Is there any possibility that plasma could selectively modify polymer surfaces?

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In order to resolve susceptibility of PTFE (polytetrafluoroethylene) and PE (polyethylene) against H_2 and O_2 plasmas, modification reactions of ETFE (ethylene-co-tetrafluoroethylene) surfaces by H_2 , O_2 , and Ar plasmas were investigated from viewpoint of chemistry. The chemical modification involved defluorination and oxidation reactions. These reactions were favorable in the remote H_2 and Ar plasmas, but were unfavorable in the remote O_2 plasma. C-H and C-F components in the ETFE surfaces were evenly modified by the remote plasma. Either of CH_2-CH_2 or CF_2-CF_2 component was not selectively modified.

Keywords: polytetrafluoroethylene, polyethylene, ethylene-co-tetrafluoroethylene, surface modification, plasma treatment, contact angle, XPS, ATR IR spectra

1. Introduction

Plasma treatment is a useful technology in the field of polymer surface modification. Once every polymer surface is exposed to plasma just for a few minutes, the exposed surface causes to be changed in surface properties such as hydrophobicity. Even polytetrafluoroethylene (PTFE) can easily be modified by plasma. For example, Figure 1 shows contact angle of water on PTFE surfaces exposed to oxygen and hydrogen plasmas as a function of the exposure time. When PTFE surfaces are exposed to the hydrogen plasma only for 60s, the surfaces show a large decrease in water contact angle from 106 to 80 degrees. Oxygen plasma cannot modify PTFE surfaces into so hydrophilic as the hydrogen plasma does. On the other hand, polyethylene (PE) surfaces are well modified into hydrophilic by both hydrogen and oxygen plasmas (Figure 1). Why is there difference in plasma susceptibility between PTFE and PE surfaces? When polymer surface containing CF_2-CF_2 and CH_2-CH_2 components is exposed to oxygen or hydrogen plasma, does the oxygen plasma modify CH_2-CH_2 component alone on the

polymer surface? Does the hydrogen plasma modify both CF_2-CF_2 and CH_2-CH_2 components

Figure 1 Contact angle of water on PTFE and PE surfaces treated with H_2 and O_2 plasmas as a function of plasma exposure time.

on the polymer surface? If such modifications are possible, polymer surfaces can be modified in nanometer scale.

Ethylene-co-tetrafluoroethylene, ETFE, is an alternating copolymer of ethylene and tetrafluoroethylene. Physical and chemical properties of ETFE are similar to those of polytetrafluoroethylene and other fluoropolymers such as copolymers of tetrafluoroethylene and hexafluoropropylene, FEP; and of tetrafluoroethylene and perfluoro(alkyl vinyl ether), PFA. When ETFE surface is exposed to plasma, what modification will occur on the ETFE surface? Can CH₂ components in the ETFE be selectively modified by oxygen plasma? Can hydrogen plasma modify homogeneously both CH₂ and CF₂ components in ETFE?

In this study, we have focused on what surface reactions occur in exposing ETFE surface to plasmas. Hydrogen plasma, oxygen plasma, and argon plasma were used for surface modification.

2. Experimental

2.1. Materials

Ethylene-co-tetrafluoroethylene, ETFE, film received from Asahi Glass Co. Ltd., Japan (trade name, Fluon ETFE; 100 μ m thickness) was provided as specimens for plasma modification. The concentration of CH₂-CH₂ and CF₂-CF₂ components in the ETFE film was 47 and 53 mol%, respectively, which were estimated from the XPS analyses.

2.2. Modifications of ETFE Films by Remote and Direct Plasmas

A special reactor of which details had been reported elsewhere [1] was used for the modification of ETFE surfaces. The ETFE specimens were positioned in the plasma reactor, and H₂, O₂, or Ar was introduced into the plasma reactor with a flow rate of 10 cm³ (STP)/min adjusted by a mass flow controller. The system was maintained at a pressure of 13.3 Pa by adjusting the vacuum valve. The plasma was operated at an rf power of 100 W at 13.56 MHz frequencies for given duration (5 - 180 s).

2.3. Contact Angle of Water on the plasma-modified PET Film Surfaces.

Contact angles of water on the ETFE film surfaces treated with the remote and direct plasmas were measured at 20°C by means of the sessile drop method [2]. A contact angle meter (Erma Co. Ltd., Japan, model G-1) was used for the

measurement. An average of the contact angle was determined from ten times measurement with an experimental error of 3 - 4 degrees.

3. Results and Discussion

When polymer surfaces are exposed to plasma, two main reactions are initiated on the surfaces. One is introduction reaction of functional groups such as carbonyl, carboxyl, etc. onto the polymer surfaces to be modified into hydrophilic. The other is degradation reaction of polymer chains. Weight loss of the polymer materials occurs, and degradation products deposit on the surfaces. The former reaction is a genuine process for the surface modification. The latter reaction is a burdensome process for the surface modification, because polymer chains on the surface are injured, and the surfaces are contaminated with degradation products. We never escape from the degradation reactions as long as we use plasma for surface modification, because the introduction and degradation reactions occur simultaneously. From this viewpoint, we have to seek modification conditions for minimizing the degradation reactions.

Preliminary experiments showed that the degradation reactions could be minimize by using the remote plasma for the modification of ETFE surfaces. We call the plasma exposures at a sample position of 0 and 80 cm from the plasma zone as the direct plasma treatment and the remote plasma treatment, respectively [1]. From now, we use the remote plasma for subsequent experiments of the ETFE surface modification.

3.1. Contact angle of water on plasma-modified ETFE surfaces

The ETFE film is an alternating copolymer of CH₂-CH₂ and CF₂-CF₂ components. Figure 1 forecasts that surface modification induced on the ETFE surfaces may be a mixture of the modifications occurring on PE and PTFE surfaces. Is the forecast of the modification true? If it is true, the contact angel on modified the ETFE surfaces has to show strong dependence on what plasma was used for the modification. Table 1 compares the contact angle among the PTFE surfaces modified by the remote H₂, O₂, and Ar plasmas. The ETFE surfaces were easily modified with the remote H₂ plasma, and the contact

angle on their surfaces was 44 degrees, which was as low as the contact angle for the modified PE surface (40 degrees). However, the ETFE sur-

Table 1 Contact angle of water on ETFE, PE, and PTFE surfaces exposed to remote plasmas for 60s

Kind of plasma	Contact angle on modified surfaces (degrees)		
	ETFE surfaces	PE surfaces	PTFE surfaces
H ₂ plasma	44	40	82
O ₂ plasma	80	44	105
Ar plasma	54	30	102
None (unmodified)	106	101	121

faces could be barely modified by the remote O₂ and Ar plasmas. Comparison in contact angle among the plasma-modified ETFE, PE, and PTFE surfaces gives us some questions.

- (1) Why could the ETFE surfaces be modified with the remote H₂ plasma as easily as the PE surfaces, even though the ETFE surfaces contain CF₂-CF₂ components in the polymer chains?
- (2) Why could the ETFE surface be barely modified with the remote O₂ plasma, even though the ETFE surfaces possess CH₂-CH₂ components in the polymer chains?

3.2. XPS spectra for the ETFE surfaces modified with remote plasmas

Atomic composition for the ETFE surfaces modified with the remote H₂, O₂, and Ar plasmas was estimated from relative intensities of

may be due to post reactions of carbon radicals formed on the ETFE surfaces by bombardment of electrons and ions in the plasmas.

Defluorination estimated from the F/C atomic ratio was 55 % by the remote H₂ plasma, 51 % by the remote Ar plasma, and 25 % by the remote O₂ plasma. The oxidation also was in the order of modification by the remote H₂ plasma > modification by the remote Ar plasma > modification by the remote O₂ plasma. These defluorination and oxidation may be closely related to the contact angle on the plasma-modified ETFE surfaces. Details of defluorination and oxidation reactions were investigated from data of narrow scanning C1s and O1s core level spectra.

The C1s spectra for the ETFE surfaces modified with the remote H₂, O₂, and Ar plasmas were decomposed into four components, which appeared at 286.1 – 286.5 eV (C1s component #1), at 287.5 – 287.9 eV (C1s component #2), at 289.0 – 290.0 eV (C1s component #3), and at 291.1 – 291.4 eV (C1s component #4). The O1s spectra also were decomposed into two components, which appeared at 531.3 – 531.4 eV (O1s component #1) and at 533.6 – 533.8 eV (O1s component #2). These analytical results are summarized in Table 2. The binding energy for the O1s components #1 and #2 gives us detailed information on chemical composition of the oxygen functional groups formed on the plasma-modified ETFE surfaces. If oxygen functional groups such as car-

Table 2 XPS spectra for plasma-modified ETFE surfaces

Kind of plasma	Atomic composition		C1s components (mol%)				O1s components (mol%)	
	F/C ratio	O/C ratio	Comp. #1	Comp. #2	Comp. #3	Comp. #4	Comp. #1	Comp. #2
H ₂ plasma	0.38	0.22	48	18	10	24	37	63
O ₂ plasma	0.68	0.17	40	11	9	40	45	55
Ar plasma	0.45	0.19	40	21	13	26	37	63
None (unmodified)	1.14	< 0.03	47			53		

C1s, F1s, and O1s core level spectra. The estimation results are summarized in Table 2. All plasma-modified ETFE surfaces showed lower F/C atomic ratio (0.38 – 0.68) than the unmodified ETFE surface (F/C ratio = 1.14), and higher O/C atomic ratio (0.17 – 0.22). These changes indicate that the plasma exposure led to defluorination and oxidation reactions on the ETFE surfaces. The oxidation reactions occurring on the ETFE surfaces

bonyl and hydroxyl groups are formed on fluorinated carbon atoms, the oxygen groups will be strongly influenced by the fluorine atoms and will appear at higher binding energy regions (by about 2 eV) than the oxygen groups formed on not-fluorinated carbons. As for the O1s components #1 and #2 at 531.3 – 531.4 and 533.6 – 533.8 eV, there is no indication that some fluorine atoms influenced their components into shifting their

binding energy. The O1s components #1 and #2 are corresponded to typical $\underline{\text{O}}=\text{C}$ groups (532.2 eV in poly(methylacrylate)) and $\underline{\text{O}}-\text{C}$ groups (533.7 eV in poly(methylacrylate)). Since there was no shift toward higher binding energy regions, the O1s components #1 and #2 could be assigned $\underline{\text{O}}=\text{C}$ groups such as $-\text{CH}_2-\underline{\text{C}}(\text{O})-\text{CF}_x-$ and $-\text{CF}_x-\underline{\text{C}}(\text{O})-\text{O}-$, and $\underline{\text{O}}-\text{C}$ groups such as $-\text{CF}_x-\underline{\text{C}}(\text{O})-\text{O}-$, $-\text{CH}_2-\underline{\text{CH}}(\text{O}-\text{R})-\text{CH}_2-$ and $-\text{CH}_2-\underline{\text{CH}}(\text{O}-\text{R})-\text{CF}_x-$, respectively.

The C1s spectra also are strongly influenced by the fluorine atoms if there are fluorine atoms on carbons. Fluorine effects will cause binding energy shift on C1s core level of 2.9 eV (α effect) and 0.9 eV (β effect). From these effects, the four C1s components constructing the C1s spectra could be assigned $-\text{CH}_2-\underline{\text{CH}}_2-\text{CF}_2-$ and $-\text{CH}_2-\underline{\text{CH}}(\text{O}-\text{R})-\text{CH}_2-$ (C1s component #1), $-\text{CH}_2-\underline{\text{CH}}\text{F}-\text{CH}_2-$ and $-\text{CH}_2-\underline{\text{CH}}(\text{O}-\text{R})-\text{CF}_x-$ (C1s component #2), $-\text{CH}_2-\underline{\text{CH}}\text{F}-\text{CF}_2-$, $-\text{CH}_2-\underline{\text{C}}(\text{O})-\text{CF}_x-$, and $-\text{CF}_x-\underline{\text{C}}(\text{O})-\text{O}-$ (C1s component #3), and $-\text{CH}_2-\underline{\text{CF}}_2-\text{CF}_2-$ (C1s component #4). The underlined carbon atoms mean the objective carbons in the assignment. As for the C1s spectrum of the unmodified ETFE surface, the components at 286.3 and 291.2 eV were assigned $-\text{CH}_2-\underline{\text{CH}}_2-\text{CF}_2-$ and $-\text{CH}_2-\underline{\text{CF}}_2-\text{CF}_2-$ groups, respectively. Their relative concentration was 47 and 53 mol%, respectively. This assignment indicates that the ETFE film is an alternating copolymer composing of CH_2-CH_2 and CF_2-CF_2 sequences, and contains no sequence of $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ and $-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-$. All plasma-modified ETFE surfaces showed large decreases of the C1s component #4, new appearance of the C1s components #2 and #3, and small changes of the C1s component #1 (Table 2). These changes indicate that C-F bonds (C1s component #4) in the ETFE polymers were modified into C-H or C-O bonds (C1s components #2 and #3) by the plasma exposure. The modification was favorably initiated by the remote H_2 and Ar plasmas, but was barely initiated by the remote O_2 plasma. However, complete modification of CF_2-CF_2 groups into CH_2-CH_2 groups (substitution of four hydrogen atoms for four fluorine atoms in CF_2-CF_2 groups) was never accomplished. If the complete modification were possible, $-\text{CH}_2-\underline{\text{CH}}_2-\text{CH}_2-$ groups (which is expected to

appear at 285.0 eV.) would appear on the C1s spectra.

How were C-H bonds in the ETFE surface modified by the plasma exposure? Table 2 shows that there were small changes in the C1s component #1 among the plasma-modified ETFE surfaces. The change was from 47 mol% to 48 mol% for the remote H_2 -plasma-modified ETFE surface, and to 40 mol% for the remote O_2 - and Ar-plasma-modified ETFE surfaces. The C-H modification by the remote H_2 plasma may be distinct from that by the remote O_2 and Ar plasmas. However, details of the C-H modification are not clear because XPS gives us no information concerning the C-H chemistry. The C-H modification will be discussed from data accumulated by IR spectroscopy.

3.5. ATR IR spectra for the ETFE surfaces modified with remote plasmas.

XPS spectra give us useful information as to chemical composition of polymer surface, but do not lead to information on chemistry of C-H structures. IR spectra give us useful information on chemistry of C-H structures in place of XPS spectra. The remote H_2 , O_2 , and Ar plasma-modified ETFE surfaces showed similar ATR IR spectra to the unmodified ETFE surface. Characteristic absorptions due to C-H and C-F bonds appeared at 2976 and 2882 cm^{-1} (C-H stretching vibration), at 1454, 1325 and 972 cm^{-1} (C-H deformation vibration), and at 1251, 1168, and 1047 cm^{-1} (C-F stretching vibration) on the IR spectra. To distinguish the plasma-modified ETFE surfaces from the unmodified ETFE surface, differential spectra were obtained using a computer processing. A chief distinction of the differential spectra was put into two categories: One was the absorptions due to C-H and C-F vibrations (3000 – 2900, 1500 – 1400, 1300 – 1200 cm^{-1}). The intensity of these absorptions was decreased by the remote plasma exposure. The other was the absorptions due to C=O vibrations (1800 – 1600 cm^{-1}). New absorptions appeared at 1757, 1720, and 1672 cm^{-1} (Figure 2).

In order to analyze the C-H and C-F modification, C-H/C-F intensity ratios for the remote H_2 , O_2 , and Ar plasma-modified ETFE surfaces were calculated from these differential spectra (Table 3). Absorptions at 2975 cm^{-1} (C-H

stretching vibration), at 1455 cm^{-1} (C-H deformation vibration), and at 1251 cm^{-1} (C-F stretching vibration) were chosen for the calculation of C-H/C-F intensity ratios. The C-H/C-F intensity

tion of the three carbonyl groups (ester, carbonyl, and α , β -unsaturated carbonyl groups) on the ETFE surfaces. The modification by the remote H_2 and O_2 plasmas formed the ester and carbonyl

Figure 2 Differential IR spectrum for remote Ar plasma-modified ETFE surface

ratios, as shown in Table 3, were in 1.0 – 1.1, and there was less difference in the C-H/C-F intensity ratios among the evenly modified by the three remote plasma-modified ETFE surfaces. The results of the calculation indicate that the C-H and C-F bonds were the remote plasma exposure, and that either of $\text{CH}_2\text{-CH}_2$ or $\text{CF}_2\text{-CF}_2$ component was not selectively modified.

On the other hand, as for the new absorptions due to C=O groups ($1800 - 1600\text{ cm}^{-1}$), is there any effect of the remote plasma exposure on the formation of the C=O groups on the ETFE surfaces? Three new absorptions appeared at 1757, 1720, and 1672 cm^{-1} when the ETFE surfaces were modified with the remote H_2 , O_2 , and Ar plasmas. These absorptions at 1757, 1720, and 1672 cm^{-1} were assigned C=O stretching vibrations in ester groups (C(O)-O-C), carbonyl groups (C=O), and α , β -unsaturated carbonyl groups (C(O)-CH=CH), respectively. The relative intensity of these absorptions against the absorption at 1757 cm^{-1} was calculated from the differential spectra data, and tabulated in Table 3. The remote plasma exposure did not always led to forma-

tion of the three carbonyl groups (ester, carbonyl, and α , β -unsaturated carbonyl groups) on the ETFE surfaces. The remote Ar plasma formed α , β -unsaturated carbonyl groups as well as ester and carbonyl groups on the ETFE surface. In this sense, the remote Ar plasma exposure is distinguished from the other two plasmas, the remote H_2 and O_2 plasmas. We cannot yet interpret here what modification reactions occurred in exposing to the remote Ar plasma to form the α , β -unsaturated carbonyl groups on the ETFE surfaces.

4. Conclusions

H_2 plasma can modify PTFE surfaces into hydrophilic, but O_2 plasma cannot modify. On the other hand, both H_2 and O_2 plasmas can modify PE surfaces into hydrophilic. In order to resolve why there is difference in plasma susceptibility between PTFE and PE surfaces, ETFE surface that was an alternating copolymer of tetrafluoroethylene and ethylene was modified by H_2 , O_2 , and Ar plasmas. What reactions occurred on the ETFE surfaces was investigated from viewpoint of chemistry. We concluded as follows.

Table 3 Absorption intensity of C-H, C-F, and C=O bonds

Kind of plasma	Intensity ratios of		Relative intensity of C=O bonds		
	C-H(I)/C-F	C-H(II)/C-F	C(O)-C	C=O	C(O)-CH=CH
H ₂ plasma	1.1	1.1	1.0	1.3	0
O ₂ plasma	1.0	1.1	1.0	1.8	0
Ar plasma	1.0	1.0	1.0	1.7	1.4

1. The chemical modification process involved defluorination and oxidation reactions on the ETFE surfaces. These modification reactions were favorable in the remote H₂ and Ar plasmas, but were unfavorable in the remote O₂ plasma.
2. Modification of C-H and C-F components by the remote plasma occurred evenly. Either of CH₂-CH₂ or CF₂-CF₂ component was not selectively modified.

Acknowledgment

We acknowledge Dr. M. Kawabe (Nitto Denko Co., Japan) for helpful assistance with ATR

IR spectroscopy measurements.

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