Sulfonic Acid Group-Containing Thin Films Prepared by Plasma Polymerization

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Synopsis

Plasma polymerization of hydrocarbon/sulfur dioxide mixtures, C_2H_2/SO_2, C_2H_4/SO_2, and CH_4/SO_2 mixtures, was investigated to obtain thin films containing sulfonic acid groups. Plasma polymerization of C_2H_2/SO_2 and C_2H_4/SO_2 mixtures gave filmlike products but that of the CH_4/SO_2 mixture did not. The plasma polymers possessed much amount of sulfur and oxygen moieties with hydrocarbon chains. The sulfur moieties involved thio, sulfite, and sulfonic acid groups. Thio groups was a main product and reached 70–80 mol % of the total sulfur moieties. The remains (20–30 mol %) were sulfonic acid and sulfite groups. The oxygen moieties were hydroxyl and carbonyl groups with small amount of carboxyl groups. The plasma polymers showed good hydrophilicity (the surface energy was 54–56 mN/m) and good antithrombogenity.

INTRODUCTION

Sulfur-containing polymers are interesting from a theoretical and a practical point of view. They include poly(sulfur nitride), polythiols, polythioethers, polythioesters, polythiazoles, polysulfoxides, polysulfones, poly(sulfonic acid)s, polysulfones, polysulfonamides, poly(sulfur nitrile)s, etc. Some of them show outstanding properties including super electroconductivity, specific ion exchange, radiation resistance, high-temperature resistance, and antibioticity.[1]

Sulfonic acid group is one of strong acids. The dissociation constant (pK) of benzene sulfonic acid is 0.70 which is fairly lower than that of sulfuric acid (pK = 1.92).[2] Moreover, the sulfonic acid group is considered to play an important role in antithrombogenic actions.[3] Therefore, if we get thin films containing sulfonic acid groups, the films will be an attractive material in electrical and physiological properties.

This study aims to obtain thin films by plasma polymerization. Tsukamoto et al.[4] tried direct plasma polymerization of benzene sulfonic acid but failed because of the instability of sulfonic acid groups in discharge state. We apply the process that sulfur dioxide tends to react with hydrocarbon radicals to form sulfonic acids.[5]

EXPERIMENTAL

Plasma Polymerization

The reaction system for plasma polymerization was an inductively coupled system operating at a frequency of 13.56 Hz (rf). It consisted of a Pyrex glass

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tube (100 mm inner diameter and 400 mm long) with a monomer inlet, pressure gauge, vacuum system, and matching network for inductive coupling of the rf power source. The plasma polymers were deposited on substrates mounted on glass plate positioned horizontally in the glass tube reactor. The details of the reaction chamber have been given in the literature.

The experimental procedures for plasma polymerization were essentially the same as reported elsewhere.[6] The reaction system was evacuated to approximately 0.13 Pa, and the substrate surfaces were exposed to argon plasma which was operated at an argon flow rate of 7 cm^3 (STP)/min, at 1.3 Pa, and at an rf power of 50 W for 10 min to eliminate water adsorbed on the substrate surfaces. The system was again evacuated to 0.13 Pa, and then the monomer gas, adjusted to a flow rate of 7 cm^3 (STP)/min at 1.3 Pa, was introduced into the reaction chamber. The rf power was turned on, and the plasma polymerization was conducted at a W/FM value of 170 MJ/kg, where W, F, and M mean the apparent input energy of the rf power (MJ/min), the monomer flow rate (mol/min), and the molecular weight of the monomer gas (kg/mol), respectively.

Methane, ethylene, acetylene, and sulfur dioxide (purchased from Takachiho Trading Co., 99.9% purity) were used as monomers without further purification.

Infrared and X-Ray Photoelectron Spectra

Flaky polymers scraped from the glass plate were used for the preparation of KBr disks. IR spectra of the polymers were recorded with a Nihon Bunko fouria transform spectrometer FT/IR-3.

Polymer films (approximately 100 nm thick, as determined by interferometry) deposited on silicon wafers were used for the measurement of XPS spectra. XPS spectra were recorded with a Shimadzu 750 electronspectrometer employing MgK_α exciting radiation at 8 kV and 30 mA. The Au core level at 84.0 eV was used for calibration of the energy scale. The complex C_{1s} and S_{2p} spectra were resolved with a Shimadzu ESCAPAC 760 data system under the assumption of Gaussian distribution. Three parameters, the position and height of the peak and the full width at half-maximum (FWHM), were varied until rough correspondence to the observed spectra was obtained.

Surface Energy

Contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate on the plasma polymers deposited on the glass plates were measured at 20°C using an Erma contact anglemeter G-I with a goniometer. The contact angle data were analyzed to estimate the surface energy according to Kaelble's method.[7]

Chemical Modification of Oxygen-Containing Groups

Oxidized moieties involving carboxyl, hydroxyl, and carbonyl groups in the plasma polymers prepared from C_2H_4/SO_2 mixture were chemically modified to be able easily to analyze them by XPS. The details of the modification have been given in the literature.[8] Carboxyl, hydroxyl, and carbonyl groups

TABLE I
Appearance of Plasma Polymers Prepared from C_2H_2/SO_2, C_2H_4/SO_2, and CH_4/SO_2 Mixtures

Mixture	SO_2 concentration (mol %)	Appearance
C_2H_2/SO_2	0	Transparent film
	40	Transparent film
	60	Transparent film
	80	Powder
C_2H_4/SO_2	0	Transparent film
	40	Transparent film
	60	Transparent film
	80	Transparent film
CH_4/SO_2	0	Transparent film
	40	Translucent powder + film
	60	Translucent powder + film
	80	Viscous liquid

were treated with 2,2,2-trifluoroethanol, trifluoroacetic anhydride, and pentafluorophenylhydrazine to yield corresponding fluorinated esters and hydrazones. The qualitative and quantitative analyses for the carboxyl, hydroxyl, and carbonyl groups were performed by XPS from a large chemical shift of the fluorinated carbon atoms and the relative intensity between fluorine and carbon atoms.

Antithrombogenity

Plasma polymers deposited on Milipore filters (VSWPO, pore size 25 nm) were immersed in cow's blood containing sodium citrate for 2 h. Afterwards, the specimens were rinsed with $0.01M$ phosphate buffer at pH 7.4, and then treated with 2.5% glutalaldehyde solution of the buffer. The number and shape of blood platelets adsorbed at the plasma polymer surfaces were visually observed from pictures by scanning electron microscopy.

RESULTS AND DISCUSSION

Preliminary experiments showed that plasma polymerization of C_2H_2/SO_2, C_2H_4/SO_2, and CH_4/SO_2 mixtures yielded oily, filmy, and powderlike products depending on reaction conditions, especially the magnitude of the W/FM value as well as the mixture composition. The operation at a moderate W/FM value of 170 MJ/kg was an adequate condition to obtain filmlike products. Table I shows the appearance of the plasma polymers prepared at 170 MJ/kg from the three mixtures. The plasma polymerization of C_2H_2/SO_2 and C_2H_4/SO_2 mixtures gave transparent films, but that of CH_4/SO_2 mixture was difficult to yield filmlike products. The formation of filmlike products may be related to the unsaturation of hydrocarbons used as monomers. Therefore, we focused mainly on plasma polymerization of C_2H_2/SO_2 and C_2H_4/SO_2 mixtures.

The polymer deposition rate in plasma polymerization of C_2H_2, C_2H_4, and CH_4 was influenced by the addition of SO_2: The deposition rate for C_2H_2, C_2H_4, and CH_4 was 4.11, 0.66, and 0.06 $\mu g/cm^2$ min, respectively. The rate for

TABLE II
Atomic Ratio of Plasma Polymers Prepared from C_2H_2/SO_2 and C_2H_4/SO_2 Mixtures

Plasma polymers	SO_2 concentration (mol %)	Atomic ratio	
		S/C	O/C
Polymers from	14	0.12	0.25
C_2H_2/SO_2 mixtures	40	0.49	0.44
	60	0.44	0.89
	80	0.63	0.57
Polymers from	3	0.07	0.15
C_2H_4/SO_2 mixtures	14	0.24	0.27
	40	0.45	0.37
	80	0.52	0.88

the C_2H_2/SO_2, C_2H_4/SO_2, and CH_4/SO_2 mixtures containing 50 mol % SO_2 was 1.20, 1.42, and 0.51 $\mu g/cm^2$ min, respectively. This indicates a possibility that SO_2 molecules in discharge state could interact with these hydrocarbons to yield plasma polymers containing SO_2 moieties.

Chemical Composition of Plasma Polymers

The wide scanning of XPS spectra showed that the plasma polymers from C_2H_2/SO_2 and C_2H_4/SO_2 mixtures possessed much amount of sulfur atoms as well as carbon and oxygen atoms. Table II shows the atomic ratios (S/C and O/C) for the plasma polymers as a function of the mixture composition, which were estimated from the relative intensity of the XPS spectra. The estimation allowed for correction of the cross section for photoionization but did not allow for correction of the escape depth and sensitivity of photoelectrons, so that the atomic ratio estimated here does not mean exactly quantitative but semiquantitative composition. The S/C atomic ratio, as shown in Table II, increased with increasing the SO_2 concentration. The O/C atomic ratio also increased with increasing the SO_2 concentration, and sulfur and oxygen concentration of the plasma polymers is a comparable amount. This indicates that the plasma polymers are hydrocarbon chains with sulfur and oxygen moieties. The details of the sulfur and oxygen moieties were analyzed by IR and XPS.

The IR spectra exhibited characteristic absorptions due to sulfur moieties. Figure 1 shows typical IR spectra for the plasma polymers prepared from C_2H_2/SO_2, C_2H_4/SO_2, and CH_4/SO_2 mixtures. The plasma polymers prepared from C_2H_2, C_2H_4, and CH_4 possess strong absorption peaks due to CH_3, CH_2, and CH groups at 2925, 1460, and 1380 cm^{-1}, and wide and weak absorption peaks due to C=O and C—O groups at 1730–1630 and 1150–1000 cm^{-1}. In addition to the absorption peaks, for the plasma polymers prepared from C_2H_2/SO_2, C_2H_4/SO_2, and CH_4/SO_2 mixtures containing 60 mol % SO_2, new and intense absorption peaks appeared at 1220, 1180, and 1070 cm^{-1}. These absorption peaks are related to the stretching vibration of S=O groups.[9]

Pouchert[10] has reported that the S=O stretching vibration is shifted by the oxidation number of sulfur atom: The stretching vibration of sulfoxide
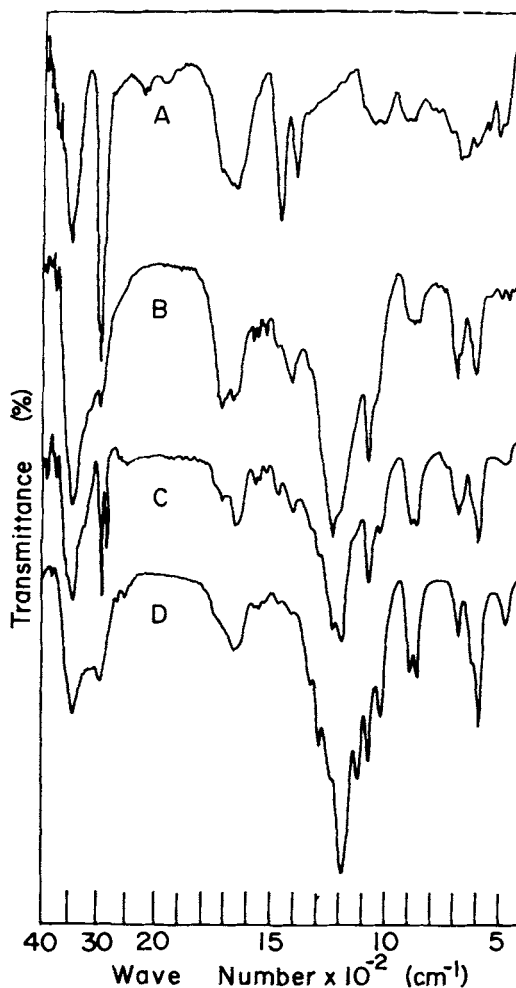
Fig. 1. IR spectra of plasma polymers prepared from acetylene (A), C_2H_2/SO_2 mixture (60 mol % SO_2) (B), C_2H_4/SO_2 mixture (60 mol % SO_2) (C), and CH_4/SO_2 mixture (60 mol % SO_2) (D).

$[-S(O)-]$ groups appears at 1025 cm^{-1}, that of sulfone $[-S(O)_2-]$ groups at 1136 and 1326 cm^{-1}, that of sulfonate $[-S(O)_2-O-]$ groups at 1176 and 1326 cm^{-1}, that of sulfonic acid $[-S(O)_2-OH]$ groups at 1070, 1168 cm^{-1}, that of sulfite $[-O-S(O)-O-]$ at 1205 cm^{-1}, and that of sulfate $[-O-S(O)_2-O-]$ groups at 1205 and 1403 cm^{-1}. With reference to Pouchert's report the new absorption peaks at 1180 and 1070 cm^{-1} could be assigned sulfonic acid groups, and the other absorption peak at 1220 cm^{-1} may be assigned either sulfite or sulfate groups. This assignment was further examined by XPS.

Figures 2 and 3 show typical C_{1s} and S_{2p} core level spectra for the plasma polymers prepared from C_2H_2/SO_2 and C_2H_4/SO_2 mixtures. The C_{1s} core level spectra, as shown in Figure 2, distributed from 283 to 292 eV with an FWHM value of 2.7 eV. These spectra were deconvoluted into three C_{1s}
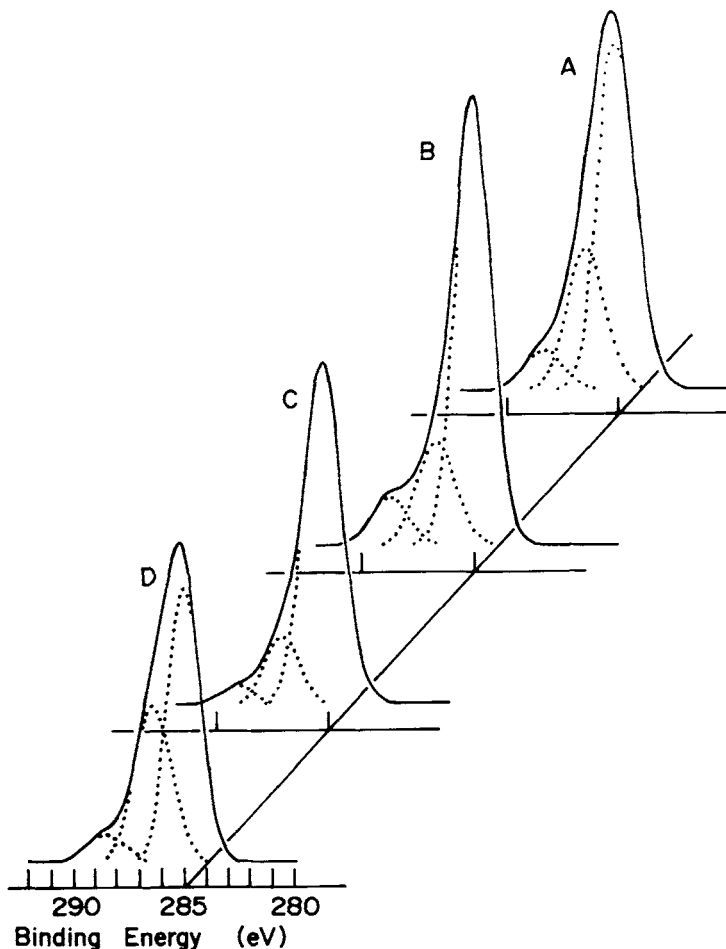
Fig. 2. XPS (C_{1s}) spectra of plasma polymers prepared from C_2H_2/SO_2 mixture (40 mol % SO_2) (A), (80 mol % SO_2) (B), C_2H_4/SO_2 mixture (40 mol % SO_2) (C), and (80 mol % SO_2) (D).

features, which were assigned CH_2 (at 285.0 eV), $C-O$, or $C-S$ (at 286.4–286.9 eV), and $C=O$ groups (at 288.5–289.0 eV). The S_{2p} core level spectra (Fig. 3) showed two peaks with an FWHM value of 2.4 eV. Each of them was deconvoluted into two components. The deconvolution is represented in dashed line in Figure 3.

Theoretically, the S_{2p} core level has two different spins, $2p_{1/2}$ and $2p_{3/2}$. The cross section for photoionization is 0.590 and 1.15 for $S_{2p_{1/2}}$ and $S_{2p_{3/2}}$ core levels, respectively.[11] Therefore, the intensity ratio for $S_{2p_{3/2}}$ and $S_{2p_{1/2}}$ core levels is expected to be 1.15/0.59 = 1.95. The relative peak ratio between the two deconvoluted components is 1.8–2.0, which corresponds to the intensity ratio (1.95) estimated theoretically. This comparison indicates that the four deconvoluted components are categorized into two pairs of $S_{2p_{3/2}}$ and $S_{2p_{1/2}}$ core level combination (163.5–163.8, 164.8–165.0; 168.0–168.3, 169.1–169.5). The $S_{2p_{3/2}}$ and $S_{2p_{1/2}}$ combination appearing at lower binding energy regions could be assigned sulfur atom having no oxygen (thio groups), and the other
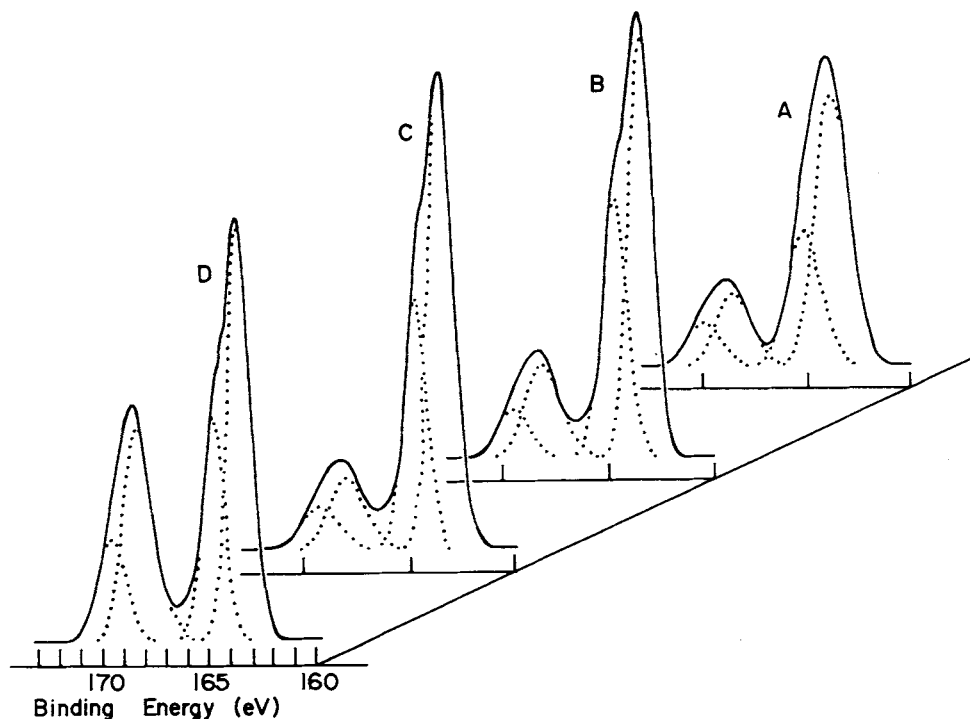
Fig. 3. XPS (S_{2p}) spectra of plasma polymers prepared from C_2H_2/SO_2 mixture (40 mol % SO_2) (A), (80 mol % SO_2) (B), C_2H_4/SO_2 mixture (40 mol % SO_2) (C), and (80 mol % SO_2) (D).

$S_{2p_{3/2}}$ and $S_{2p_{1/2}}$ combination appearing at higher binding energy regions could be assigned sulfur atom attached to two or three oxygen atoms (sulfone, sulfite, or sulfonic acid).[12] The presence of sulfate groups in the plasma polymers is excluded because sulfate groups will appear at 169.4 eV for $S_{2p_{3/2}}$ core level.

Table III shows a typical chemical composition of the oxygen moieties generated in the plasma polymers during the plasma polymerization of

TABLE III
Oxidized Moieties at Surface of Plasma Polymers Prepared from C_2H_4/SO_2 Mixture

Polymers	Oxidized moieties at surface (number/100 carbon atoms)			
	OH	C=O	COOH	Total
Plasma polymers from C_2H_4/SO_2 mixture (2/3)	0.7	1.0	0.3	2.0
Plasma polymers from C_2H_4/SO_2 mixture (1/4)	1.2	2.2	0.2	3.6
Polyethylene exposed to O_2 plasma	0.02	5.3	1.6	6.9
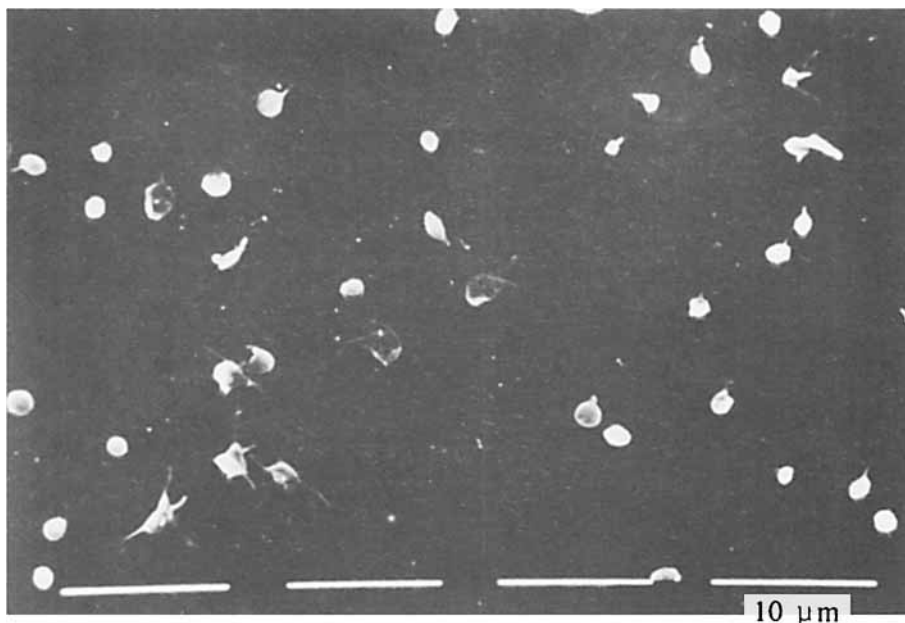
(A)
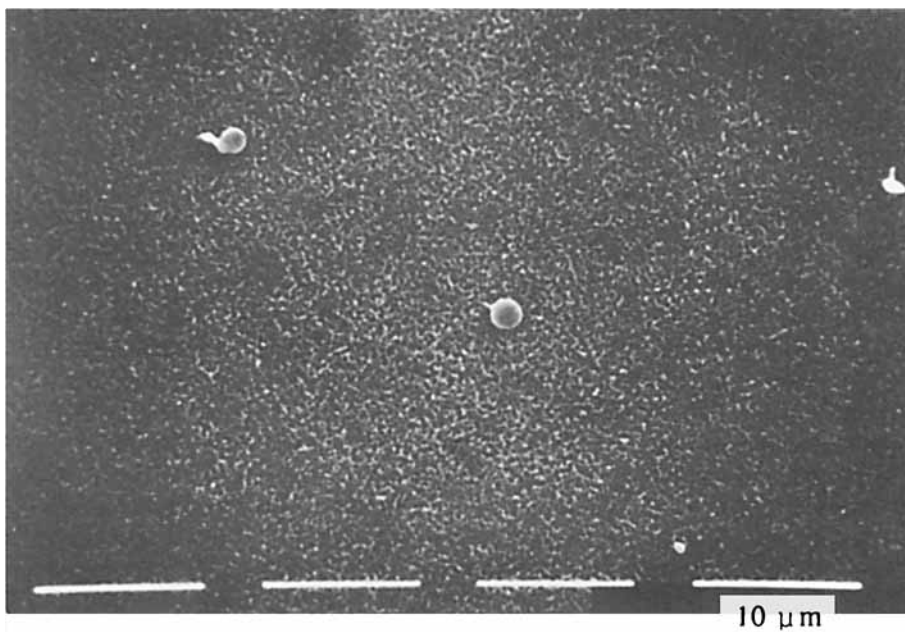
(B)

Fig. 4.   SEM pictures of plasma polymer surface prepared from C_2H_4/SO_2 mixture (80 mol % SO_2); (A), blank (Milipore filter); (B), plasma polymer.

C_2H_4/SO_2 mixtures. Hydroxyl, carbonyl, and carboxyl groups were modified by fluorination and were determined by XPS. This determination does not exclude the presence of ether links as an oxygen moiety. Table III shows that the oxygen moieties such as hydroxyl, carbonyl, and carboxyl groups exist at the plasma polymer surfaces. Carbonyl and hydroxyl groups were main products. Similar oxygen moieties are formed by oxygen plasma (Table III). The concentration of the oxygen moieties formed by oxygen plasma was more than twice as much as that formed by C_2H_4/SO_2 plasma. This indicates that C_2H_4/SO_2 plasma may be not so oxidative atmosphere compared with oxygen plasma.

From these IR and XPS results we summarize the chemical composition of plasma polymers prepared from C_2H_2/SO_2 and C_2H_4/SO_2 mixtures.

1. Similar polymers are plasma-polymerized from C_2H_2/SO_2 and C_2H_4/SO_2 mixtures. These polymers contain a large amount of sulfur and oxygen moieties.
2. The sulfur moieties of the plasma polymers are thio, sulfite, and sulfonic acid groups. Thio group is a main product and reached 70–80 mol % of the total sulfur moieties. The remains (20–30 mol %) are sulfonic acid and sulfite groups.
3. The oxygen moieties of the polymers are hydroxyl, carbonyl, and carboxyl groups. The hydroxyl and carbonyl groups are main products.

Surface Properties of Plasma Polymers

Plasma polymers which were prepared from C_2H_2/SO_2 and C_2H_4/SO_2 mixtures showed hydrophilic properties: The surface energy for the plasma polymer prepared from C_2H_2/SO_2 mixture containing 60 mol % SO_2 was 55.6 mN/m, and that for the plasma polymer prepared from C_2H_4/SO_2 containing 80 mol % SO_2 was 53.7 mN/m, while the plasma polymers prepared from C_2H_2 and C_2H_4 were hydrophobic (the surface energy was 32.9 mN/m). The increased hydrophilicity may be due to polar groups including sulfonic acid, hydroxyl, and carbonyl groups.

The plasma polymer surface showed antithrombogenity. Figure 4 shows SEM pictures of the plasma polymer surface after immersion in cow's blood. The plasma polymers which were prepared from C_2H_4/SO_2 mixture containing 80 mol % SO_2 and which were deposited on Milipore filter were used as specimens. Significantly, from the pictures the number of blood platelets adsorbed at the plasma polymer surface is fewer than the original Milipore filter. Sulfonic acid groups of the plasma polymers might contribute to the antithrombogenity. This indicates a possibility that the coating with the plasma polymers may be available to improve antithrombogenity of biomaterials.

CONCLUSION

The following conclusions may be drawn from this study regarding plasma polymerization of hydrocarbon/sulfur dioxide mixtures.

1. Plasma polymerization of C_2H_2/SO_2 and C_2H_4/SO_2 mixtures gives film-like products having a large amount of sulfur and oxygen moieties.
2. The sulfur moieties involve thio groups, sulfite groups, and sulfonic acid groups. The thio group is a main product and reaches 70–80 mol % of the total sulfur moieties. The remains (20–30 mol %) are sulfonic acid and sulfite groups. The oxygen moieties are hydroxyl and carbonyl groups with small amount of carboxyl groups.
3. The plasma polymers give hydrophilic and antithrombogenic surfaces.

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