Durable and Hydrophobic Surface Modification by Plasma Polymers Deposited from Acetylene/ Hexafluoroacetone Ethylene/ Hexafluoroacetone, and Ethane/ Hexafluoroacetone Mixtures

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Synopsis

Plasma polymerization of mixtures of ethane/hexafluoroacetone (HFA), ethylene/HFA, and acetylene/HFA deposit hydrophobic and thin films. The IR and XPS measurements of the deposited films show that fluorination with HFA occur to yield hydrophobic plasma films which possess CF_3, CF_2, and CF moieties. The advancing contact angle of water on the surface of the deposited films increases with increasing the HFA concentration, especially plasma polymer films prepared from the acetylene/HFA mixture (87.5 mol % HFA) show an advancing contact angle of 126 degrees. Such high hydrophobicity of the plasma polymer surface is attributed to high concentration of fluorinated carbons, especially CF_3 side groups. The CF_3 concentration in the plasma polymers reach about 30 mol % of the total carbon units. These surfaces show no change in advancing contact angle even when stored in a moist atmosphere of 60% RH at 20°C for at least 2 weeks.
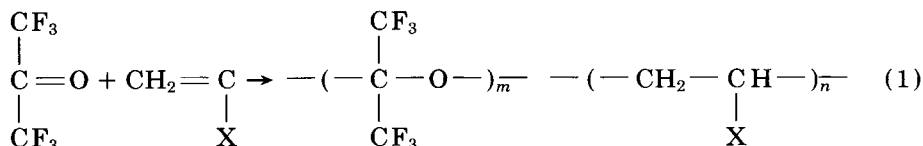
INTRODUCTION

Surface fluorination calls potentially attention for modifying the surface characteristics of polymers without affecting the bulk properties of the polymer materials. For surface fluorination two techniques have been proposed: one is a direct fluorination process with fluorine gas[1-6] and the other is a plasma fluorination process.[7-14] The former process is conventional but suffers from nuisances: uncontrolled fluorination, degradation of polymer surface, and hazardous fluorine gas.[5,6] The plasma fluorination process is preferred rather than the direct fluorination process with fluorine gas because of easy treatment. The fluorination of polymer surfaces is accomplished only by exposing them to plasma of fluorine-containing compounds. Inorganic compounds involving SF_6, NF_3, and BF_3 and organic fluorocarbons involving CF_4 and C_2F_6 are frequently used as plasma gases for the plasma fluorination process.[7-10]
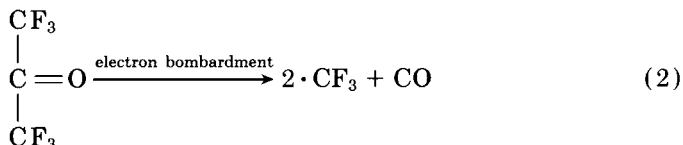
In the practice of surface modification we should direct attention to the durability of the hydrophobic surfaces modified in addition to how hydrophobic the polymer surface is modified. Hydrophobic moieties being present at air/ polymer interface begin to move away from the surface into the bulk of the polymer when the polymer surface is exposed to humid atmosphere or is immersed in water, and the surface changes from hydrophobic to hydrophilic.[15]

The decay of the hydrophobicity is closely related to the rotational and diffusional movement of the polymer chains near the surfaces. The highly crystalline polymers show slower decay of the hydrophobicity than low-crystalline polymers.[12] Thus the durable hydrophobic surface may be accomplished by the restriction of the polymer chain movement (crosslinking).

Plasma polymers are highly crosslinked and show low mobility of polymer chains because of crosslinking. It is expected that plasma polymers will give durable and hydrophobic surfaces. Hexafluoroacetone (HFA) is able to be copolymerized with vinyl monomers by radical initiators to yield random copolymers,[16]

$$
\begin{array}{ccc}
CF_3 & & CF_3 \\
| & | & | \\
C=O + CH_2=C \rightarrow & -(-C-O-)_m & -(-CH_2-CH-)_n \qquad (1) \\
| & | & | \\
CF_3 & X & CF_3 \qquad\qquad X
\end{array}
$$

while HFA in plasma state is subjected to degradation and CF_3 radicals are generated with liberation of CO molecules,[10]

$$
\begin{array}{c}
CF_3 \\
| \\
C=O \xrightarrow{\text{electron bombardment}} 2 \cdot CF_3 + CO \qquad (2) \\
| \\
CF_3
\end{array}
$$

Accordingly, our interests are: (1) What interaction between HFA and unsaturated compounds occurs in a discharge state? Is the interaction either copolymerization of HFA and unsaturated monomers or fluorination with CF_3 moieties? (2) How hydrophobic are the formed plasma polymers? (3) How durable are the plasma polymer surfaces? This study focused on plasma polymerization of the mixture of HFA and hydrocarbons, ethane, ethylene, and acetylene. Chemistry of the formed plasma polymers and their hydrophilicity were investigated.

EXPERIMENTAL

Plasma Polymerization

A handmade reactor which was inductively coupled with a radio frequency (rf) (13.56 MHz) generator (Nihon Koshuha Co., Japan, model SKN-05P, max. power 500 W) was used in this study for plasma polymerization. It consisted of a Pyrex glass tube (100 mm inner diameter and 400 mm long) with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for the inductive coupling of the rf generator. Plasma polymers were deposited on high- and low-density polyethylene sheets (10 × 20 mm × 1.6 mm thick, and 10 × 30 mm × 30 μm thick) which were mounted on a glass plate with double-side adhesive tape and which were positioned horizontally in the glass tube reactor. The details of the reactor have been given in a literature.[17]

The experimental procedures for plasma polymerization were essentially the same as reported elsewhere.[17] The reaction system was evacuated to approximately 0.13 Pa, and the substrate surface was exposed to argon plasma for 2 min in order to eliminate water adsorbed on the substrate surfaces. The system was again evacuated to 0.13 Pa, and then monomer gas, adjusted to a flow rate of 2 cm^3 (STP)/min at 1.3 Pa, was introduced into the reaction chamber. The plasma polymerization was continued at a rf power of 100 W for 0.5 to 1.0 h.

Hexafluoroacetone (HFA) (purchased from Central Glass Co., Japan, more than 99% purity), ethane, ethylene, and acetylene (purchased from Takachiho Trading Co., Japan, 99.9% purity) were used as monomers.

Infrared and X-Ray Photoelectron Spectra

IR spectra of the plasma polymers were recorded on a Nihon Bunko fourie transform spectrometer FT/IR-3 by means of attenuated total reflection (ATR). For ATR the crystal of KRS-5 was used and the purity of the crystal surface was monitored before each analysis by recording spectrum of the bare crystal. The incidence angle of infrared light was 45°. The spectral resolution was 2 cm^{-1} and 1000 scans were recorded on each sample.

Polymer films (approximately 100 nm thick, as determined by interferometry) deposited on polyethylene sheets were used for measurement of XPS spectra. XPS spectra were recorded on 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} spectra were subjected to the curve-fitting procedure using a Shimadzu ESCAPAC 760 data system. Gaussian distribution was assumed and 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 accomplished. The sensitivity factors (S) for following core levels were used to calculate the relative atomic concentration on the plasma polymer surfaces: $S(C_{1s})$ = 1.00, $S(F_{1s})$ = 4.30, $S(O_{1s})$ = 2.90.

Surface Energy

Advancing contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate on the plasma polymers deposited on the polyethylene sheets were measured at 20°C using an Erma contact anglemeter G-I with a goniometer. From the contact angle data the surface energy was estimated according to Kaelble's method.[18]

RESULTS AND DISCUSSION

Polymer Deposition and Chemical Composition of Plasma Polymers prepared from Ethane/HFA, Ethylene/HFA, and Acetylene/HFA Mixtures

Figure 1 shows the polymer deposition rate in plasma polymerization of ethane/HFA, ethylene/HFA, and acetylene/HFA mixtures as a function of the HFA concentration. The polymer deposition rate in plasma polymerization of the three mixture systems is enhanced by the HFA addition and reaches
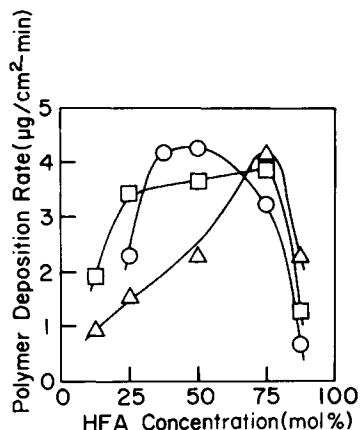
Fig. 1.   Polymer deposition rate in plasma polymerization of ethane/HFA (△), ethylene/HFA (□), and acetylene/HFA mixtures (○) as a function of HFA concentration.

maximums at HFA concentration of 50 to 75 mol %. This indicates that HFA in the presence of hydrocarbons such as ethane, ethylene, and acetylene acts as a comer of plasma polymerization although HFA alone is not plasma-polymerized and give no polymer deposition. This enhanced deposition rate indicates a capability of HFA to be interacted with the hydrocarbons in a discharge state. What interaction occurs in a discharge state?

Table I shows the elemental composition (the F/O, F/C, and O/C atomic ratio determined by XPS) for the plasma polymers prepared from the ethane/HFA, ethylene/HFA, and acetylene/HFA mixtures. If HFA is copolymerized with the hydrocarbons according to eq. (1) the formed plasma polymers will involve $(CF_3)_2C-O-$ unit as HFA component and CH_x units as hydrocarbon component. The polymer should possess a F/O atomic ratio of 6 independent of the HFA concentration. The F/O atomic ratio for the plasma polymers prepared from the mixtures, as shown in Table I, is 7.3 to 19 depending on the

TABLE I
Elemental Composition and Surface Energy of Plasma Polymers Prepared from Ethane/HFA,
Ethylene/HFA, and Acetylene/HFA Mixtures as a Function of HFA Concentration

Starting mixture	HFA concentration (mol %)	Atomic ratio			Surface energy (mJ/m)		
		F/O	F/C	O/C	γ_s	γ_s^d	γ_s^p
Ethane/HFA	62.5	—	—	—	49.0	48.9	0.1
	75.0	11	1.1	0.1	43.4	41.9	1.5
	87.5	7.3	2.2	0.3	11.1	11.0	0.1
Ethylene/HFA	62.5	—	—	—	48.7	48.0	0.7
	75.0	9	0.9	0.1	41.0	40.0	1.0
	87.5	10	2.2	0.2	12.4	12.1	0.3
Acetylene/HFA	62.5	—	—	—	61.5	59.3	2.2
	75.0	8	1.6	0.2	18.6	17.8	0.8
	87.5	19	1.9	0.1	9.7	9.6	0.1

HFA concentration. Therefore we conclude that the interaction attributed to the enhanced deposition rate is not the copolymerization between HFA and hydrocarbons.

The F/C atomic ratio for the plasma polymers prepared from the three mixtures containing 75 mol % HFA was about 1.0 to 1.5 and increased to about 1.9 to 2.2 when HFA of 87.5 mol % was mixed. This result show that the plasma polymers have highly fluorinated carbon units. Details of these fluorinated carbon units were investigated by FT/IR and XPS.

Figure 2 shows typical IR spectra of the plasma polymers prepared from the ethane/HFA, ethylene/HFA, and acetylene/HFA mixtures containing 87.5 mol % HFA. In the spectra a strong absorption peak due to C-F stretching vibration appeared at 1230 cm^{-1} and weak absorption peaks due to $C(O)F$, $C=O$, and CF_3 groups appeared at 1850 and 980; 1740, 1720, 1700, and 1665; and 740 cm^{-1}, respectively.[19] Figure 3 shows the XPS (C_{1s}) spectra for the same plasma polymers as used for the inspection of IR spectra. At sight we can understand that the C_{1s} spectra involve at least four C_{1s} features having different binding energy. The spectra were deconvoluted into four components which could be assigned to $\underline{C}F$, $\underline{C}F-CF_n$, $\underline{C}F_2$, and $\underline{C}F_3$ units with the assistance of the substituent effects of fluorine atoms. The chemical shifts are 2.9 and 0.7 eV for the primary and secondary effect of fluorine substituent at α and β carbon position, respectively.[20] However the component assigned to CF units involves $C=O$ and $C(O)F$ groups because the plasma polymers contain somewhat oxygen-containing groups. The relative peak area of each unit shows that the three plasma polymers possess no hydrocarbon unit but fluorocarbon units. Highly fluorinated carbon units (CF_2 and CF_3 groups) reach about 60 mol % of the total carbon units. The terminal CF_3 groups which will contribute to the enhancement of hydrophobicity occupy about 30 mol %.

Therefore we conclude from these results that HFA acts as a fluorinating reagent in plasma polymerization of the HFA/ethane, HFA/ethylene, and
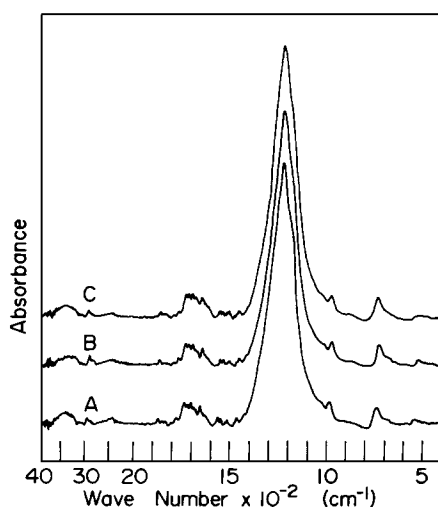

Fig. 2. IR spectra of plasma polymers prepared from ethane/HFA (A), ethylene/HFA (B), and acetylene/HFA mixtures (C) containing 87.5 mol % HFA.
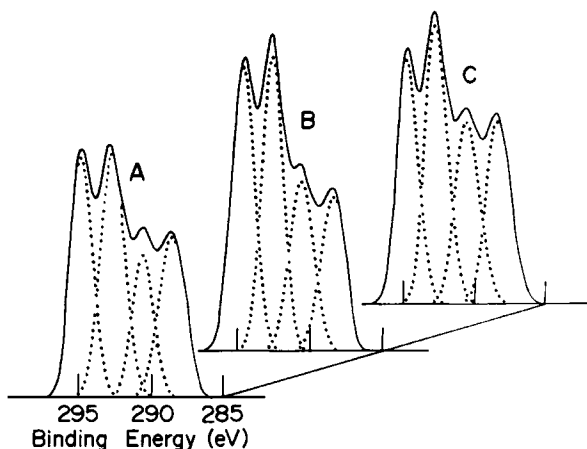
Fig. 3.   XPS (C_{1s}) spectra of plasma polymers prepared from ethane/HFA (A), ethylene/HFA (B), and acetylene/HFA mixtures (C) containing 87.5 mol % HFA.

HFA/acetylene mixtures. HFA in a discharge state is degraded into CF_3 radicals according to eq. (2), and the CF_3 radicals would proceed the fluorination of CH_2 and CH moieties of the plasma polymers and the addition to polymer chain radicals. This is the interaction bringing about the enhanced polymer deposition rate.

Hydrophobicity of Plasma Polymers prepared from HFA/Ethane, HFA/Ethylene, and HFA/Acetylene Mixtures

Figure 4 shows the advancing contact angle of water against the surface of the plasma polymers deposited on polyethylene sheet as a function of the HFA concentration. The advancing contact angle increased with increasing the HFA concentration. At a HFA concentration of 87.5 mol %, the water contact angle
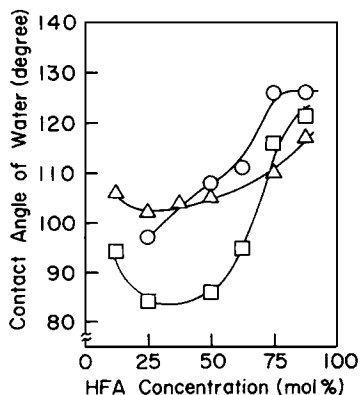

Fig. 4.   Advancing contact angle of water on surface of plasma polymers prepared from ethane/HFA (△), ethylene/HFA (□), and acetylene/HFA mixtures (○) as a function of HFA concentration.

reaches 126, 122, and 112 degrees for the plasma polymers prepared from the acetylene/HFA, ethylene/HFA, and ethane/HFA mixtures, respectively. The reproducibility of the advancing contact angle measurement is within 2 degrees. Observation using scanning electron microscopy at a resolution of about 0.1 μm showed that surfaces of the deposited plasma polymers were smooth without roughness. Surface topographical changes having dimensions less than 0.1 μm are expected to have an affect on contact angle of water.[9] Thus we conclude that the contact angle changes result from the chemical modification of deposited plasma polymers. The plasma polymer surfaces prepared from the acetylene/HFA, ethylene/HFA, and ethane/HFA mixtures are superior or comparable in hydrophobicity to polytetrafluoroethylene (an advancing contact angle of 116 degrees).

Furthermore to evaluate the hydrophobicity the surface energy was estimated from the data of the advancing contact angles of five liquids according to the Kaelbe's method.[18] Table I shows the surface energy of the plasma polymers prepared from the acetylene/HFA, ethylene/HFA, and ethane/HFA mixtures as a function of the HFA concentration. The surface energy decreased with increasing the HFA concentration. The surface energy is about 43, 41, and 19 mJ/m for the plasma polymers prepared from the ethane/HFA, ethylene/HFA, and acetylene/HFA mixtures, respectively when HFA of 75 mol % is added, and at 87.5 mol % HFA addition, reaches about 11, 12, and 10 mJ/m. This indicates that the powerful fluorination occurs when the HFA concentration increases from 75 to 87.5 mol %.

Durability of Hydrophobic Surface

Figure 5 shows the advancing contact angle of water against surface of the plasma polymers prepared from the acetylene/HFA mixture containing 87.5 mol % HFA as a function of storage time. The specimens for the durability inspection were the plasma polymers which were deposited on a high-density polyethylene sheet and stored in a moist atmosphere of 60% RH at 20°C. The surface, stored at 20°C, shows no change in advancing contact angle of water until at least two weeks (Fig. 5): the water contact angle is 126 degrees as deposited and 125.6 degrees when two weeks passed from the deposition.

Strobel et al.[10] have reported that the HFA-plasma irradiation is able to fluorinate a polypropylene sheet to obtain hydrophobic surface whose water contact angle is 114 degrees. We also tried the surface fluorination of polyeth-

TABLE II
C_{1s} Component of Plasma Polymers Prepared from Ethane/HFA,
Ethylene/HFA, and Acetylene/HFA Mixtures

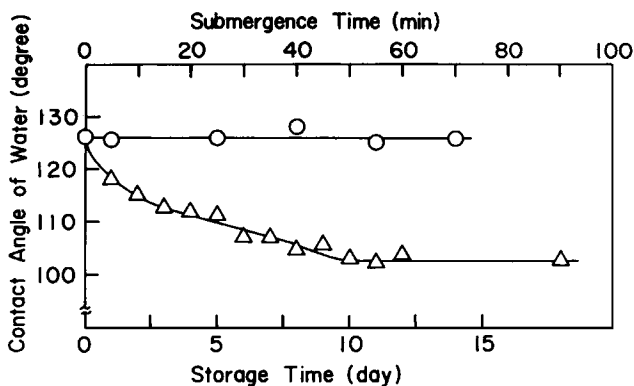| Starting mixture	HFA concentration (mol %)	C_{1s} component (mol %)			
		$\underline{C}F$	$\underline{C}F\text{-}CF_n$	$\underline{C}F_2$	$\underline{C}F_3$
Ethane/HFA	87.5	23	16	32	29
Ethylene/HFA	87.5	19	20	30	31
Acetylene/HFA	87.5	22	21	31	26

Fig. 5.   Advancing contact angle of water on surface of plasma polymers prepared from acetylene/HFA mixture (87.5 mol % HFA) as function of storage time ($\bigcirc$) in 60% RH at 20°C and submergence time ($\triangle$) in hot water of 80°C.

ylene sheet by the HFA-plasma irradiation. The advancing contact angle of water against the sheet irradiated for 10 min, which showed an advancing contact angle of 128° just after the irradiating gradually decreased with the lapse of the storage time. Finally when a storage time of 10 min passed the advancing contact angle of water reached 97 degrees which was just close to that of the original polyethylene sheet (97 degrees). Such decay of hydrophobicity in a moist atmosphere is not a special case but other evidences have been reported. Yasuda and colleagues[12,13] have discussed the durability of polymer surfaces (Nylon 6 and poly(ethylene terephthalate) fluorinated by the CF_4-plasma irradiation. They concluded that the decay of the hydrophobicity is controlled by the rotational and the diffusional migration of the fluorine-containing moieties from the air/polymer interface into the bulk phase of the polymers, and that durable polymer surfaces would be obtained by the restriction of the polymer chains movement.

In the sense of durability we can say that the plasma polymers prepared from the acetylene/HFA mixture offer stable and hydrophobic surface. This high durability of the plasma polymers may be attributed to the crosslinked polymer chain which is an inherent character of plasma polymers.

When the plasma polymers deposited on a high-density polyethylene sheet are submerged in hot water at 80°C, the advancing contact angle of water decreases gradually with the lapse of the submergence time, and reaches a constant of 103 degrees after 50 min or more (Fig. 5). The surface energy of the plasma polymers submerged for 90 min is estimated to be about 21 mJ/m. The plasma polymers prepared from the acetylene/HFA mixture do not offer perfectly stable surface without the movement of hydrophobic moieties.

CONCLUSION

Plasma polymerization of mixtures of ethane/HFA, ethylene/HFA, and acetylene/HFA were investigated from the viewpoint of polymerization reaction and surface properties. Results are summarized as follows:

1. HFA acts as fluorinating reagent in plasma polymerization of the mixtures. The plasma polymers prepared from the three mixtures contain high concentration of fluorine atoms (the F/C atomic ratio is 1.9 to 2.2), and are mainly consist of CF, CF_2, and CF_3 units. The CF_3 side groups in the plasma polymers occupy about 30 mol % of the total carbon units.

2. Plasma polymers prepared from the three mixtures show hydrophobic property. The advancing contact angle of water on the plasma polymer surfaces increases with increasing the HFA concentration, and at 87.5 mol % HFA addition the water advancing contact angle of water reaches 126, 122, and 112° for the plasma polymers prepared from the acetylene/ HFA, ethylene/HFA, and ethane/HFA mixtures, respectively.

3. The surface of the plasma polymers deposited from the acetylene/HFA mixture show no change in advancing contact angle of water as far as stored in a moist atmosphere of 60% RH at 20°C.

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