

# Surface Coating Protective Against Oxidative Plasma Etching of Polypropylene

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**ABSTRACT:** Polypropylene (PP) sheets were coated with the ultrathin polymer layers by plasma polymerization of hexamethyldisiloxane and two other Si-containing monomers, and the protection effects from oxidative plasma etching were investigated. Etching was evaluated by the weight loss of PP sheets after the exposure to an oxidative plasma of O<sub>2</sub> or air. The effects of plasma polymer coating on the etching resistance were investigated with respect to the type of plasma polymer, thickness of a coating layer, oxidative plasma etching conditions, etc. Weight of the coated PP sheets was less changed and the substrates remained stable after a certain period of oxidative plasma treatments, during which time the original PP film had prominently lost weight. The importance of the crosslinked network with —Si— components in plasma polymers on the etching resistance was suggested from the results. Infrared spectra were taken and analyzed with the plasma polymers after O<sub>2</sub>-plasma treatments, and the increase in the Si—O structure was indicated by the increase in the peak intensity at 1023 cm<sup>-1</sup>. Stabilization against oxidative etching was attributed to the crosslinked Si—O structure on the surface layer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1049–1057, 1997

**Key words:** polypropylene; plasma polymer; hexamethyldisiloxane; oxidative plasma etching; Si—O structure

## INTRODUCTION

Plasma polymerization is an advantageous procedure to prepare ultrathin polymer membranes, and much interest has been directed toward the practical application.<sup>1,2</sup> Conventional plasma polymerization is carried out under vacuum or reduced pressure. The reactive intermediates can travel in the longer distance range without mutual collision under such vacuum condition, and as a result, the more uniform deposition of a polymer and the treatments are expected by the control of discharge conditions.<sup>2</sup> Such uniformity is

an advantage of plasma polymerization compared to other treatments such as corona treatments.

Plasma polymerization has been attempted with various organic compounds, and the nature is, of course, dependent on the chemical composition of a starting monomer. Siloxanes are, in general, effectively polymerized, and the mechanically stable membranes are formed. Hexamethyldisiloxane (HMDSiO) is one of the popular siloxane compounds, and the plasma polymerization has been investigated extensively; for example, the chemical structures have been analyzed with the spectroscopic procedures of IR<sup>3–9</sup> and ESCA,<sup>4,6</sup> and the surface morphology has been investigated by SEM and AFM.<sup>10</sup> Plasma polymerization of HMDSiO in the presence of O<sub>2</sub> has been also attempted, and it was found that oxygen

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is introduced in the crosslinked —Si— network.<sup>11</sup> HMDSiO/O<sub>2</sub> plasma polymer coating functioned effectively as a barrier layer against permeation of oxygen.<sup>12</sup> Generation of the SiO<sub>x</sub> structure was also suggested by the remote plasma reaction of O<sub>2</sub> made simultaneously with plasma polymerization of some siloxane monomers without special heating.<sup>13</sup>

Incidentally, polypropylene (PP) is susceptible to oxidation and degraded by the active oxygen, and various additives were used for the stabilization. Construction of a protection layer from the attack of such reactive species should be effective for the stabilization of PP, and from this aspect the appropriate coatings have been considered. Stabilization of PP should be due to the suppressed permeation of active oxygen as well as the direct protection against etching by the tight plasma polymer layers. Indeed, ultrathin plasma polymer coating of HMDSiO has been attempted, and some improvements in the weatherability of PP were achieved with respect to the retention of mechanical properties such as tensile strength.<sup>14</sup>

In the present work, PP films were coated with the plasma polymers of HMDSiO and two other silicon-containing monomers, and the protection against oxidative plasma etching was investigated. The results were discussed from the effects of the type of a plasma polymer, the coating thickness, and so forth. The chemical structure of the polymers after the oxidative plasma etching treatments was analyzed by IR, and the chemical effects were discussed. If the present oxidative plasma etching can be applied as an alternative method of an outdoor weathering method, it is profitable as a time-saving and simplified test.

## EXPERIMENTAL

### Materials

Monomers used for plasma polymerization in the present work were; HMDSiO (C<sub>6</sub>H<sub>18</sub>Si<sub>2</sub>O, MW = 162.4), hexamethyldisilane (HMDSi; C<sub>6</sub>H<sub>18</sub>Si<sub>2</sub>, MW = 146.4), and hexamethyldisilazane (HMD-SiZ; C<sub>6</sub>H<sub>18</sub>Si<sub>2</sub>N, MW = 161.4). Toluene (C<sub>6</sub>H<sub>8</sub>, MW = 92) was also used as a hydrocarbonic plasma polymer source for comparison. These chemicals were subjected to plasma polymerization as supplied without further purification, but fully degassed under vacuum to remove the dissolved air.

Polymer sheets were prepared by hot pressing

of atactic PP (density = 0.866, Scientific Polymer Products). Film sheets of poly(dimethylsiloxane) (PDMSiO; Silastic) and poly(ethylene terephthalate) (PET; Mylar) were also used, and the oxidative plasma etching behaviors were compared to that of PP.

### Plasma Polymerization

The procedure of the plasma polymerization was principally the same as that described before.<sup>15,16</sup> Glow discharge plasma was generated by an inductively coupled radio frequency of 13.56 MHz, and the plasma reaction was carried out in a reactor made of Pyrex glass tubing (40-cm length and 4.4-cm diameter). A monomer vapor was introduced through a vacuum valve (SS-4BMG, Nupro Co.), and the system pressure was controlled by the opening.

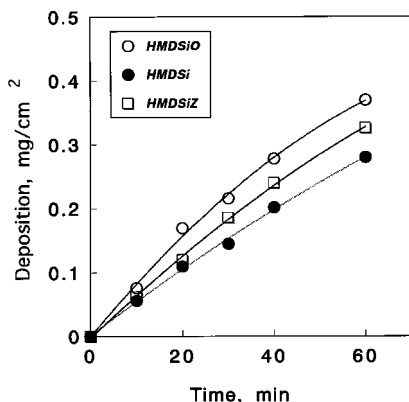
Monomer vapor was supplied at a fixed flow pressure of 3.5 Pa, and the plasma polymerization was made at 50 W in general. The flow rate was calculated from the pressure increase after closing the stop cock valve of the pumping site in the system, and 2.4–2.5 mL (STP)/min was given at 3.5 Pa for these monomers. The power was intensive enough to provide the full glow in the present system for plasma polymerization. The weight of the plasma polymers deposited on a micro cover glass plate (1.8 × 1.8 cm) was measured, and the deposition rate of polymers was determined. Thus, the thickness of plasma polymer layer was obtained from the deposition weight considering the density of polymers, and controlled by the polymerization time.

### Oxidative Plasma Etching

PP substrate films (2.5 × 2.5 cm) were coated with these plasma polymers at a certain thickness, and subjected to further oxidative plasma etching by O<sub>2</sub> or air. The oxidative plasma was generated in the same reactor system as the plasma polymerization (4.4-cm diameter, 40-cm length). The film size is smaller than the reactor, and therefore, the uniform polymerization and also uniform oxidative etching result. Oxidative etching treatments were repeated at the 10–20 min intervals, and the susceptibility of PP films to etching was evaluated by the weight loss.

### IR

Infrared (IR) spectra were taken using an IR-photometer (Paragon-1000, Perkin-Elmer) with the



**Figure 1** Deposition profile of plasma polymers of HMDSiO, HMDSi, and HMDSiZ (3.5 Pa, 50 W).

plasma polymers deposited on a KBr disc. The deposited polymers were directly exposed to O<sub>2</sub>-plasma, and the measurements of IR were repeated at the 5–10 min intervals of treatments. The IR absorbance peak intensity was obtained from the height from the base line, and the changes in the intensities were followed against the oxidative etching time.

## SEM

The surface morphology of the HMDSiO-plasma polymers was observed by a scanning electron microscopy (SEM) with an apparatus of DS-720 (Topcon Co. Ltd., Japan) at 15 kV.

## RESULTS AND DISCUSSION

### Polymer Deposition Profile

Figure 1 shows the deposition profiles of plasma polymers of HMDSiO, HMDSi, and HMDSiZ obtained at 3.5 Pa and 50 W in the present reactor system. The deposition amount increased with the polymerization time, and the order was related to the molecular weight of a supplied compound.

The discharge power dependence of the polymer deposition was also investigated in the power range of 10–100 W. The results for HMDSiO and HMDSi are shown in Figure 2. Here, the deposition weight was compared after the reaction of 20 min. The deposited amounts became constant beyond 30–40 W, and it is indicated that the plasma polymerization reached equilibrium at the power higher than this range. When the power was lower, the activation of monomers did not sufficiently take place, and as a result plasma po-

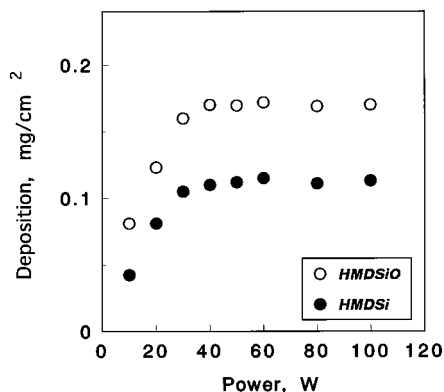
lymerization was not completed, i.e., the supplied monomer was not fully converted to a polymer deposit.

It should also be noted here that the deposition of these Si-monomers did not decrease even at the higher power condition of 100 W. In other words, the formed polymers were not degraded at the higher power. The reaction of organic compounds in glow discharges is competitive between the polymer deposition and the degradation, and the tendency is dependent on the nature of chemical composition. Some fluorine monomers such as CF<sub>2</sub>=CF<sub>2</sub> are much degraded, and a plasma polymer deposition amount becomes smaller gradually with the power increase beyond the critical point.<sup>16</sup> Hydrocarbon compounds having a aromatic structure such as benzene and toluene are more polymerizable to give much deposition, but lead also to gradual degradation under the drastic power condition.

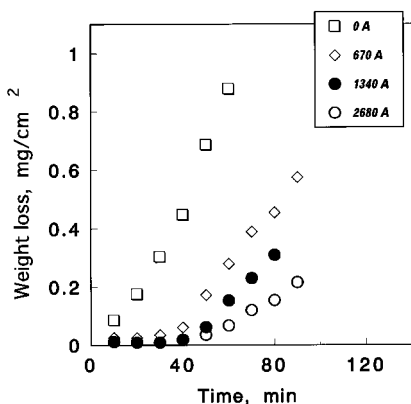
On the contrary, Si-containing monomers were much more stable in glow discharges compared to other conventional plasma polymers. This means that the plasma polymer coating is the candidate of protective coating against the etching by high energy sources.

### Oxidative Etching Resistance

Ultraviolet (UV) light at the much shorter wavelength is indeed generated in plasma, and the energy should be sufficient to cause the cleavage of C—C and other chemical bonds from the surface of the substrate polymer. According to the wavelength sensitivity study<sup>18</sup> of photo oxidation, the increase in the carbonyl peak absorption of IR



**Figure 2** Discharge power dependence of the plasma polymer deposition of HMDSiO and HMDSi (3.5 Pa, 20 min).



**Figure 3** Weight loss of HMDSiO-plasma polymer-coated PP films at the various thickness by O<sub>2</sub>-plasma etching (15 Pa, 20 W).

and the decrease in tensile strength of PP become more prominent when the polymer is exposed to UV of a shorter wave length.

Incidentally, the PP substrates should have been exposed to UV during the present protective plasma polymer coating treatments. However, as the exposing time is comparatively short, the degradation of the bulk PP should be negligible.

#### Coating Thickness Effects

Figure 3 shows the O<sub>2</sub>-plasma etching time dependencies of weight loss of HMDSiO-plasma polymer-coated PP films at the various thickness up to 2680 Å. Here, the coated films were exposed to O<sub>2</sub>-plasma (15 Pa, 20 W) and the oxidative etching was evaluated by the degree of weight loss of the substrates.

Weight was unchanged practically at the first stage of plasma exposure with the coated PP films, but gradually decreased after a certain period of time lag. Thus, the resistance effect is evident from the comparison with that of untreated PP film. The time at which the weight decrease practically starts is an indication of the degradability of polymers.<sup>19</sup> The induction period ( $T_{ind}$ ) was taken and utilized to see the stabilizing effects. Although  $T_{ind} = \sim 0$  min for the original PP, the time became longer than 50 min for HMDSiO-plasma-coated PP, and thus the stabilization effects by plasma polymer coating were suggested.

Decrease of weight was also dependent on the degree of coating thickness, and the rate was suppressed with the coating thickness. The slope of the curve of weight loss vs. oxidative plasma treatment time after  $T_{ind}$  was taken, and the weight

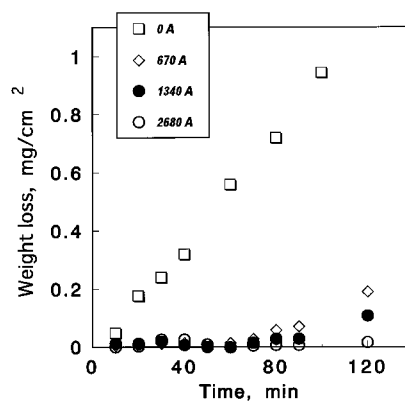
decreasing rate was evaluated. The rates after  $T_{ind}$  were estimated as  $0.59 \times 10^{-3}$ ,  $0.48 \times 10^{-3}$ , and  $0.28 \times 10^{-3}$  g/cm<sup>2</sup>h, respectively, for the coating thickness of 670 Å, 1340 Å, and 2680 Å. The weight loss rate was smaller than that for the original PP, i.e.,  $1.2 \times 10^{-3}$  g/cm<sup>2</sup>h, and the resistance effects by Si-plasma polymer coating were evident again.

Weight loss by plasma etching is dependent on the oxidative potential of the plasma gas source. Figure 4 shows the results by the less oxidative air plasma etching (15 Pa, 20 W).  $T_{ind}$  became longer and reached 70–80 min on the HMDSiO-plasma polymer-coated PP. The weight decreasing rate was estimated  $0.17 \times 10^{-3}$ ,  $0.10 \times 10^{-3}$ , and  $0.02 \times 10^{-3}$  g/cm<sup>2</sup>h, and smaller than the rates by O<sub>2</sub>-plasma etching.

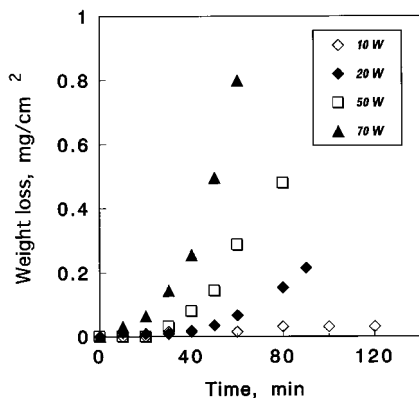
When an inert Ar was used as a plasma gas source, the weight loss rate was much smaller, and even the HMDSiO-plasma polymer-coated PP at the smaller thickness of 670 Å did not lose the weight until more than 120 min of plasma exposure.

#### Discharge Power Effects

Above results were based on the etching by a discharge power at 20 W. However, plasma intensity and, therefore, the susceptibility to etching should be naturally changed by the applied power. Figure 5 shows the discharge power dependence of weight loss by O<sub>2</sub>-plasma etching in the power range of 10–70 W for the PP samples coated with an about 3000 Å-thick HMDSiO-plasma polymer. The weight loss became prominent with power, especially beyond 50 W. However, the resistant effects were evident when the results were



**Figure 4** Weight loss of HMDSiO-plasma polymer-coated PP films by air-plasma etching (15 Pa, 20 W).



**Figure 5** Weight loss of 3000 Å-thick HMDSiO-plasma polymer-coated PP films by O<sub>2</sub>-plasma etching at 10, 20, 50, and 70 W.

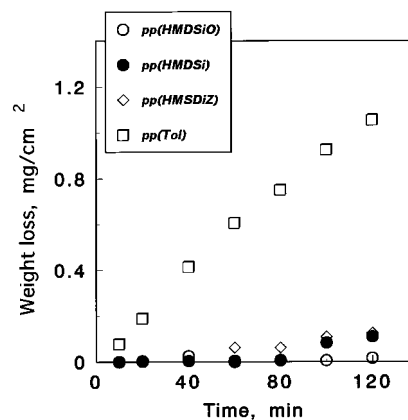
compared with the weight loss of the original PP film.

In the present reactor system, temperature was not controlled, and as a result, the samples were directly exposed to heat generated at the reactor surface during plasma exposure. The equilibrium temperature on the reactor wall measured with a thermometer was 39°C for the treatment at 20 W of O<sub>2</sub>-plasma exposure, and 59°C for that at 70 W. When the untreated PP was exposed to O<sub>2</sub>-plasma at 70 W, the sheet had shrunk by melt during plasma exposure, and the weight loss rate became much faster. The observation indicates that the wall surface temperature in the reactor raised above the melting temperature of PP. On the contrary, the coated PP film did not melt after O<sub>2</sub>-plasma exposure under the same discharge power, and the protecting effects became evident.

By the way, we employed here the oxidative plasma exposure method to see the etching resistance of Si-plasma polymer-coated PP sheets, and also expected the procedure to be utilized as an alternative method of the standard outdoor weathering tests of polymer materials. The plasma etching method provides the more convenient and cost-effective approach. However, more improvements such as temperature control during plasma exposure seem to be quite necessary for the practical substitution.

**Effects of Si Components in Plasma Polymers**

The etching resistance was also compared to those by other plasma polymer coating from HMDSi and HMDSiZ. Figure 6 shows the weight loss results for the coated samples at the thickness of

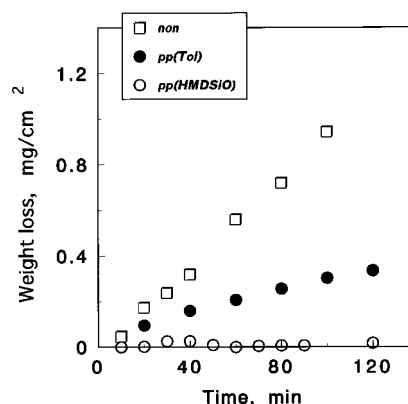


**Figure 6** Comparison of weight loss behaviors of the coated PP films with HMDSiO, HMDSi, HMDSiZ, and toluene-plasma polymers at 3000 Å by O<sub>2</sub>-plasma etching (15 Pa, 20 W).

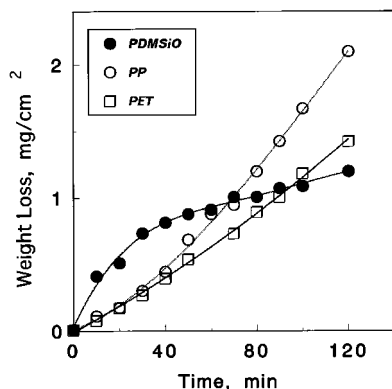
about 3000 Å. The results are also compared to that by hydrocarbonic toluene plasma polymer coating.

The plasma polymer-coated PP films with HMDSiO and HMDSiZ did not lose their weight by O<sub>2</sub>-plasma etching for a long time, and the resistant effects were evident. On the contrary, the substrate coated with a toluene plasma polymer had lost the weight at quite the same rate as the original PP film (see Fig. 3). Thus, the etching resistant effects were not practically observed in the toluene plasma polymer sample. It should be noted, however, that the hydrocarbonic plasma polymer coating was still effective against the less oxidative plasma etching.

Figure 7 shows the results of weight loss by



**Figure 7** Comparison of weight loss behaviors of the original PP and the coated PP films with HMDSiO and toluene-plasma polymers at 3000 Å by air-plasma etching (15 Pa, 20 W).



**Figure 8** Comparison of weight loss of PDMSiO, PP, and PET by  $O_2$ -plasma etching (15 Pa, 20 W).

air-plasma etching (15 Pa, 20 W). Although the weight-decreasing rate of a toluene plasma polymer-coated PP was greater than that of the HMDSiO-plasma polymer-coated one, the rate was smaller than that of the original PP. Thus, the coating was more or less effective against the less oxidative plasma etching. When the Ar-plasma treatments were applied, the weight loss was much less even on the toluene plasma polymer-coated PP, and the etching resistance effects against nonoxidative plasma were evident.

### Effects of Crosslinked Structure

The tight crosslinked structure of plasma polymers should thus participate in the stabilization of polymers against plasma etching. Effects of such network structure were further confirmed by the comparison of the weight loss behaviors of some other linear polymers. Figure 8 shows the dependence on the  $O_2$ -plasma etching time (15 Pa, 20 W), respectively, for PDMSiO, PET, and PP. PDMSiO was selected as a typical siloxane polymer with a  $-\text{Si}(\text{CH}_3)_2\text{O}-$  unit.

The weight loss of PDMSiO was much greater than that of HMDSiO-plasma polymer-coated PP, and was more or less the same level as other linear hydrocarbonic polymers. This indicates that the linear siloxane structure alone is not necessarily so effective for the resistance against oxidative etching, but the crosslinked network with the tight  $-\text{Si}-$  component is necessary for the stabilization.

It should be noted here that the weight-decreasing behavior of PDMSiO was somewhat different from those of other polymer sheets. In other words, the weight loss rate decreased gradually

with the plasma exposure time beyond 40 min, although the weight-decreasing rate is faster at the first stage of oxidative plasma exposure. The suppression of weight loss and, therefore, the stabilization after the longer plasma exposure should be attributed to the simultaneously formed cross-linked  $\text{Si}-\text{O}$  structure on the surface.

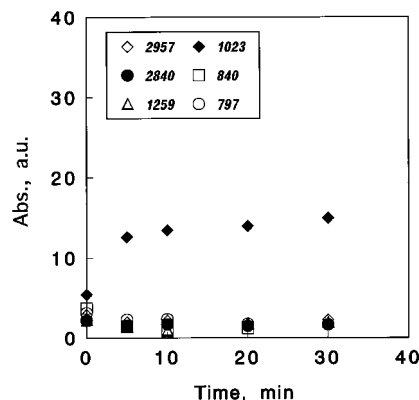
## IR Analyses of $O_2$ -Plasma-Treated Polymers

### HMDSiO-Plasma Polymer

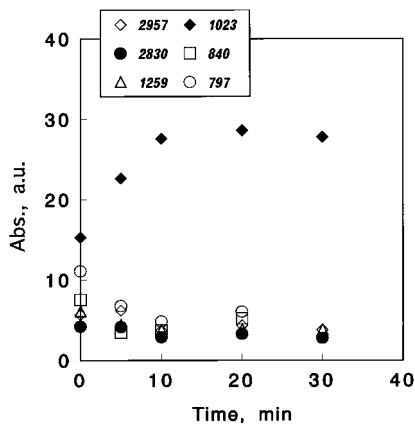
Although the identification of IR peaks of silane and siloxane plasma polymers has been provided, the oxidative changes in the chemical structure by  $O_2$ -plasma etching treatments have so far not been reported. In the present study, IR spectra were repeatedly obtained and the changes of peak intensity were followed to analyze the chemical structure of plasma polymers by the  $O_2$ -plasma exposure.

Figures 9 and 10 show the changes in the IR absorption peak intensities during the  $O_2$ -plasma treatments (15 Pa, 20 W), respectively, for the 500-Å thick and the 2000-Å thick HMDSiO-plasma polymers formed on a KBr disc. The IR peaks at  $2957\text{ cm}^{-1}$  ( $-\text{CH}_3$ ),  $2840\text{ cm}^{-1}$  ( $-\text{CH}_2-$ ),  $1259\text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ ),  $1023\text{ cm}^{-1}$  ( $\text{Si}-\text{O}$ ),  $840\text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ ), and  $797\text{ cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ ) were taken and compared. Besides these peaks, there appeared a small peak at  $2107\text{ cm}^{-1}$  for  $\text{Si}-\text{H}$ , which should have been generated through the rearrangement of hydrogen from a methyl group during plasma polymerization of HMDSiO.

The following are pointed out from the results. (1) The absorption peak at  $1023\text{ cm}^{-1}$  for  $\text{Si}-\text{O}$



**Figure 9** IR peak changes of 500 Å-thick HMDSiO-plasma polymer by  $O_2$ -plasma treatments (15 Pa, 20 W).



**Figure 10** IR peak changes of 2000 Å-thick HMDSiO-plasma polymer by O<sub>2</sub>-plasma treatments (15 Pa, 20 W).

increased, while other peaks decreased by O<sub>2</sub>-plasma exposure. (2) The IR peaks other than that for Si—O became negligible in the 500-Å thick sample. (3) The change in the IR peak intensities was prominent at the first stage of about 10 min of O<sub>2</sub>-plasma exposure and then reached constant.

The siloxane structure exists, of course, in HMDSiO and, therefore, in the plasma polymers, but the IR peak for Si—O components increased unexpectedly after the oxidative etching treatments. This indicates that the —Si— network on the surface of plasma polymers was attacked and oxygen was incorporated to form the more dense

Si—O structure. The peak for  $\begin{matrix} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{matrix}$  was not observed practically in these O<sub>2</sub>-plasma-etched polymers, and the detachment of carbon component rather than the carbonylation was suggested.

Thus, the SiO<sub>x</sub>-like structure should be formed on quite the surface layer. Incidentally, the chemical composition of C<sub>2.0</sub>O<sub>0.62</sub>Si<sub>1.0</sub> was obtained for the HMDSiO-plasma polymer by the elemental analyses according to the peak intensity analyses by ESCA, which was operated at the incident angle of 90° to the sample surface. The elemental analyses data by ESCA should, therefore, represent the composition of several tens Å layer on the surface. Because the theoretical chemical composition of HMDSiO is C<sub>6.0</sub>O<sub>1.0</sub>Si<sub>2.0</sub>, the detachment of carbon and the incorporation of oxygen were suggested in the plasma polymer. After the O<sub>2</sub>-plasma treatments, the Si<sub>2p</sub> peak area increased relatively, but interestingly small

amounts of C<sub>1s</sub> peak were still observed in the ESCA spectra.

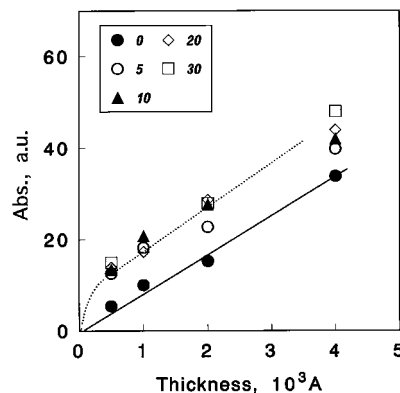
**HMDSi- and HMDSiZ-Plasma Polymers**

Similar changes in the IR peak were observed in the plasma polymers of HMDSi and HMDSiZ. The starting monomers of HMDSi and HMDSiZ do not naturally contain oxygen, but small peak for the Si—O structure was observed in the plasma polymers. The oxidized structure should have been formed by oxidation during storage in air by the reaction of the radically active plasma polymer with oxygen. The peak for Si—O was, of course, very small at the first stage, but the intensity became gradually greater with the O<sub>2</sub>-plasma exposure.

In the HMDSiZ-plasma polymer, the peaks for a Si—N bond appeared at 1181 cm<sup>-1</sup>. The IR peak intensity gradually decreased with the longer oxidative plasma treatments and the detachment of Si—N bonds during the oxidation was suggested.

**Coating Thickness Dependence**

The penetrating effects of oxidative plasma from the surface of the polymers were investigated from the increase in the IR peak intensity at 1023 cm<sup>-1</sup> for Si—O. For this purpose, the HMDSiO-plasma polymers were formed at the various thickness on a KBr disc and exposed to O<sub>2</sub>-plasma, and then the IR spectra were repeatedly taken. Dependence of the peak intensity on the thickness is shown in Figure 11, respectively for the original HMDSiO-plasma polymer (15 Pa, 50



**Figure 11** Thickness dependence of IR peak intensity at 1023 cm<sup>-1</sup> (Si—O) of the HMDSiO-plasma polymer and the O<sub>2</sub>-plasma-treated polymer (15 Pa, 20 W, 5–30 min).

W) and for those exposed to the O<sub>2</sub>-plasma for 5, 10, 20, and 30 min.

In the untreated HMDSiO-plasma polymer, the absorption peak intensity of Si—O increased linearly with the thickness of the deposited layer, and the relationship of  $A = 8.54 \times d$  was given from the result. Here,  $d$  is the thickness in  $10^{-3}$  Å and  $A$  is the peak intensity in an arbitrary unit.

In contrast to this, somewhat different relationship was observed for the O<sub>2</sub>-plasma-treated polymers. The peak intensity for Si—O became greater at the first stage, and increased linearly with the thickness beyond this critical point. The behavior was commonly observed in the O<sub>2</sub>-plasma-treated samples for 5–30 min. The difference in the peak intensity before and after the O<sub>2</sub>-plasma treatments should correspond the thickness for the layer with a Si—O component. Then, the thickness of the Si—O layer formed by oxidation can be calculated. The thickness of the oxidized layer was estimated as about 1000 Å, although the direct plasma oxidation effects should be confined to quite the surface layer.

### Surface Morphology by SEM

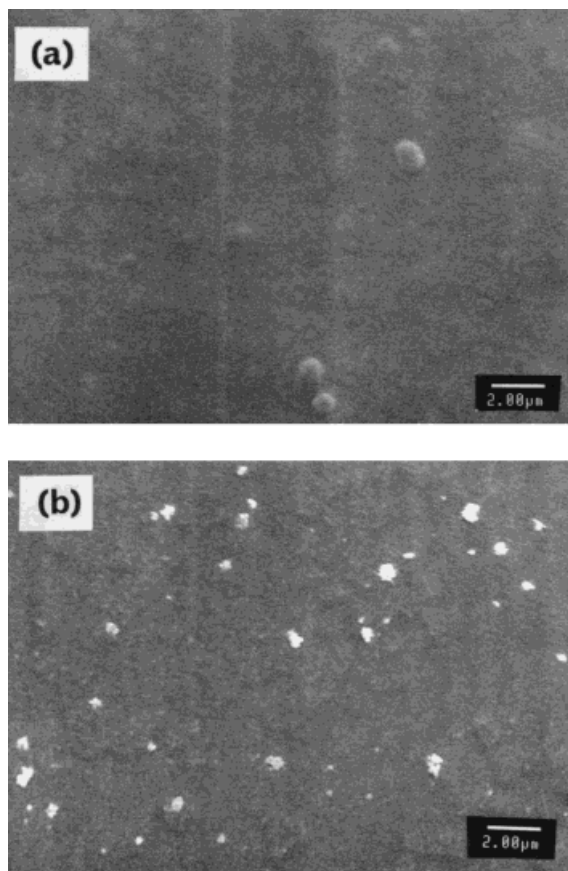
Figure 12 shows the SEM photo pictures, respectively, for the HMDSiO-plasma polymer-coated PP surface of the thickness of about 3000 Å (a) and the O<sub>2</sub>-plasma-exposed surface for 30 min (b). Under the oxidative plasma treatment condition, the weight loss of the coated PP film was negligible, as indicated from the result shown in Figure 3.

The oxidized surface was comparatively smooth, but small particles that are supposed to be composed of inorganic SiO<sub>x</sub>-like materials were formed after the oxidation treatments. Diameter of the particle was smaller than several hundred Å.

### CONCLUSION

Ultrathin plasma polymer coating of some Si-monomers was found to be effective to impart the stabilization of PP against oxidative plasma etching. The stabilization effects should be due both to the direct blocking effects of etchants in plasma and to the formation of the more stable Si—O structure.

We have previously observed some resistant effects on the outdoor weathering of PP<sup>14</sup>, and, therefore, expected the present plasma oxidation could be used as a substitution method of outdoor



**Figure 12** SEM pictures of 3000 Å-thick HMDSiO-plasma polymer (a) and the O<sub>2</sub>-plasma-etched polymer (15 Pa, 20 W, 30 min) (b).

weathering tests. However, the reliable relationship between the two procedures has not been obtained at present. The discrepancy should be due to the difference in the degradation mechanism by active species during the exposures; i.e., activated oxygen functions mainly in the oxidative plasma exposure, while much penetrative UV light takes part in the outdoor weathering. Further investigation is therefore necessary for the application of the oxidative plasma etching to an alternative and simple method for the accelerated tests of weathering. For example, the temperature rise during plasma exposure should be controlled.

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