Photochemical Surface Modification of Poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) Film with Triethylamine

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Thin film of poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) reacted with triethylamine (TEA) upon UV irradiation to give hydrophilic and oleophilic surface through complicated defluorination reactions such as introduction of diethylaminoethyl group and formation of unsaturated bonds. Solvent and additive effects on the photoreaction strongly suggested the involvement of an electron transfer process from TEA to FEP.

Surface modification of fluoropolymers is an important process in their fabrication especially in adhesion since raw material strongly refuses adhesive, ink, or other chemicals. In general, treatment with alkali metal in liquid ammonia or with oxygen plasma is performed to modify the surface.[1] Several attempts with laser irradiation have been reported for physical and chemical surface modification of fluoropolymers, which will be advantageous from viewpoints of convenient and short-time operation, and spatial control.[2-4] For the chemical reactions with vapor[3] and solution,[4] introduction of some chemical functionality and defluorination were observed. We describe here a photochemical reaction of poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) with triethylamine (TEA) giving hydrophilic and oleophilic surface.

An FEP film (4 x 4 cm^2, 100 μm thickness) was placed on a cell in contact with a nitrogen-purged acetonitrile solution of TEA (1 x 10^{-2} mol dm^{-3}) and was irradiated with a KrF laser (248 nm; 35 mJ cm^{-2} $pulse^{-1}$) through the film to excite the solution at interface. The irradiated surface was analyzed by measuring contact angles with water (θ_W) and with hexadecane (θ_{HD}) and by X-ray photoelectron spectroscopy (XPS). Figure 1 shows changes in the contact angle of the FEP film with water and those with hexadecane droplet with laser shot number, which indicates that the irradiated surface gradually becomes both hydrophilic and oleophilic. After 6000 shot, the contact angle with water increased probably because of decomposition of hydrophilic functionalities. When the contact angle of an FEP film irradiated in acetonitrile was measured with buffer droplets of various pH values (contact angle titration),[5] a sigmoidal behavior with pH showing an abrupt increase from pH6 to pH7 was observed to indicate introduction of basic diethylaminoethyl group to the surface (Figure 2). This group will show high hydrophilicity in an acidic media through protonation to give quaternary ammonium salt. On the other hand, the contact angle of a film irradiated in water was almost independent of pH. The film irradiated in acetonitrile colored yellow to light brown, but those irradiated in water and in cyclohexane were less colored. UV-visible absorption spectrum of the film irradiated in acetonitrile showed broad absorption from 200 to 600 nm, which was decreased by treatment with bromine vapor to indicate the presence of conjugated olefinic bondings. Elementary analysis of the film surface by XPS indicated considerable decrease in fluorine and introduction of nitrogen and oxygen by the irradiation (Table 1). Since similar irradiation in the absence of TEA little affected the contact angles and atomic ratios, the changes described above are attributed to a photochemical reaction between FEP and TEA. Though source of oxygen is not clear at present, it may be derived from oxygenation or hydrolysis of the introduced functionalities. The properties of the irradiated surface will satisfy practical adhesivity as compared to the previous results.[1,2b,4c]

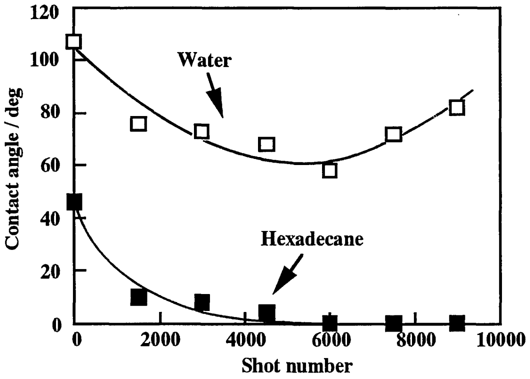

Figure 1. Plots of contact angles of water and hexadecane droplets with irradiated FEP films: [TEA] = 0.01 mol dm^{-3} in acetonitrile, KrF laser 35 mJ cm^{-2} $pulse^{-1}$.

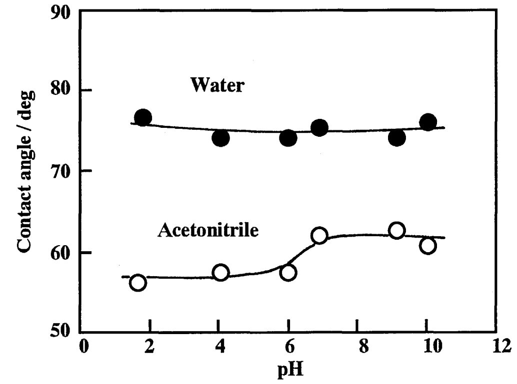

Figure 2. Contact angle titration of an FEP film irradiated with KrF laser in contact with aqueous and acetonitrile solutions of TEA: [TEA] = 0.01 mol dm^{-3}, KrF laser 35 mJ cm^{-2} $pulse^{-1}$, 6000 shot.

As summarized in Table 1, the preference of polar solvent for the present reaction suggests the involvement of ionic intermediates. Use of water, however, was ineffective probably owing to rapid protonation to quench the excited singlet state of TEA giving $(CH_3CH_2)_3NH^+\ldots OH^-$.[6,7] We also studied the light source effect on the photoreaction in acetonitrile, which was monitored by the contact angle and XPS measurements (Table 2). TEA showed two broad absorption bands ranging from 220 to 260 nm (S_1-S_0 transition) and from 210 to 190 nm (S_2-S_0

Table 1. KrF-laser induced surface modification of FEP film with triethylamine[a]

Solvent (ε)[b]	θ_W/deg	θ_{HD}/deg	F/C[c]	N/C[c]	O/C[c]
before irradiation	107	48	2.11	0.00	0.02
cyclohexane (2.0)	107[d]	48[d]	2.14[d]	0.00[d]	0.01[d]
	90	20	1.47	0.02	0.08
acetonitrile (35.9)	107[d]	48[d]	2.15[d]	0.00[d]	0.02[d]
	58	<5	0.29	0.06	0.13
water (80.2)	102[d]	40[d]	2.16[d]	0.00[d]	0.02[d]
	76	16	1.49	0.02	0.08

[a] [TEA] = 1 x 10^{-2} mol dm^{-3}; KrF laser: 35 mJ cm^{-2} $pulse^{-1}$, 6000 shot. [b] Dielectric constant. [c] Measured by XPS. [d] In the absence of TEA.

Table 2. Light source effect on the surface modification of FEP film with triethylamine in acetonitrile[a]

Wavelength/nm	θ_W/deg	θ_{HD}/deg	F/C[b]	N/C[b]	O/C[b]
before irradiation	107	48	2.11	0.00	0.02
185[c]	66	<5	0.04	0.12	0.06
248[d]	58	<5	0.29	0.06	0.13
	96[e]	30[e]	1.47[e]	0.04[e]	0.06[e]
254[f]	78	<5	0.21	0.04	0.11
	102[g]	40[g]	1.92[g]	0.00[g]	0.02[g]
308[h]	107	48	2.12	0.00	0.01
	76[g]	7[g]	0.34[g]	0.05[g]	0.16[g]

[a] [TEA] = 1 x 10^{-2} mol dm^{-3}. [b] Measured by XPS. [c] 30-W super low-pressure Hg lamp, 2 h. [d] KrF laser: 35 mJ cm^{-2} $pulse^{-1}$, 6000 shot. [e] In the presence of CCl_4; [CCl_4] = 0.1 mol dm^{-3}. [f] 30-W super low-pressure Hg lamp, UV-D33S glass filter, 5 h. [g] In the presence of naphthalene (N); [N] = 5 x 10^{-3} mol dm^{-3}. [h] XeCl laser: 45 mJ cm^{-2} $pulse^{-1}$, 6000 shot.

transition) in cyclohexane. Upon direct excitation at 185 and 254 nm with a super low-pressure Hg lamp, similar results were obtained as observed with KrF laser. On the other hand, irradiation at 308 nm with XeCl laser (45 mJ cm^{-2} $pulse^{-1}$; 6000 shot) did not induce the reaction to rule out non-resonant two-photonic excitation, though two-photon energy at 308 nm is enough for excitation of TEA. The reaction with KrF laser was considerably quenched by the addition of 0.1 mol dm^{-3} of CCl_4. Irradiation with XeCl laser in the presence of naphthalene (N) induced the reaction,[8] whereas no considerable change was observed upon irradiation at 254 nm with a Hg lamp in the presence of N.[9] These quenching and sensitizing effects suggested the involvement of an electron transfer process from TEA to FEP, where two mechanisms can be considered: direct electron transfer and photoionization of TEA followed by capture of solvated electron (e_s^-) by FEP. Details are now in progress and will be given elsewhere. The intermediacy of radical cation of TEA ($TEA^{\cdot+}$) and radical anion of FEP ($FEP^{\cdot-}$) in both the mechanisms, however, will result in the introduction of diethylaminoethyl group to the FEP surface as observed for various organic acceptors such as halo- and cyano-aromatics and aliphatic amines.[10]

The present results have demonstrated an example of photochemical activation of inert fluoropolymer surface by the use of Hg lamps and XeCl laser as well as ArF and KrF lasers as reported before.[3,4,11]

References and Notes

†† Student research assistant of JAERI from Osaka University, Apr. 1994 - Mar. 1995.

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