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Surface Modification of Polymeric Materials by Remote Plasma

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SUMMARY: Remote plasma treatment has been proposed here as a special technique to modify polymer surfaces. A concept for the remote plasma treatment rises from the anticipation that radicals rather than electrons and ions in plasma contribute to introduction reactions of functional groups and the radicals have longer lifetime than electrons and ions. As a result, effective surface modification at a position far from the plasma zone (remote plasma treatment) will be done because radicals rather than electrons and ions become a predominant species for the modification.

Fluoropolymers, poly(tetrafluoroethylene), tetrafluoroethylene-hexafluoropropylne copolymer, and tetrafluroethylene-perfluoroalkylvinylether copolymer, were modified by the remote hydrogen plasma. Their surface morphology and surface chemistry were demonstrated. An application of the remote hydrogen plasma treatment for improvement of adhesion between copper metal and the fluoropolymers was also demonstrated.

Introduction

Plasma treatment is a technique to modify surface properties and surface topology of polymeric materials. Modification of polymeric surfaces from hydrophobic to hydrophilic or from hydrophilic to hydrophobic is easily accomplished by means of exposing their surfaces to plasmas for a few minutes. Table 1 shows typical results of hydrophilic and hydrophobic modification of polyethylene surfaces by eight different plasmas1). In these modification processes, hydrophilic or hydrophobic groups are introduced on the polyethylene surfaces by reactions with plasma (introduction of functional groups). Radicals in the plasmas play an important role in the introduction reactions. The radicals abstract hydrogen atoms from polymer chains to form carbon radicals in the polymer chains, and the carbon radicals react with other radicals in plasma to form hydrophilic or hydrophobic groups on the polymer surface. These are essential reactions for the introduction reactions of functional groups. On the other hand, the other species besides in the plasmas, electrons and ions, bombard the polymer surface during the process of introduction reactions, and initiate degradation reactions on the polymer surface. As a result, degradation products with low-molecular weight and an injur-

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ed layer (weak boundary layer) are formed on the polymer surface.

Therefore, in the surface modification by plasma, two different processes, introduction of functional groups and degradation, occur simultaneously on the polymer surfaces. In the sense of chemistry, the degradation of polymer surfaces is an uncalled-for process in the surface modification. As long as plasma is used as reactive species for the modification, degradation on the polymer surfaces is never avoided from the surface modification by plasma treatment. Is there any amelioration for plasma treatment without degradation of polymer surfaces? We propose here remote plasma as a possible amelioration.

Table 1 Water contact angle on polyethylene surfaces treated with plasmas

Kind of plasma	Water contact anlge (degree)
-	99
CO	16
CO_2	8
NO	25
NO_2	37
O_2	35
SF_6	117
CF_4	121
C_2F_6	114

Introduction of functional groups and degradation on polymer surface

Table 2 compares effects of plasma treatment on polyethylene (PE) and polypropylene (PP). PE and PP surfaces were modified with Ar and O_2 plasmas and then adhered with epoxy adhesive[2]. Peel strength for the PE/epoxy adhesive and PP/epoxy adhesive systems was evaluated from the viewpoint of effects by the plasma treatment. Surface modification by the Ar and O_2 plasma was effective for PE in improving the adhesion with epoxy adhesive. On the other hand, the Ar and O_2 plasmas were no effective for PP in the adhesion improvement. This disparity between PE and PP in effects of the plasma treatment

Table 2 Effects of plasma treatment on adhesion between polymers and epoxy adhesive

Polymers	Kind of plasma	90° Peel strength (N/25 mm)
PE	-	0.1
	Ar	17.4
	O_2	28.6
PP	-	0
	Ar	0.1
	O_2	0.1

may be due to not only introduction reactions of functional groups but also degradation reactions. When PE and PP were exposed to Ar plasma, weight loss and degradation products were formed on their surfaces.

Table 3 shows weight loss and water-soluble degradation products formed on PE and PP surfaces, when their surfaces were exposed to Ar plasma at 25W for 2 min2). Weight loss and water-soluble product formed on the PE surface were very small. On the other hand, weight loss and degradation products on the PP surface were about ten times larger than those from PE. Therefore, the PP surface is easy to be degraded by the Ar plasma, and as a result, the PP surface is deposited by degradation products. The deposition of degradation products on the PP surface may be a factor to disturb the adhesion with epoxy adhesives.

Table 3 Degradation products formed by Ar plasma treatment (at 25W for 2 min)

Polymers	Weight losss by Ar plasma treatment ($\mu g/cm^2$)	Fromation of water-soluble products ($\mu g/cm^2$)
PE	2	1
PP	16	11

The two tables (Tables 2 and 3) indicate an important aspect on modification of polymer surfaces by plasma. Actions by plasma on polymer surfaces contain an introduction reaction of functional groups and a degradation reaction. The introduction reaction does not isolate from the degradation reaction but coexists always with the degradation reaction during the surface modification process (Fig. 1). How much the introduction reaction or the degradation reaction occurs depends on the nature of polymers as well as plasma conditions. Even when

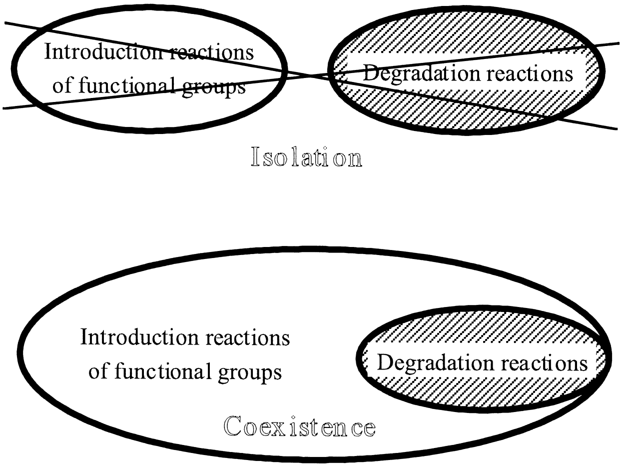


Fig.1: Aspect of plasma treatment process

the same plasma is used for the surface modification, different effects of the plasma treatment will appear in the case of polymers having different plasma susceptibility, as an example, PE and PP. We can not get out of the degradation process, as long as plasma is used as a reactive species for the surface modification. In the sense of chemistry, the degradation reaction is uncalled-for one in the surface modification. How to minimize the degradation reaction is an important factor to make a success of effective surface modification.

Surface modification by remote plasma

We propose here a special technique, "Remote Plasma Treatment" to minimize degradation reactions occurring during the plasma treatment. A concept for the remote plasma treatment rises from the anticipation that radicals rather than electrons and ions in plasma contribute to introduction reactions of functional groups and the radicals have longer lifetime than electrons and ions$^{3)}$.

Plasma contains electrons, ions, and radicals that can interact with polymer surfaces. The interaction leads to introduction reactions of functional groups on the surfaces and degradation reactions of the polymer surfaces. The introduction reactions are mainly initiated by interaction with radicals. On the other hand, the degradation reactions are initiated by the bombardment of electrons and ions. If radicals alone are separated from the plasma and then, interact with the polymer surface, the introduction reactions will occur on the polymer surfaces without degradation reactions. Fig. 2 shows typical elemental reactions in hydrogen plasma$^{4-8)}$. There is a small difference in rate constant between the generation reactions of hydrogen radical (H) and hydro-

1. Generation of active species

$$e + H_2 \xrightarrow{k_1} H_2^+ \qquad k_1 = 2.32\text{x}10^{-11}\text{cm}^3/\text{s}$$

$$e + H_2 \xrightarrow{k_2} 2H \qquad k_2 = 4.49\text{x}10^{-12}$$

2. Disappearance of active species

$$H_2^+ + e \xrightarrow{k_3} H_2 \qquad k_3 = 5.66\text{x}10^{-8}$$

$$2H + H_2 \xrightarrow{k_4} 2H_2 \qquad k_4 = 8.3\text{x}10^{-33}$$

Fig. 2: Typical elemental reactions in hydrogen plasma

gen ion (H_2^+), but there is a large difference between the disappearance reactions of the hydrogen radical and hydrogen ion. The rate constant (k_4) of the disappearance of hydrogen radicals is negligibly small compared with that of hydrogen ions (k_3). As a result, the hydrogen radical will be a predominant component if the hydrogen plasma elapses after discharge.

Fig. 3 shows a special reactor to separate hydrogen radicals from hydrogen plasma[9]. The reactor consisted of a cylindrical Pyrex glass tube (45 mm diameter, 1000 mm long) and a columnar stainless steel chamber (300 mm diameter, 300 mm height). The Pyrex glass tube had two gas inlets for the injection of hydrogen and argon gases and a copper coil for the energy input of rf power (13.56 MHz frequency) at an end of the tube. The Pyrex glass tube at the other end was jointed with the stainless steel chamber in a manner of Viton O ring flange. The stainless steel chamber was contained a vacuum system of a combination of a rotary pump and a diffusion pump. Polymer samples for modification were positioned in the Pyrex glass tube at a constant distance of 800 mm from the center of the copper coil.

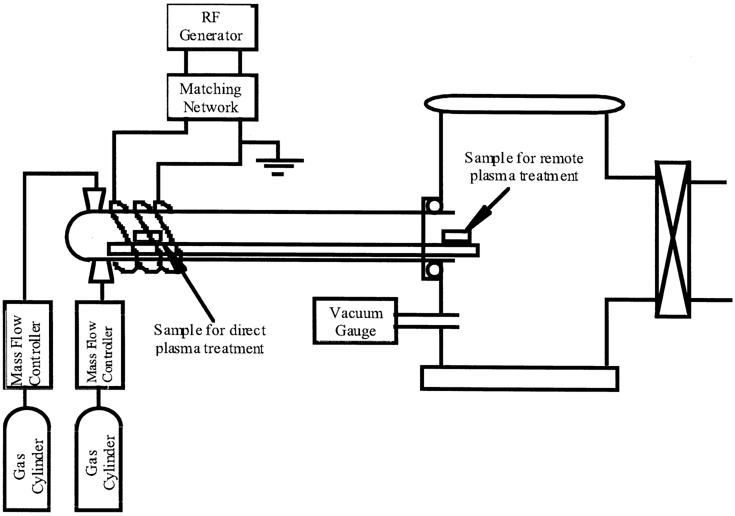
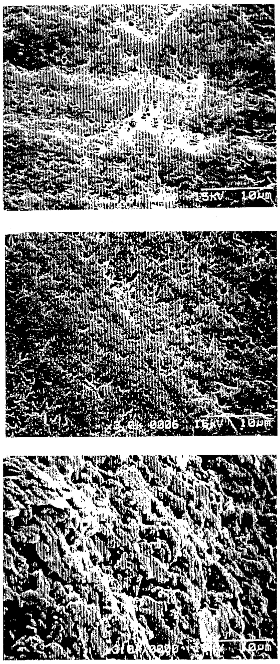


Fig. 3: Schematic presentation of reactor for remote plasma treatment

Hydrogen gas (10 cm^3/min) was injected from the gas inlet, and discharged at the copper coil to make hydrogen plasma. Active species, electrons, hydrogen ions, and hydrogen radicals, in the hydrogen plasma traveled in the direction of the stainless steel chamber with hydrogen gas stream and streamed out from the reactor. At a distance of 800 mm from the plasma zone, hydrogen radicals will be a predominant component and electrons and hydrogen ions will be minor component, because of a large difference in lifetime. This is a basic concept of "Remote Plasma Treatment". Difference between the remote and conventional plasma treatments is the relative position of polymer samples from the plasma zone. We call here the conventional plasma treatment "direct plasma treatment".

Comparison of remote and direct plasma treatments

Fig. 4 shows SEM pictures of poly (tetrafluoroethylene), PTFE, surfaces treated with the remote and direct hydrogen plasmas (at 100W, at 13.56 MHz)10). The PTFE surface treated with the remote hydrogen plasma (The PTFE sample was set up at a distance of 80cm far from the hydrogen plasma zone.) showed a scabrous surface that contained many micropores of 0.2 – 0.4 μm wide and 1 – 2 μm long. This SEM picture is similar surface morphology to the original PTFE. On the other hand, the PTFE surface treated with the direct hydrogen plasma (The PTFE sample was set up in the hydrogen plasma zone.) showed distinctly different one in the surface morphology from the remote hydrogen plasma-treated PTFE surface. The surface roughness was increased to 1 – 2 μm wide and 3 – 7 μm long. This comparison indicates that less degradation occurred in the remote hydrogen plasma, and heavy degradation reaction occurred in the direct hydrogen plasma.



Original PTFE

PTFE treated with
remote hydrogen
plasma at 100W
for 120s

PTFE treated with
direct hydrogen
plasma at 100W
for 30s

Fig. 4: SEM pictures of PTFE surfaces treated with remote and hydrogen plasmas

The two PTFE surfaces treated with the remote and direct hydrogen plasmas were analyzed with XPS (Table 4)9). The PTFE surface treated with the remote hydrogen plasma showed a large decrease in F/C atom ratio and increase in O/C atom ratio. Similarly, the PTFE surface treated with the direct hydrogen plasma showed similar decrease in F/C atom ratio and increase in O/C atom ratio. This result indicates that defluorination and oxidation occurred in the remote hydrogen plasma treatment as well as in the direct hydrogen plasma. Even when the PTFE surface did not touch directly to the hydrogen plasma, defluorination occurred effectively. The formation of oxygen moieties on the PTFE surface by the remote hydrogen plasma may be due to post reactions of carbon radicals with oxygen in air after the plasma treatment. Carbon radicals are formed by means of abstraction reactions of fluorine atoms from the PTFE surface by hydrogen atoms and by means of the bond scission of the C-F and C-C bonds by electron and ion bombardment.

Table 4 Atom composition of remote and direct hydrogen-plasma-treated PTFE surfaces

Plasma	Atom composition on treated PTFE surfaces	
	F/C atom ratio	O/C atom ratio
Remote H_2	0.41	0.12
Direct H_2	0.60	0.07
(Untreated)	1.90	0.05

XPS spectra gave us useful information on the chemical composition of the PTFE surfaces treated with the remote and direct hydrogen plasmas. Fig. 5 shows typical XPS (C_{1s}) spectra for the two PTFE surfaces[9]. The C_{1s} spectra for the untreated PTFE showed a peak at 292.5 eV due to CF_2CF_2 groups. The remote- and direct-hydrogen plasma-treated PFTE showed, as shown in Fig. 5, complex C_{1s} spectra having two peaks. The spectra were decomposed into five components appearing at 285.9-296.0, 287.6-287.9, 289.6-289.8, 292.5, and 293.7-294.1 eV. These five components are assigned to the $\underline{C}H_2CHF$ groups at 285.9-296.0 eV, $\underline{C}HFCH_2$ and C=O groups at 287.6-287.9 eV, $\underline{C}H(OR)CHF$ groups at 289.6-289.8 eV, $\underline{C}F_2CF_2$ groups at 292.5 eV, and $\underline{C}F_3CF_2$ and $\underline{C}F(OR)_2CF_2$ groups at 293.7-294.1 eV. The underlined carbon atoms are objective atoms for the assignment. This analysis shows that there is no difference in chemical composition between the PTFE surfaces treated with the remote and direct hydrogen plasmas. The remote hydrogen plasma as well as the direct hydrogen plasma has a high capability of the surface modification of PTFE. Hydrogen substitution on the PTFE surface occurs in the modification process by the remote hydrogen plasma.

The O_{1s} spectra also gave us useful information on oxygen moieties formed on the PTFE surfaces. The spectra are not represented here for shortness' sake. The O_{1s} spectra were decomposed into two components, O=C and O-C groups, appearing at 532.3-532.4 and 533.6-533.7 eV, respectively. This analysis shows that oxidation occurred on the carbon atoms to form C=O and C-O groups.

From these results, we conclude that the remote hydrogen plasma leads to effective modification of PFTE surfaces without heavy degradation on their surfaces.

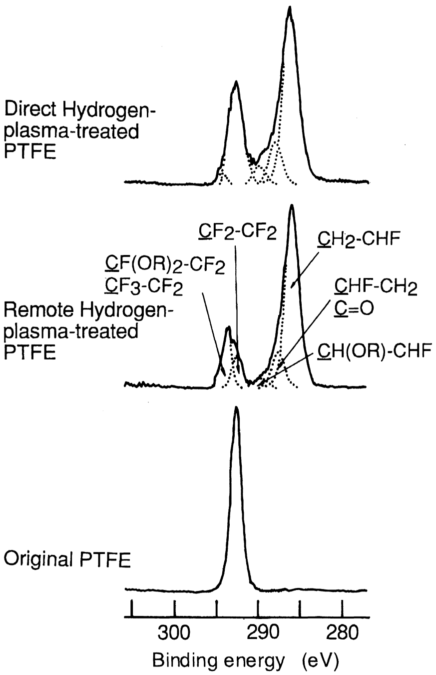


Fig. 5: C_{1s} spectra for PTFE surfaces treated with remote and direct hydrogen plasmas

Application of Remote Hydrogen Plasma Treatment – Copper Metallization on Fluoropolymer Surfaces -

Fluoropolymers; poly(tetrafluoroethylene), PTFE; tetrafluroethylene-hexafluoropropylene copolymer, FEP; and tetrafluroethylene-perfluoroalkylvinylether copolymer, PFA; show distinguished physical and chemical properties such as high-temperature resistance and chemical resistance as well as hydrophobic properties. In addition to these distinguished properties, these polymers show excellent electrical-properties which are high resistivity of more than 10^{18} Ωcm, a low dielectric constant of 2.1, and a low dissipation factor of less than 2 x 10^{-4}. Furthermore, FEP and PFA can be fabricated easily in conventional melt processes because of amorphous structure. From this aspect, we believe that the fluoropolymers may be an outstanding insulator from electrical currents with high frequency (GHz), for example, a printed wiring board for integrated circuits and an insulator for electrical wires. To apply the fluoropolymers for the electrical materials, copper metallization on the fluoropolymer surfaces was investigated here using the surface modification by the remote hydrogen plasma.

The fluoropolymer (PTFE, FEP, and PFA) sheets (50 μm thickness) were treated with the remote hydrogen plasma (at 13.56 MHz and at 25 – 100W), and then metallized by a combination of an electroless- and electro-platings. The total thickness of the deposited copper metal on the fluoropolymer surfaces was about 30 μm (0.2 μm thickness by the electroless plating and 30 μm thickness by the electroplating). The adhesion between the copper metal layer and the fluropolymer sheet was evaluated as T-type peel strength at a peel rate of 10 mm/min.

Fig. 6 shows typical results for the peel strength as a function of the plasma exposure time in the remote hydrogen plasma treatment[11]. PFA sheets (5 mm wide) were used as a fluoropolymer substrate for the copper metallization experiment. The peel strength, as shown in Fig. 6, increased with increasing the plasma exposure time, reached a maximum of 101 mN/5mm, and then leveled off. This indicates that the surface modification by the remote hydrogen plasma treatment contributes improvement of adhesion between copper metal and PFA. The surface modification by the direct hydrogen plasma also was effective in improving the adhesion, but the improvement was not as powerful as that by the remote hydrogen plasma (shown in Fig. 6). The peel strength was increased from 0 to 24 mN/5mm by the direct hydrogen plasma treatment, but further increase was never seen. This indicates that the direct hydrogen plasma was not effective in modifying the PFA surfaces, although defluorination occurred effectively on the PFA surfaces. The ineffectiveness may be due to heavy degradation reactions on the PFA surface.

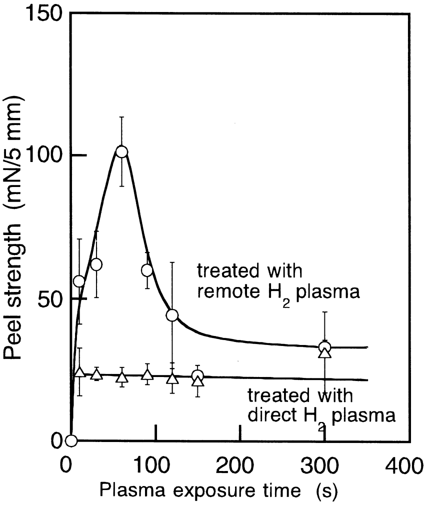


Fig. 6: Peel strength for copper metal/ PFA composites as a function of plasma exposure time in remote and direct hydrogen plasma treatment processes.

XPS (C_{1s}, F_{1s}, and Cu_{2p}) spectra for surfaces of the PFA and copper metal layers failed from the copper metal/PFA system showed a mechanism of the failure mode from the composites[11]. The PFA and copper metal layers peeled off from the copper metal/PFA system showed similar C_{1s} and F_{1s} spectra and no Cu_{2p} spectrum. The C_{1s} spectra contained an intense and sharp peak at 292.8 eV and a small but widely distributed peak at 287 – 284 eV. The F_{1s} spectra contained a symmetrical peak at 690 eV. These spectra show that the PFA and copper metal layers peeled off from the copper metal/PFA system are similar in chemical composition. The failure occurred in an inner layer of plasma-treated PFA polymer rather than at the interface between the copper metal and PFA layers.

The other fluoropolymers, PTFE and FEP, also were modified by the remote hydrogen plasma, and the adhesion with copper metal was improved effectively (Table 5)[12]. The surface modification by the remote hydrogen plasma contributes to improvement of the adhesion between copper metal and fluoropolymers.

Table 5 Peel strength for copper metal/fluoropolymer systems

Fluoropolymers	Peel strength (mN/5mm) Untreated	Treated with remote H_2 plasma
PTFE	7.5	92
FEP	0	195
PFA	0	101

Conclusion

We have proposed here a special technique, “Remote Plasma Treatment” to minimize degradation reactions occurring in the plasma treatment. A concept for the remote plasma treatment rises from greatly longer lifetime of radicals than electrons and ions. Capability of the remote hydrogen plasma has been demonstrated in modifying fluoropolymer surfaces and applying the modification into the copper metallization of the fluoropolymer surfaces. We believe that the remote hydrogen plasma treatment is a preferable technique for surface modification of fluoropolymers.

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