Effect of I₂ Plasma on the Properties of Polyethylene

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ABSTRACT: Polyethylene surfaces were treated with I₂ plasma. From ESCA analysis, it became apparent that iodine atoms were bound chemically to the surface of polyethylene substrate by the treatment of I₂ plasma. Also, iodine bonded chemically to polyethylene increased by the exposure of I₂ vapor after I₂-plasma treatment of the substrate. The reaction of I₂-plasma treated polyethylene with aminoalcohol made the polyethylene substrate hydrophilic.

KEY WORDS Plasma / Iodine / Surface / Treatment / Polymer /

In glow-discharge low-temperature plasma, atoms and/or molecules are activated to give ions, radicals or excited species. Plasma are expected to be applied in various fields, such as forming thin films with high functionality, etching a substrate surface, and treating the surface of organic material substrates. Though plasma chemistry has been widely investigated, further studies on plasma chemistry are required in order to create the various functional thin films or surfaces.

Recently, plasma treatment of polymer has been done to introduce various functionalities onto the surface of organic materials. Functionalities, such as wettability, water repellency and adhesion, are attributed to chemical structures and functional groups on polymer surface. Plasma treatment of a polymer is useful method for reforming a polymer surface, which changes the surface properties of an organic material, such as hydrophobicity or hydrophilicity. The treatment of the organic materials by O₂, N₂, or Ar plasma produces the functional groups, such as hydroxyl, carbonyl, amino or nitrile groups, and adds various functionalities, such as hydrophilicity, wettability or adhesion property.^{1,2} Plasma

treatment of a polymer by fluorine derivatives such as tetrafluoromethane or fluorine is used for etching a material surface, and gives water repellency to polymer surface.³ Also, plasma treatment of organic materials by chloroform is reported.⁴ However, plasma treatment by iodine (I₂) gas has not been reported, although plasma polymerization using iodomethane was carried out to form thin films containing iodine linked chemically.⁵ This article reports that I₂-plasma treatment of polymer forms organic materials linking chemically iodine atoms. The functionality of I₂-plasma-treated polyethylene was investigated.

EXPERIMENTAL

As shown in Figure 1, the plasma apparatus is made of a pyrex glass, 5 cm in diameter and 40 cm in length, fitted with an iodine (I₂) gas inlet, argon (Ar) gas inlet, pressure gauge and vacuum system. The plasma was generated by application of a high voltage amplified by a neon transformer to the tungsten (W) electrodes. The plasma power was controlled using a variable resistor. The plasma apparatus was evacuated to about 200—400 mTorr, and then

Figure 1. Schematic diagram of the apparatus for I_2 -plasma treatment.

the vapor of I_2 sublimed at 0°C was introduced. Before the plasma treatment by I_2 vapor, the atmosphere was replaced with Ar gas. As a sample for ESCA analysis, polyethylene thin film (PE, $30\text{ mm} \times 25\text{ mm} \times 0.8\text{ mm}$) was used. The polyethylene substrate ($50\text{ mm} \times 25\text{ mm} \times 2\text{ mm}$) was used to measure the contact angle.

The reaction of the treated polyethylene with amine was carried out as follows. The I_2 -plasma-treated polyethylene substrate was placed in a beaker containing a solution of various amines (200 ml) for a specified period. The substrate was washed by ethanol, and dried under reduced pressure.

ESCA spectra were recorded with a Shimadzu electron spectrometer, ESCA 750. Wettability of the treated polyethylene substrate was estimated by the contact angle with water. Contact angles with water were measured at room temperature using a contact-angle meter (ERMA Inc., Model G-I).

RESULTS AND DISCUSSION

I_2 -Plasma Treatment of Polyethylene

Vapor of iodine (I_2) was introduced into the reactor without generating plasma, and the polyethylene substrate was exposed to I_2 vapor. The polyethylene substrate was analyzed by ESCA. The iodine doublet at 630 and 619 eV was not detected, thus showing that iodine did not link chemically and was not adsorbed

Figure 2. ESCA spectra of I_2 -plasma, I_2 -plasma/ I_2 -vapor-treated polyethylene and untreated polyethylene. a) polyethylene substrate without treatment; b) polyethylene substrate treated by I_2 -plasma for 1 hour; c) polyethylene substrate treated by I_2 -plasma for 1 hour and exposed to I_2 vapor for 1 hour.

physically to the surface of the polyethylene substrate only by exposure of I_2 vapor without plasma generation.

Polyethylene substrate was treated by I_2 plasma at 200 mTorr. The I_2 -plasma-treated polyethylene was analyzed by ESCA. As shown in Figure 2b, I_2 -plasma-treated polyethylene showed peaks at 630.60 eV and 619.10 eV, which were assigned to iodine atoms of $3d_{3/2}$ and $3d_{5/2}$ respectively. These peaks are indicative of iodine bonded chemically to carbon by I_2 plasma, since iodine was not detected on polyethylene exposed to I_2 vapor.

The iodine in polyethylene surface depended on the time of I_2 -plasma treatment. As shown in Figure 3, iodine became approximately constant at 25% at an I/C molar ratio over

Figure 3. Effects of I₂-plasma treatment time on iodine bonded to polyethylene. (Plasma voltage, 3.6 kV)

20 min.

The ac voltage applied to the W electrodes was set at 3.0 kV, 3.6 kV, and 4.8 kV, because iodine bonded to the polyethylene was very low below 3.0 kV and I₂ plasma was unstable over 4.8 kV. At each plasma voltage, I₂-plasma treatment was carried out for 1 h. Iodine bonded to polyethylene surface is shown in Table I. Iodine in polyethylene increased with plasma voltage.

The depth profile of iodine bonded to polyethylene was measured by varying the incident angle of X-ray to the surface of the polyethylene film. From Table II, it was confirmed that iodine was present at a depth of *ca.* 100 Å from the topmost layer of the polyethylene surface. It has been reported that the escape depth of photoelectron is the outermost few tens of Angstroms of the sample (in the range ~ 100 Å).⁶

Treatment of Polyethylene by I₂ Plasma and I₂ Vapor

Radical species are present at the surface of organic material treated by plasma and the life span is very long in comparison with that of the organic radical species. Halogen molecules are known to react easily with radical species.

The surface of the polyethylene substrate was treated for 1 h with I₂ plasma generated at plasma voltages of 3.6 kV, and thereafter,

Table I. Surface composition of I₂-plasma-treated and I₂-plasma/I₂-vapor-treated polyethylene

Plasma voltage (kV)	I ₂ -plasma (1 h)	I ₂ -plasma (1 h)/ I ₂ -vapor (1 h)
	I/C	I/C
3.0	0.04	0.16
3.6	0.22	0.43
4.8	0.29	—

Table II. Depth profile of I₂-plasma-treated polyethylenes surface^a

	0° (<i>d</i>)	30° (0.87 <i>d</i>)	45° (0.71 <i>d</i>)	60° (0.5 <i>d</i>)
I/C	0.04	0.08	0.05	0.02

^a (*d*, escape depth of photoelectron in the range ~ 100 Å).

iodine vapor was introduced into the reactor for 1 h without plasma generation. The surface of polyethylene substrate after this treatment was analyzed by ESCA. As shown in Figure 2 and Table II, exposure to I₂ vapor after I₂-plasma treatment caused the introduction of iodine more than that of iodine by I₂-plasma treatment only. This suggests that I₂-plasma treatment of polyethylene forms carbon-iodine bonds and radical species on polymer surface, and thereafter that radical species surviving on the polymer surface react with I₂ vapor introduced into the reactor without activation by plasma, to form the additional carbon-iodine bonds.

Reactions of Polyethylene Containing Iodine with Amine Derivatives

The hydrophobic/hydrophilic properties of I₂-plasma-treated polyethylene or I₂-plasma/I₂-vapor-treated polyethylene were determined by measurement of the contact angle with water. The contact angle with water ranged from 56 to 104°, because the contact angle depended on the amount of oxygen and iodine bonded to the polymer surface. To import hydrophilicity to the polymer surface, the

reaction of polyethylene containing iodine with amine was carried out. Polyethylene containing iodine was prepared by I₂-plasma treatment for 1 h at 3.6 kV and thereafter treatment with I₂ vapor alone for another 1 h without plasma. Alkyl iodide easily reacts with amine to give the ammonium iodide salt, as follows.

After reactions with various amines, iodine in polyethylene containing iodine decreased, and the introduction of nitrogen atoms to polyethylene substrate was apparent from the results of ESCA measurement (Table III). The nitrogen (N_{1s}) peak appeared at 403 eV, which was assigned to the nitrogen atoms of ammonium salts. It is considered that the decrease of iodine contents resulted from the exchange reaction of iodide ion (I[−]) with hydroxide ion (OH[−]) and the elimination reaction of hydrogen iodide (HI) from polyethylene containing iodine by interaction of the amine. The contact angle with water decreased slightly, after reactions of I₂-plasma-/I₂-vapor-treated polyethylene with amines (Table III, No. 1–3). Similarly, after reactions with aminoalcohol derivatives (No. 4–6), iodine in polyethylene containing iodine decreased and nitrogen atoms were bound to polyethylene substrate. The contact angle with water decreased at all surfaces of the polyethylene substrate treated by I₂-plasma-/I₂-vapor/aminoalcohol, causing the surface to become hydrophilic.

Treatment of polyethylene substrate by I₂-plasma, I₂-plasma/I₂-vapor, or I₂-plasma/I₂-vapor/aminoalcohol makes it possible to change the hydrophobicity/hydrophilicity of polyethylene.

Table III. Elemental composition of substrate surface treated by the reaction of I₂-plasma-/I₂-vapor-treated polyethylene with various amines^a

Amines	Element ratios		Contact angles
	N/C	I/C	
1 <i>n</i> -Propylamine	0.20	0.03	76°
2 Isopropylamine	0.31	0.06	58°
3 Triethylamine	0.15	0.04	60°
4 2-Methylaminoethanol	0.33	0.03	24°
5 2-Dimethylaminoethanol	0.40	0.04	27°
6 2-Ethylaminoethanol	0.33	0.05	21°

^a I₂-plasma/I₂-vapor treated polyethylene: I/C; 0.43, contact angle; 73°.

CONCLUSIONS

In this study, iodine was bonded chemically to polyethylene surface by treatment of I₂ plasma. By exposure of I₂ vapor after I₂-plasma treatment, more iodine than that by I₂-plasma treatment only became bound to the surface of polyethylene.

The I₂-plasma-treated polyethylene surface reacted with aminoalcohols, causing the surface to become hydrophilic.

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