Surface Modification of Polyethylene Powder Using Plasma Reactor with Fluidized Bed

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SYNOPSIS

The fluidization technique was applied for the surface modification of powder by plasma, and whether the technique was a practically useful one in the surface modification of powder or not was discussed. Polyethylene powder was used as a specimen to be modified. The oxygen plasma treatment of the polyethylene powder in the fluidized state showed a capability that the surface of the powder was changed from hydrophobic to hydrophilic. The contact angle of water for the treated powder surface was 51°, which was estimated from the dynamic wicking data. The hydrophilic surface modification of the polyethylene powders in the fluidized bed required the operation of the plasma treatment for at least 3 h. The requirement of the plasma operation for long time rises mainly from large surface area of the powder. The oxygen plasma treatment led to the formation of oxygen functionalities including $C = O$ and $C(O) - O -$ groups at the outermost layer of the powder. The concentration of the $C = O$ and $C(O) - O -$ functionalities reached 10 and 6% of the total carbon elements being in the XPS sampling depth, respectively. From these results we conclude that the fluidization technique is a useful manner in the surface modification of powder by plasma.

INTRODUCTION

Plasma treatment is a useful technique to modify the surface properties of the polymeric materials from hydrophobic to hydrophilic or inversely from hydrophilic to hydrophobic without change in bulk properties. The technique for hydrophilic surface modification has commercially applied for adhesion improvement between polymer films and adhesive glue and wicking and printing improvement of polyester fabrics and polyolefine films.[1,2] Essentials of the technique are that electrons, atoms, and radicals in the plasma attack the surface of the polymeric materials, then abstract hydrogen atoms from the polymeric surface to form radical sites at the surface, and finally oxygen atoms react with the radical sites to form oxygen functionalities including OH, $C = O$, and COOH groups.[3] Therefore good contact of the polymeric surface with the plasma is an important factor to operate efficiently the surface modification.

Powders including carbon black, zinc oxide, ferric oxide, titanium oxide, pigment, silica gel, and zeolite are useful raw materials in rubber, electronic, paint, and petrochemical industries. Investigators in these industries focus their attention on the surface modification of these powders. Powder is difficult to be handled in the plasma treatment because of aggregation and large surface area per the unit mass of the powder. In the surface modification by plasma it is necessary to touch the surface of the powder with the plasma. The untouched regions of the powder surface are never modified. Therefore the aggregation of the powder should be destroyed in the plasma and all of the powder surface should be coercively touched with the plasma.

A reactor with the fluidized bed is frequently used for chemical reactions with solid and gas or liquid.[4] Powder is placed on the porous plate in the reactor, which is positioned vertically, and a gas is injected from the gas inlet at the bottom of the reactor. The gas passes up through a bed of the powder. At more than a critical flow rate of the gas stream the pressure drops and the drag on individual powder increases. As result, the powders start to move and

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become suspended in the fluid. This state is called "fluidization" and means the condition of fully suspended particles.[4]

In this study we applied the fluidization technique for the surface modification of powder by plasma. We discussed whether the fluidization technique was a practically useful manner in the surface modification of powder or not. The hydrophilicity of the plasma-treated powder was evaluated from the dynamic wicking measurement and the chemical composition of the powder surface was analyzed by FTIR spectroscopy and XPS. Polyethylene powder was used as a specimen to be modified because polyethylene was a convenient substrate in determination of the hydrophilicity and in analysis of the chemical composition of the modified surface.

EXPERIMENTAL

Plasma Treatment Reactor with Fluidized Bed and Plasma Treatment

A reactor used this study for the plasma treatment of polyethylene powder was home-made with a fluidized bed. It consisted of a cylindrical Pyrex glass tube (35 mm inner diameter, 887 mm long) with a glass filter (No. 2) as a porous plate to support the bed of polyethylene powders at a distance of 92 mm from the bottom, pressure gauges for monitoring the pressure drop between a gas inlet and the fluidized bed, a gas inlet with a mass flow controller at the bottom. The tube was opened at the top and was connected through a trap for deposition of polyethylene powders flied-off from the fluidized bed with the combination of a mechanical booster pump (108 m^3/h) and a rotary pump (160 L/min). A pair of electrodes (150 × 150 mm) for glow discharge at 13.56 MHz frequency was placed at a distance of 63 mm from the bottom and was connected with a matching network and an rf (13.56 MHz) generator (Samco International Inst. Co., Japan; model PM-43, 300W). The arrangement of these components is schematically shown in Figure 1.

Polyethylene powders of 5 g [Idemitsu Petrochemical Co., Japan; density of 0.95 g/cm^3; powder size of 100/200 mesh (0.074–0.147 mm diameter)] were filled into the reactor, which was vertically placed, and oxygen gas was injected from the gas inlet at the bottom of the reactor. When the oxygen gas was passed at low flow rate up through a bed of polyethylene powders, the powders did not move. However, when the oxygen flow rate increased, the pressure dropped and the drag on individual powders

increased. As a result, the powders started to move and became suspended in the fluid. This is the fluidization state, the condition of fully suspended particles. A relationship between the gas flow rate and the pressure drop is shown schematically in Figure 2. If the powders in the bed are quite small, the gas flow channels between the powders will be laminar and the pressure drop between the gas inlet and the bed will be proportional to the gas flow rate. At a certain flow rate the pressure drop will counterbalance the weight of the bed, and the fluidization will initiate. The condition for fluidization in this study was determined from the relationship of the pressure drop versus gas flow rate. The fluidization of the polyethylene powders [Idemitsu Petrochemical Co., Japan; density of 0.95 g/cm^3; powder size of 100/200 mesh (0.074–0.147 mm diameter)] using the reactor shown in Figure 1, occurred at an oxygen flow rate of more than 30 cm^3/min at a pressure in the fluidized bed of 133 Pa.

The polyethylene powders in the fluidized state were plasma treated at a rf power of 150 W for 2–9 h at an oxygen flow rate of 30 cm^3/min at a pressure of 133 Pa.

Surface Properties of Polyethylene Powder

The dynamic wicking property of the plasma-treated polyethylene powders was determined as hydrophilicity of the powder surface using Lesca dynamic wicking meter (model WET-300). A schematic representation of the dynamic wicking meter is shown in Figure 3, and essentials of the dynamic wicking measurement are as follows. A polyethylene powder of 1 g was tapped 200 times and filled in the cylindrical glass tube (11.5 mm inner diameter, 55 mm long) of which an end was sealed with nylon mesh (pore size 20 μm). The tube was vertically placed, and the end (nylon mesh-sealed side) of the tube was contacted with water in the beaker. As the surface of the nylon mesh touched the water surface, water penetrated up into the column of the polyethylene powders by the capillary attraction. The weight of the penetrating water into the column increased with increasing time after the water contact. When the weight of the penetrating water was counterbalanced with the capillary attraction, the penetration of water into the column of the polyethylene powder was finished. In the determination of the dynamic wicking property, the weight of the penetrating water into the column was measured using an electric balance as a function of time after the water contact.
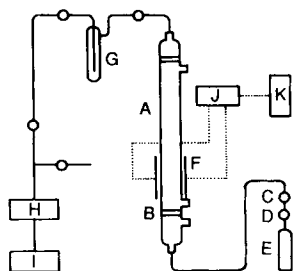
Figure 1(a) Schematic presentation of oxygen plasma treatment reactor with fluidized bed. (a) Reaction chamber, (b) porous plate, (c) mass flow controller, (d) body valve, (e) gas cylinder, (f) electrodes, (g) cold trap, (h) mechanical booster pump, (i) rotary pump, (j) matching network, (k) RFGenerator.
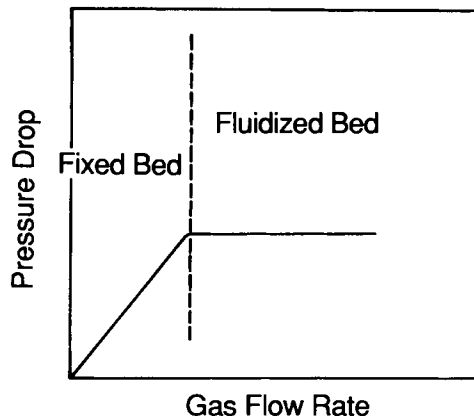

Figure 2 Typical relationship between gas flow rate and pressure drop.

The contact angle of water on the surface of the polyethylene powder was tentatively calculated from the Eq. (1):[5]

$$\left(\frac{W}{S}\right)^2 = \frac{1}{S_p} \times \frac{\rho_1^2}{\rho_p} \times \frac{\epsilon^3}{1-\epsilon} \times \frac{\gamma_{1\cos\theta}}{2\eta} \times t \qquad (1)$$

where W, S, S_p, ρ_1, ρ_p, ϵ, γ_1, θ, η, and t are the weight of the penetrating water, the cross section of the cylindrical tube, the surface area of the polyethylene powder per unit weight, the density of water, the density of the polyethylene powder, the porosity of the polyethylene column, the surface energy of water, the contact angel of water, the viscosity of water, and the time after the water contact, respectively. The porosity of the polyethylene column, ϵ, was estimated from the relationship,[5] $\epsilon = 1 - \{W_p/(hS\rho_p)\}$, where W_p, h, S, and ρ_p were the weight

of the polyethylene powder tapped in the column, the height of the polyethylene powder in the column, the cross section of the cylindrical column, and the density of the polyethylene powder, respectively. The surface area of the polyethylene powder tapped in the column was estimated from the relationship,[5] $S_p = 6(1 - \epsilon)/(D_p\rho_p)$, where ϵ, D_p, and ρ_p were the porosity of the polyethylene column, the diameter of the polyethylene powder, and the density of the polyethylene powder, respectively. In estimation of the surface area of the polyethylene powder tapped in the column, the powder was assumed to be sphere with 0.11 mm diameter, although it distributed from 0.147 to 0.074 mm diameter.
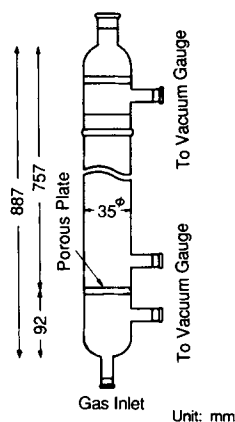
Figure 1(b) Schematic presentation of reaction chamber.
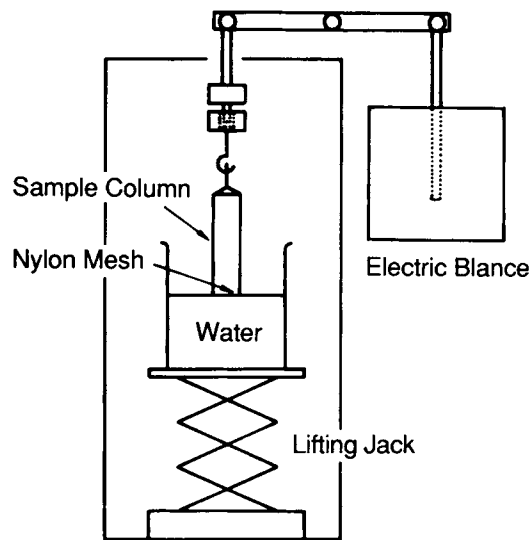
Figure 3 Schematic presentation of apparatus for measurement of penetrating rate.

IR and XPS Spectra of Polyethylene Powder

IR spectra of the plasma-treated polyethylene powders were recorded on a Nihon Bunko FTIR-3 spectrometer with a diffuse reflector (Spectra Tech Inc., U.S.A., model 0030). The spectral resolution was 2 cm, and 1000 scans were recorded on each sample.

XPS spectra of the plasma-treated polyethylene powder were obtained on a Shimadzu spectrometer 850 using Mg K_α photon source. The anode voltage was 8 kV, the current 15 mA, and the background pressure in the analytical chamber 2×10^{-6} Pa. The C_{1s} spectra were decomposed by fitting Gaussian function to the experimental curve using a nonlinear, least-squares curve-fitting program supplied by Shimadzu. The sensitivity factor (S) for core levels was $S(C_{1s}) = 1.00$, $S(N_{1s}) = 1.77$, and $S(O_{1s}) = 2.85$.

RESULTS AND DISCUSSION

Wicking Properties of Plasma-Treated Polyethylene Powder

Figure 4 shows the weight of the penetrating water into the polyethylene column as a function of the water contact time. The untreated polyethylene powder shows no water penetration, but the oxygen-plasma-treated polyethylene powders show much water penetration. The weight of penetrating water increases linearly with time after the touching water, and levels off after 13–3 min. The time required for the water penetration to level off depends on the plasma treatment time: 13 min for the polyethylene powders plasma treated for 2 h, 4 min for the powders plasma treated for 3 h, and 3 min for the pow-
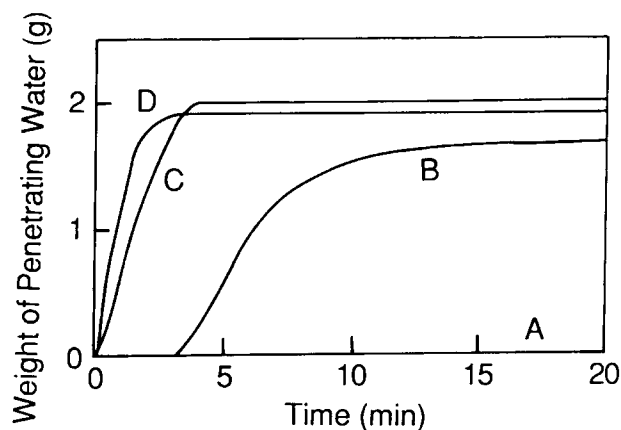
Figure 4 Penetrating rate of water into oxygen-plasma-treated polyethylene powder column: (a) untreated, (b) treated for 2 h, (c) treated for 3 h, (d) treated for 6 h.

ders plasma treated for 6 h. The total weight of penetration water also shows an effect of the plasma treatment time; negligible amount for the untreated polyethylene powder, 1.64 g for the polyethylene powders plasma treated for 2 h, 1.99 g for the powders plasma treated for 3 h, and 1.91 g for the powders plasma treated for 6 h. These results show that the oxygen plasma treatment of the polyethylene powder in the fluidized bed has a capability that the surface of the polyethylene powder could change from hydrophobic to hydrophilic.

Table I shows the comprehensive results in dynamic wicking measurement. Equation (1) indicates that the weight of penetrating water is proportional to the cosine of the water contact angle against the polyethylene surface and time after the touching water if the mass of polyethylene powder filled in the cylindrical tube, the porosity, and the density of the polyethylene powder are constant. Namely, the penetration rate (the weight of the penetration water divided by the water contact time) means comparison in the contact angle of water against the surface of the polyethylene powder. The water penetration rate is negligible for the untreated polyethylene powder, 6.5×10^{-3} g/cm^2 s for the polyethylene powders plasma treated for 2 h, 1.6×10^{-2} g/cm^2 s for the powders plasma treated for 3 h, and 1.9 $\times 10^{-2}$ g/cm^2 s for the powders plasma treated for 6 h. The estimation of the contact angle of water from the water penetration rate according to the Eq. (1) is summarized in Table I. The contact angle of water for the untreated polyethylene powder is not able to be estimated from the Eq. (1) because of no penetration of water but is expected to be more than 90°. The contact angle of water is estimated to be 75°, 54°, and 51° for the polyethylene powders plasma treated for 2, 3, and 6 h, respectively. It is definite that the oxygen plasma treatment in the fluidized bed makes the surface of the polyethylene powders hydrophilic. The plasma treatment for more than 3 h is not effective in hydrophilic modification. When polyethylene film instead of the polyethylene powder was plasma treated using the same reactor under the identical plasma conditions, the contact angle of water against the plasma-treated film was 48°. This comparison emphasizes low efficiency of the plasma actions because of short contact of the polyethylene powder with the plasma. The polyethylene powders are assumed to be spheres with 0.11 mm diameter, although the powders are distributed from 0.147 to 0.074 mm diameter, the powders of 5 g occupy a surface area of about 1200 cm^2. The large surface area per the unit mass of the powder may be a factor of low efficiency of the plasma actions.

Table I Wicking Properties of Oxygen-Plasma-Treated Polyethylene Powder

Oxygen-Plasma Treatment Time (h)	Porosity of Polyethylene Column	Total Weight of Penetrating Water (g)	Penetration Rate $(g/cm^2\ s)$	Contact Angle of Water (degree)
0	0.540	0	0	>90
2	0.535	1.64	6.50×10^{-3}	75
3	0.556	1.99	1.65×10^{-2}	54
6	0.564	1.91	1.89×10^{-2}	51

The homogeneity of the powder surface also is an important subject in the modification of powders. However, we have no idea how to examine the homogeneity, and have not dealt with the homogeneity.

Chemical Composition of Plasma-Treated Polyethylene Powder

From the XPS survey the relative elemental composition for the oxygen-plasma-treated polyethylene powders was determined (Table II). The untreated polyethylene powder contains a small amount of oxygen (the O/C atomic ratio is 0.007) but no nitrogen element. The oxygen plasma treatment makes the powder rich in oxygen. The O/C atomic ratio increases from 0.007 to 0.15–0.19 (21–27 times higher) and the N/C atomic ratio is negligibly small (less than 0.01). This indicates that the polyethylene powders in the fluidized bed were fully oxidized by the oxygen plasma. Immaterial of the shape of specimens to be plasma treated, powder or film, the oxygen concentration incorporated by the oxygen plasma is not distinguished between the polyethyl-

ene powders and films. We have reported on the hydrophilic surface modification of polyethylene films by plasmas including oxygen, nitrogen oxide, and nitrogen dioxide plasma.[6] The polyethylene films, when treated for 10 min with the oxygen plasma at an rf power of 50 W, showed a water contact angle of 46° and an O/C atomic ratio of 0.172. This indicates that the plasma treatment of polyethylene powders in the fluidized bed is a process with low efficiency compared with that of the polyethylene films. The treatment time requisite to the formation of the oxidized surfaces with an O/C atomic ratio of 0.15 is 3 h for the polyethylene powders and 10 min for the polyethylene films. This inefficiency may be due to the polyethylene powders with large surface area per unit mass and to the plasma operation with low input energy of the rf power per unit mass of oxygen molecule. The plasma treatment of the polyethylene powders was operated at an oxygen flow rate of 30 cm³/min, at a pressure of 133 Pa, and at an rf power of 150 W; and that of the polyethylene films was at an oxygen flow rate of 2 cm³/min, at a pressure of 1.3 Pa, and at an rf

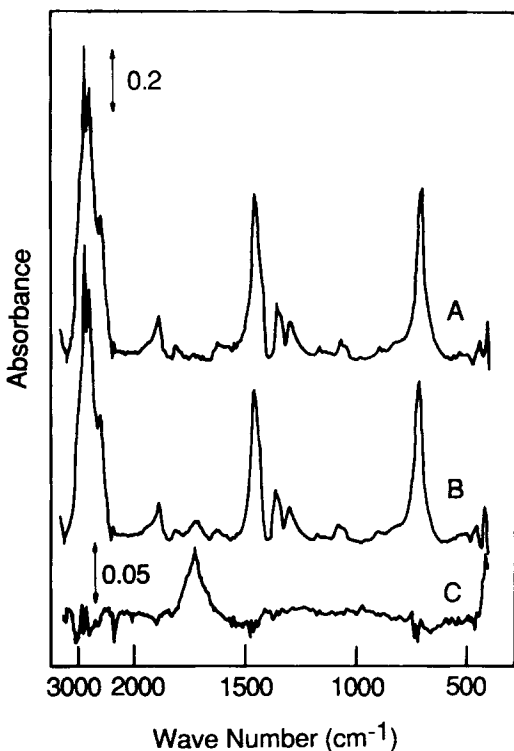**Table II XPS Spectra of Oxygen-Plasma-Treated Polyethylene Powder**

Plasma Treatment Time (h)	Atomic Ratio O/C	Atomic Ratio N/C	C_{1s} Component (Peak Position and Peak Area) Peak 1	C_{1s} Component (Peak Position and Peak Area) Peak 2	C_{1s} Component (Peak Position and Peak Area) Peak 3
0	0.007	0	285.0 eV[a] (95%)[b]	286.7 eV (5%)	
3	0.15	0.45×10^{-2}	285.0 (88)	287.1 (8)	289.2 (4)
6	0.15	0.71×10^{-2}	285.0 (86)	287.1 (10)	298.2 (5)
9	0.19	0.68×10^{-2}	285.0 (84)	287.1 (10)	289.2 (6)

[a] Peak position in eV.
[b] Relative peak area in %.

power of 50 W. The magnitude of the input energy of rf power for a glow discharge is evaluated conventionally by the W/FM parameter. The W/FM parameter means an apparent input energy per unit mass of plasma gas to maintain a glow discharge, where W, F, and M are the input rf power, the flow rate of oxygen gas, and the molecular weight of oxygen, respectively.[7] The W/FM parameter is estimated to be 120 MJ/kg on the plasma treatment of the polyethylene powder and 1050 MJ/kg on that of the polyethylene film. The fluidization requires indispensably a gas stream with a high flow rate for suspension of the polyethylene powders. From the viewpoint of plasma treatment this requirement is an unfavorable factor.

Figure 5 shows typical IR spectra of the oxygen-plasma-treated polyethylene powders. On the IR spectrum for the untreated polyethylene powder strong absorption peaks due to CH_2, CH_3, and terminal vinyl groups appear at 2934, 2859, 1897, 1820, 1636, 1623, 1472, 1368, 1305, and 772 cm^{-1}.[8] The oxygen-plasma-treated polyethylene powders show similar IR absorption peaks to that of the untreated, but new absorption peaks due to oxygen function-
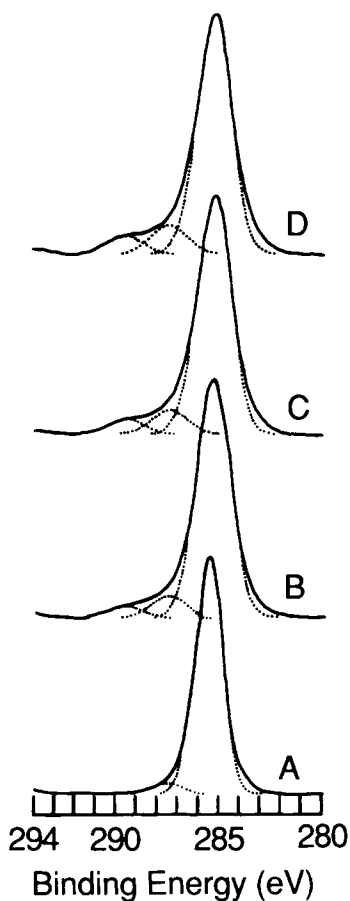

Figure 5 IR spectra of oxygen-plasma-treated polyethylene powders. (a) Untreated, (b) treated for 6 h, (c) difference spectrum between (b) and (a).

alities appear near 1730 cm^{-1}. The difference spectrum between the oxygen-plasma-treated and the untreated polyethylene powder show distinguishes feature of the oxygen functionalities. On the difference spectrum a strong but broad absorption peak appears at 1720 cm^{-1} ($C=O$ groups).[9]

XPS (C_{1s}) spectra for the plasma-treated polyethylene powders give detailed information on the oxygen functionalities (Fig. 6). The C_{1s} spectrum for the untreated polyethylene powder is symmetrical and the full width at half-maximum is small, 1.54 eV. The C_{1s} spectrum is decomposed into a main component and a small component, which are assigned CH_2 and $C=O$ groups, respectively. The C_{1s} spectra of the polyethylene powders oxygen plasma treated for 3, 6, and 9 h are distinguished from that of the untreated powder. The spectra have a main peak with a tail and the full width at half-maximum is 1.92–2.00 eV. These C_{1s} spectra are decomposed into a main component and two small components of which the peak lies at 285.0 (CH_2 groups), 287.1 ($C=O$ groups), and 289.2 eV [$C(O)-O-$ groups].[10] The decomposition is summarized in Table II. The assignment of these decomposed peaks was done from comparison with the Golub and Cormia results.[10] Golub and Cormia investigated on XPS spectra for the polyethylene film exposed to oxygen plasma and observed the formation of oxygen functionalities including $C-O$ (at 286.1–286.5 eV), $C=O$ (at 287.6–287.8 eV), and $C(O)-O-$ groups (at 289.2 eV). Except for disappearance of $C-O$ groups the polyethylene powders oxygen plasma treated in the fluidized bed show similar XPS spectra to the reported. It is obvious that the oxygen plasma treatment of the polyethylene powders in the fluidized bed leads to the formation of $C=O$ and $C(O)-O-$ functionalities at the outermost layer of the powders. The relative concentration of the $C=O$ and $C(O)-O-$ functionalities shows a tendency to increase slightly with the plasma treating time: The $C=O$ concentration is from 5% of the total carbon elements being in the XPS sampling depth (about 50–100 Å) for the untreated to 10% at a treating time of 9 h, and the $C(O)-O-$ concentration is from 0 for the untreated to 6% at a treating time of 9 h.

From these results we conclude that the polyethylene powders in the fluidized bed can be modified by the oxygen plasma to form oxygen functionalities such as $C=O$ and $C(O)-O-$ groups at the outermost layer of the powders. The concentration of the $C=O$ and $C(O)-O-$ functionalities reaches 10 and 6% of the total carbon elements being in the XPS sampling depth, respectively.

Figure 6 XPS (C_{1s}) spectra of oxygen-plasma-treated polyethylene powders. (A) untreated, (B) treated for 3 h, (C) treated for 6 h, (D) treated for 9 h.

CONCLUSION

Polyethylene powders in the fluidized bed were modified by the oxygen plasma, and the surface properties and chemical composition of the powder were investigated. Results are summarized as follows.

1. The oxygen plasma treatment of the polyethylene powder in the fluidized state showed a capability that the surface of the powder was changed from hydrophobic to hydrophilic.
2. The plasma-treated polyethylene surface showed a contact angle of water of 51°, which was estimated from the dynamic wicking data and was comparable in hydrophilicity to that of polyethylene film plasma treated under the identical plasma conditions.
3. The hydrophilic surface modification of the polyethylene powders in the fluidized bed required the operation of the plasma treatment for at least 3 h. The requirement of the plasma operation for long time rises mainly from large surface area of the powder.
4. The oxygen plasma treatment led to the formation of oxygen functionalities including $C{=}O$ and $C(O){-}O{-}$ groups at the outermost layer of the powder. The concentration of the $C{=}O$ and $C(O){-}O{-}$ functionalities reached 10 and 6% of the total carbon elements being in the XPS sampling depth, respectively.

From these results we conclude that the fluidization technique is a useful manner in the surface modification of powder by plasma.

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