for γ_S^d and the fractional

TABLE IX

Fractional polar contribution in the total critical surface energy of untreated and plasma treated polymers

	(B) γ_S^p/γ_S			
(A) Condition	PTFE	TFE–ET copolymer	PVDF	PE
(1) Untreated (a)	0.00	0.05	0.14	0.08
(b)	0.06	0.09	0.15	0.03
(2) He–p, fresh	0.08	0.12	0.26	0.34
N_2–p	0.07	0.20	0.26	0.36
O_2–p	0.15	0.25	0.26	0.42
(3) He–p, 3 days later	0.11	0.20	0.29	0.38
N_2–p	0.07	0.09	0.16	0.33
O_2–p	0.03	0.21	0.22	0.42

(a) Data of this work.

(b) Data of D. H. Kaelble in *J. Adhesion* **2**, 66 (1970).

polar contributions. The effect of plasma exposure is the most prominent for PE. The total critical surface energies, γ_S, increase by more than 1.5 times, and most of the contribution can be attributed to the polar terms, γ_S^p.

SUMMARY AND CONCLUSIONS

Some aspects found in this study may be summarized as follows:

(1) Wettability of fluorine polymers is increased by plasma exposure, and several tens of seconds of exposure is long enough for causing the changes. However the effect is much less than that occurring in PE.

(2) The effects of the type of plasma and the aging after plasma exposure on the wettability are not so prominent as for PE.

(3) One of the important factors participating in the changes of the surface characteristics is the polar term in the critical surface energies.

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