

Surface Modification of Polyethylene and Magnetite Powders by Combination of Fluidization and Plasma Polymerization

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SYNOPSIS

A new surface modification process of powders was attempted, using the combination of fluidization and plasma polymerization techniques. This study shows that the combination of the fluidization and plasma polymerization techniques is useful in the surface modification of powders.

Polyethylene and magnetite powders were first fluidized, and then were modified in the fluidization state by the plasma polymers of tetrafluoroethylene (TFE). XPS spectra of the modified powders showed that the surfaces of the polyethylene and magnetite powders were coated with fluorine-containing polymers, and that the polymers were mainly composed of CH, CF, and CF₂ groups. The elemental composition (F/C atomic ratio) and the composition of the fluorinated carbons in the plasma polymers were dependent on the *W/FM* parameter, as well as the TFE concentration in the TFE/Ar mixture. It is emphasized that the *W/FM* parameter is a factor used to control the chemistry of the plasma polymerization reactions. The triboelectric charge of the magnetite powders, when modified by the plasma polymerization of the TFE/Ar mixtures, was higher than the unmodified by about two. The static electrification properties of the powders can be changed by the plasma-polymer-coating. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Powders, including carbon black, zinc oxide, ferric oxide, titanium oxide, pigment, silica gel, and zeolite, are useful raw-materials in the rubber, electronic, paint, and petrochemical industries, and these powders are frequently blended with polymer solutions or resins. The blended products serve as paints, music and video tapes, rubber composites, and plastic composites. In these blending processes, good contact of the powders with the polymer solutions and polymer resins, namely, dispersion in the polymer solutions and adhesion with the polymer resins, is an important factor to yield high performance of the composites. From the viewpoint of good contact, surface modification of the powders is emphasized,

and many modification processes have been proposed for basic research and industrial applications.

Magnetite powder is frequently used as a carrier of toner (carbon black powder) in the plain paper copier, PPC. The static electrification of the carrier and toner is one of important properties in the development process of the PPC technique. To obtain copies of good quality, investigators focus their attention on controlling the static electrification of the carrier and toner by the surface modification. When two polymers are rubbed against each other and separated, one is positively charged and acts as an electron donor, and the other negatively charged and acts as an electron acceptor. The sequence of polymers, according to their charging properties, is called the triboelectric series.¹ Polytetrafluoroethylene is the polymer with the strongest electron acceptor properties of the commercial polymers, and polyethylene, polyvinyl chloride, cellulose acetate, and Nylon 6,6 follow in the triboelectric series.¹ In the PPC development, generally, a negatively-

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charged carrier and a positively-charged toner are used. Therefore, the means by which the carrier and toner surfaces are controlled in charging them negatively and positively, respectively, is of importance. In this study, surface modification of the carrier was attempted by coating of polytetrafluoroethylene to form a negatively-charged surface.

Plasma polymerization is a thin film process, and all surfaces of the substrates in the plasma zone are covered with the thin films of the plasma polymers. In this sense, plasma polymerization is a polymer-coating process, and the surface properties of materials are able to be changed easily by the plasma-polymer coating. The plasma polymerization of tetrafluoroethylene yields fluoro polymers, which are similar in hydrophobic properties, but are not identical in chemical structure to polytetrafluoroethylene. The surface modification of powders by the plasma polymerization of tetrafluoroethylene was attempted.

Powder is difficult to handle in the polymer-coating process because of aggregation and the large surface area per unit mass of the powder. In the polymer-coating process using plasma polymerization, 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 between solid and gas or liquid. Powder is placed on a porous plate in the reactor, which is positioned vertically, and 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 gas stream, the pressure drops, and the drag on individual powder increases. As a result, the powders start to move and become suspended in the fluid. This state is called "fluidization," and means the condition of fully suspended particles.² If the powders in the fluidization state are introduced into the zone of the plasma polymerization, each of the powders is coated with the plasma polymers without aggregation.

This study is the first attempt to modify the powder surface by plasma polymerization in a fluidized reactor. Polyethylene and magnetite powders were used as specimens, and the surfaces of these powders were coated with plasma polymers of tetrafluoroethylene. The plasma-polymer-coated powders were also analyzed by FTIR spectrometry and XPS. We discussed whether the combination of fluidization and plasma polymerization techniques was of practical use in the polymer-coating of powders.

EXPERIMENTAL

Materials

Polyethylene powders [Idemitsu Petrochemical Co., Japan; density 0.95 g/cm³ and powder size 100/200 mesh (0.074–0.147 mm diameter)] and magnetite powders, without any surface modification [Tomoe-gawa Paper Co. Ltd., Japan; apparent density 2.45 g/cm³, powder size 200/350 mesh (44–63 μm diameter)], were used as powder specimens. Tetrafluoroethylene was purchased from PCR Inc., USA, (99% purity) and were used as a monomer for plasma polymerization without further purification. A toner, composed of styrene-acrylonitrile copolymer (Tomoe-gawa Paper Co. Ltd., Japan; powder size 11–12 μm diameter), was used for measuring the triboelectric charge in the carrier-toner contact.

Plasma Polymerization Reactor with Fluidized Bed and Plasma Polymerization Reactor and Plasma Polymerization Procedures

The reactor used this study for the plasma polymerization was a homemade one with a fluidized bed. It consisted of a cylindrical Pyrex glass tube (35 mm inner diameter, 887 mm long) with a glass filter (#2) as a porous plate to support the bed of the 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, and a gas inlet with a mass flow controller at the bottom. The tube was open at the top and was connected through a trap for deposition of the powders that flew from the fluidized bed with the combination of a mechanical booster pump (108 m³/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, 300 W). The arrangement of these components is schematically shown in Figure 1.

Five g of the polyethylene or magnetite powder was filled into the reactor, which was vertically placed, and the mixtures of tetrafluoroethylene (TFE) and argon (Ar) gas were injected from the gas inlet at the bottom of the reactor. When the gas mixture was passed at low flow rate up through a bed of the powders, the powders did not move. However, when the flow rate of the gas mixture increased, the pressure dropped and the drag on individual

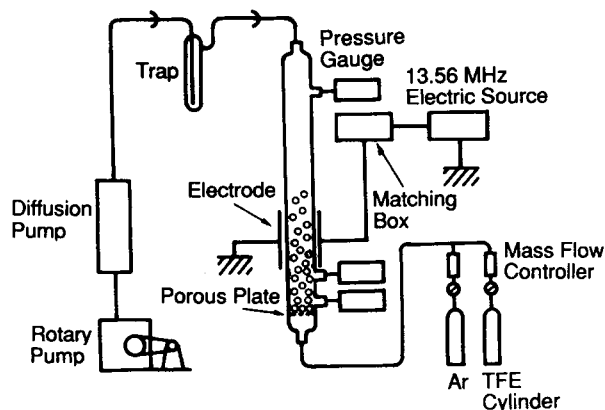


Figure 1 Schematic of plasma polymerization reactor system with fluidized bed.

powders increased. As a result, the powders started to move and became suspended in the fluid. This state is called "fluidization," and is defined as the condition of fully suspended particles. The fluidization of the powders, using the reactor shown in Figure 1, occurred at a flow rate of more than $23 \text{ cm}^3/\text{min}$ for the polyethylene powder, and at a rate of $40 \text{ cm}^3/\text{min}$ for the magnetite powder at a pressure of 133 Pa in the fluidized bed.

The powders in the fluidized state were coated by the plasma polymerization of tetrafluoroethylene at an Rf power of 70–150 W at a pressure of 133 Pa for 1 h.

IR and XPS Spectra of Polyethylene and Magnetite Powders

IR spectra of the plasma-polymer-coated polyethylene and magnetite powders were recorded on a Horiba Fourier transform infrared spectrometer, FT-300, with a MCT detector and a diffuse reflector (Spectra Tech Inc., USA, model 0030). The spectral resolution was 0.5 cm^{-1} , and 500 scans were recorded for each sample.

The XPS spectra of the plasma-polymer-coated polyethylene and magnetite powders were obtained on a Shimadzu spectrometer 850, using Mg K_{α} photon source. The anode voltage was 8 kV, the current was 15 mA, and the background pressure in the analytical chamber was 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 $S(C_{1s}) = 1.00$, $S(N_{1s}) = 1.77$, $S(Fe_{2p}) = 10.50$, and $S(O_{1s}) = 2.85$.

Static Electrification Properties of Magnetite Powders

Nineteen g of the plasma-polymer-coated magnetite powder was mixed with a toner (Tomoe-gawa Paper Co. Ltd., DP-58), using a blender at a blending rate of 100 rpm. Afterwards, the mixture was placed in a Faraday cage with a stainless steel mesh screen, the toner in the mixture was blown off by a stream of nitrogen gas introduced from the top of the Faraday cage, and the carriers remained on the mesh screen. The capacity of the triboelectric charge, generated on the surfaces of carriers, was measured with a Toshiba powder-charge measuring device, TB-200³. Figure 2 shows a schematic diagram of the powder charge measuring equipment.

When the capacity of charges generated at the surface of carriers at time zero and T , after the separation of the carrier-toner contact is Q_0 and Q_T , respectively, the Q_0 is as shown in eqs. (1) and (2).³

$$Q_0 = CV_0 \left(1 + \frac{T}{2\tau} \right) \quad (1)$$

$$V_T = \left(1 - \frac{T}{\tau} \right) V_0 \quad (2)$$

where τ is the time constant of the charge measuring equipment, and V_0 and V_T are the electric potential of the capacitor at time zero and T , respectively. From eqs. (1) and (2), eq. (3) is derived.

$$Q_0 = CV_0 \left(1 + \frac{V_0 - V_T}{2V_0} \right) \quad (3)$$

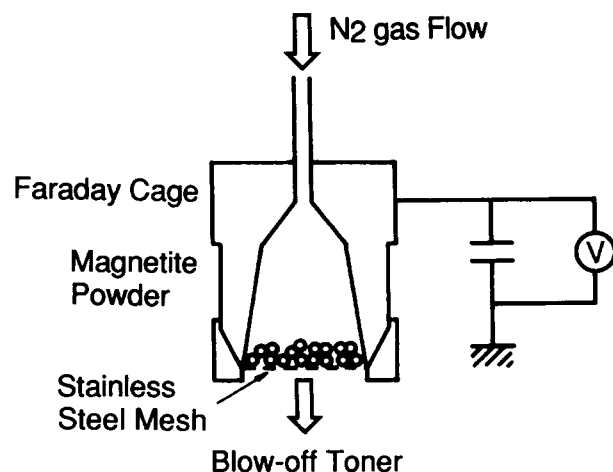


Figure 2 Schematic of triboelectric charge measuring equipment.

In our measurements, T is 5–30 sec, and $(V_0 - V_T/2V_0)$ is less than 0.001, and is negligible. Therefore, eq. (4) is shown as³

$$Q_0 = CV_T \quad (4)$$

Practically, the capacity of charges was measured at 30 sec after the separation of the carrier-toner contact.

RESULTS AND DISCUSSION

Surface Analysis of Plasma-Polymer-Coated Polyethylene Powders

In the plasma polymerization process, generally, polymer-forming and ablation processes compete (the CAP mechanism, proposed by Yasuda⁴), and the deposited plasma polymers result from the balance of the two processes. The balance is controlled by the W/FM parameter, where W , F , and M are defined as the apparent *rf* power to sustain glow discharge in Joule/min, a flow rate of the monomer in mol/min, and the mol wt of the monomer in kg/mol, respectively.⁴ The W/FM parameter in Joule/kg is defined as the apparent electric-input energy per unit of the monomer in plasma polymerization. When plasma polymerization is operated at low W/FM parameters, the polymer-forming process rather than ablation process is predominant, and the polymer deposition rate increases with increasing W/FM parameter (in the energy-deficient region). On the other hand, plasma polymerization operates at high W/FM parameters, the ablation process rather than the polymer-forming process is predominant, and the polymer deposition rate decreases with an increase in the W/FM parameter (in the energy-sufficient region). The effects of the W/FM parameter on plasma polymerization are schematically illustrated in Figure 3. Plasma polymerization in the energy-deficient region yields plasma polymers with less damage by the ablation process, and plasma polymerization in the energy-sufficient region deposits plasma polymers with damage. When TFE is plasma-polymerized at extremely high W/FM parameters, all fluorine atoms in TFE are sputtered off, and no fluorine-containing plasma polymers are deposited.⁴ Therefore, the W/FM parameter is an important factor in the control of the plasma polymerization process.

Preliminary experiments showed that the plasma polymerization of TFE should be operated at W/FM parameters of less than 100 MJ/kg, because of

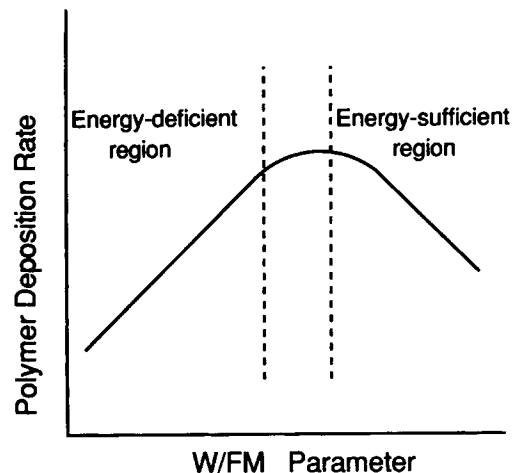


Figure 3 Schematic of dependence of plasma polymerization on W/FM parameter.

less elimination (ablation) reaction of fluorine atoms. So, plasma polymerizations in this study were operated at W/FM parameters of 67 and 97 MJ/kg. Table I shows the effects of the TFE concentration in the TFE/Ar mixture, as well as the W/FM parameter on the plasma polymerization, and Figure 4 shows that the F/C atomic ratio at the surface of the plasma-polymer-coated polyethylene powders is plotted against the TFE concentration and the W/FM parameter. The F/C atomic ratio, at the surface of the polyethylene powders, was determined from the relative intensity of the F_{1s} and C_{1s} core level spectra. The polyethylene surfaces, plasma-polymerized at a W/FM parameter of 97 MJ/kg, show a higher F/C atomic ratio than those at a W/FM parameter of 67 MJ/kg. And the F/C atomic ratio, when the polyethylene surfaces were plasma-polymerized at the same level of the W/FM parameter, increases linearly with increasing TFE concentration in the TFE/Ar mixture (Fig. 4). From these results, we conclude that the plasma polymerization at high W/FM parameters up to 100 MJ/kg, and at high TFE concentrations up to 35 mol %, is favorable for the coating process with fluorine-containing polymers.

IR spectra for the polyethylene powders, coated with TFE plasma polymers, showed characteristic and strong absorption at near 1250 cm^{-1} , due to C—F stretching vibration,⁵ but the fine structure of the fluorine functionalities, such as CF, CF_2 , and CF_3 groups, could not be determined from the IR spectra. XPS (C_{1s}) spectra yield information on the fine structure of the fluorine functionalities. Figure 5 shows typical C_{1s} core level spectra for the polyethylene powders coated with TFE plasma polymers.

Table I Atomic Composition of Polyethylene Powders Treated with TFE Plasma Polymerization

Sample No.	Plasma Polymerization Conditions				Atomic Ratio F/C
	FR Power (W)	TFE Flow Rate (cm ³ /min)	Ar Flow Rate (cm ³ /min)	W/FM (MJ/kg)	
A-1	70	8 (35 mol %)	15	67	0.72
A-2	100	8	15	96	0.79
B-1	78	8 (30 mol %)	19	67	0.62
B-2	111	8	19	96	0.72
C-1	88	8 (25 mol %)	24	67	0.48
D-2	146	8 (20 mol %)	32	96	0.62
Untreated					< 0.01

The C_{1s} spectra expand into a high binding energy region up to 295 eV and are decomposed into six C_{1s} components, which appear at 285.0 (CH groups), 286.8–287.2 (CH—CF or C=O groups), 288.8–289.4 (CF groups), 291.0–291.8 (CF₂ groups), 292.1–292.8 (CF₂–CF_n groups), and 293.3 eV (CF₃ groups).⁶ The relative concentration of these C_{1s} components is summarized in Table II. The surfaces of the plasma-polymerized polyethylene powders, except the A-1 and A-2 samples as shown in Table II, are mainly composed of CF and CF₂ groups, as well as CH groups. The A-1 and A-2 samples, which were plasma-polymerized at a high TFE concentration of 35 mol %, possess CF groups at their surfaces,

in addition to CF₂, CF, and CH groups. The appearance of the CF and CF₃ groups enables one to predict that the cleavage of C—F bonds in TFE and the rearrangement of F atoms would occur in the plasma polymerization process. From the relative concentration of the C_{1s} components, we estimated the average number of fluorine substituents per the fluorinated carbon atoms (F/fluorinated C atomic ratio). The calculation is summarized in the last column in Table II. The ratio for the A-1 and

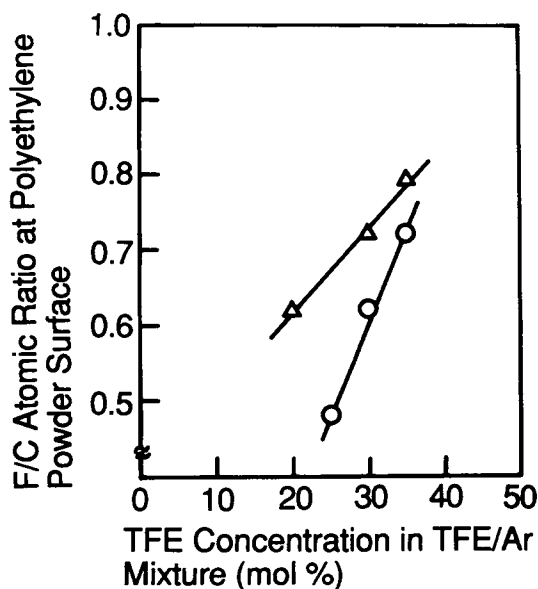


Figure 4 Effects of TFE concentration and *W/FM* parameter on plasma polymerization in TFE/Ar mixture system: (○) plasma-polymerized at a *W/FM* parameter of 67 MJ/kg, (△) plasma-polymerized at 96 MJ/kg.

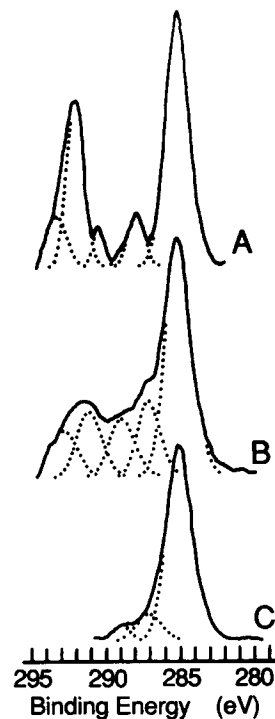


Figure 5 C_{1s} spectra for polyethylene powder surfaces, treated with plasma polymerization of TFE. (A) Plasma-polymerized at 35 mol % TFE at 96 MJ/kg, (B) plasma-polymerized at 20 mol % at 96 MJ/kg, (C) untreated.

Table II Fluorinated Carbon Composition of Polyethylene Powders Treated with TFE Plasma Polymerization

Sample No.	Fluorinated Carbon Composition (mol %)			F/Fluorinated C Atomic Ratio
	CH Groups	CF Groups	CF ₂ Groups	
A-1	63	13	24	1.9
A-2	54	11	34	2.3
B-1	65	8	27	1.8
B-2	57	12	30	1.7
C-1	71	8	20	1.7
D-2	63	12	25	1.7

A-2 samples is 1.9 and 2.3, respectively, and the ratio for the other samples (B-1, B-2, C-1, and D-2 samples) is 1.7–1.8. This comparison indicates that the formation of highly fluorinated carbon groups is favorable in the plasma polymerization at a high TFE concentration of 35 mol %.

The C_{1s} spectra also show that the plasma-polymerized polyethylene surfaces contain no-fluorinated carbon groups of about 57–71% of the total carbon atoms existing at the topmost layer of the polyethylene surface. This indicates three possibilities: (1) the polyethylene surface is not completely coated with the TFE plasma polymers, (2) the polyethylene surface is completely covered with the TFE plasma polymers, but the TFE plasma polymers contain no-fluorinated carbon groups as well as fluorinated carbon groups (Fluorine atoms in TFE will be eliminated by electron sputtering or by HF elimination reactions with activated hydrogen atoms liberated from the polyethylene surfaces, and plasma polymer with no-fluorinated carbon groups will be formed.), or (3) the polyethylene surface is completely covered with the TFE plasma polymers, but the sampling depth of photoelectrons is deeper than the thickness of the deposited TFE plasma polymers. We cannot as yet interpret that either of the possibilities is the probable reason.

Surface Analysis of Plasma-Polymer-Coated Magnetite Powders and their Triboelectric Properties

The magnetite powders require a higher flow rate of the Ar stream in the fluidized bed for fluidization than the polyethylene powders, because of high density of the powders. In practice, an Ar flow rate of 30 cm³/min was used for the fluidization of the magnetite powder, and the concentration of TFE was 25 and 35 mol %. In these TFE/Ar mixture systems, the plasma polymerization was performed at *W/FM* parameters of 48–77 MJ/kg, and the surface of the magnetite powders was coated with the TFE plasma polymers. The elemental analyses for the plasma-polymer-coated magnetite powders, except for the Fe-1 sample, which were determined by the relative intensity of the F_{1s}, O_{1s}, and C_{1s} core level spectra, as shown in Table III, show an increase in the F/C atomic ratio from < 0.001 to 1.41–1.55 and decreases in the O/C atomic ratio from 0.81 to 0.07–0.13 by the plasma polymerization. This indicates that the powder surfaces were surely coated with fluorine-containing polymers.

The C_{1s} spectra for the plasma-polymer-coated magnetite surfaces showed the peak shift, due to the high-electron negativity of fluorine atoms, toward

Table III Atomic Composition of Carrier Powders Treated with TFE Plasma Polymerization

Sample No.	Plasma Polymerization Conditions				Atomic Ratio	
	RF Power (W)	TFE Flow Rate (cm ³ /min)	Ar Flow Rate (cm ³ /min)	<i>W/FM</i> (MJ/kg)	F/C	O/C
Fe-1	100	10 (25 mol %)	30	61	0.26	1.01
Fe-2	125	10	30	77	1.47	0.07
Fe-3	100	16 (35 mol %)	30	48	1.41	0.11
Fe-4	125	16	30	60	1.55	0.13
Untreated					< 0.01	0.81

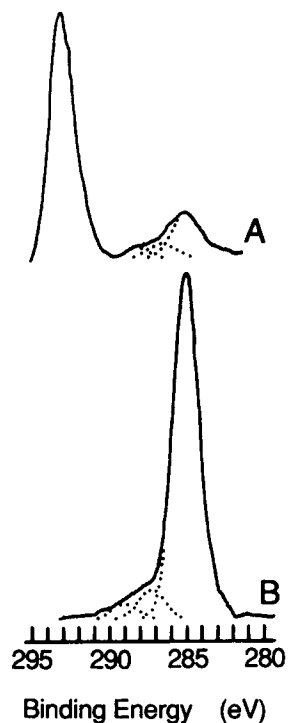


Figure 6 C_{1s} spectra of magnetite powder surfaces, treated with plasma polymerization of TFE. (A) Plasma-polymerized at 35 mol % TFE at 60 MJ/kg, (B) untreated.

the high binding energy regions (about 292 eV). A typical C_{1s} spectrum for the plasma-polymer-coated magnetite powders (Fe-4 sample) is compared with that for the original magnetite powder in Figure 6. The C_{1s} spectrum for the original magnetite powder shows a main peak at 285 eV (CH groups) with a full width at half-maximum (FWHM) of 1.9 eV and a small lump, which is temporarily decomposed into two components of C—O and C=O groups. The relative peak area between the main and collateral peaks is 9 : 1. This indicates that the surface of the magnetite powders is not pure ferric oxide, but is contaminated with carbonaceous materials. The C_{1s} spectrum for the Fe-4 sample, as shown in Figure 6, shows a main peak at 292.5 eV (CF_2 groups) with

a FWHM value of 1.8 eV and a small lump at 285–288 eV, which is temporarily decomposed into three components (CH, CH—CF or C=O, and CF groups).⁶ The relative peak area between the main and collateral peaks is 8 : 2. This XPS analysis indicated that the surface of the plasma-polymer-coated magnetite powders is mainly covered with CF_2 groups containing polymers. The plasma polymers, deposited at the surface of the magnetite powders, are different in the composition of the fluorinated carbons from those of the polyethylene powders, although the same monomer, TFE, was used for plasma polymerization and the plasma polymerizations were performed under similar operational conditions. The plasma polymers, deposited on the magnetite powder surfaces, are rich in CF_2 groups, and those deposited on the polyethylene powder surfaces are mixtures of CF and CF_2 groups. At the present time, we cannot interpret why the plasma polymers, rich in CF_2 groups, were deposited on the surface of the magnetite powders, and why the plasma polymers, rich in CF_2 groups, were not deposited on the polyethylene surface.

TFE polymers plasma-polymer-coated magnetite powders of 19 g were mixed with a toner of 1 g, and the mixture was blended using a blender at a rate of 100 rpm for 5–60 min. Afterwards, the triboelectric properties of the magnetite powders were compared with the untreated powders. Table IV shows the capacity of triboelectric charge for the plasma-polymer-coated magnetite powders (Fe-4 sample) and the untreated powder. The capacity of the triboelectric charge, as shown in Table IV, was markedly changed by the TFE plasma-polymer coating. The untreated magnetite powder, when stirred at 100 rpm with a toner for 5–60 min, shows a capacity for a triboelectric charge of 10–13 $\mu C/g$, and the plasma-polymer-coated magnetite powder shows a capacity of 23–27 $\mu C/g$, which is about two times higher than the untreated powder. It is obvious that the TFE plasma-polymer coating contributes to the enhancement of the triboelectric charging. The enhancement may be due to high dielectric constant

Table IV Static Electrification Properties of Plasma-Polymer-Coated Magnetite Powders

Sample No.	Capacity of Triboelectric Charge ($\mu C/g$)			
	Stirring Time 5 ^a	Stirring Time 10	Stirring Time 30	Stirring Time 60
Fe-4	23	26	26	27
Untreated	10	10	13	13

^a Stirring at 100 rpm.

of fluorine-containing polymers deposited on the magnetite surfaces.

From these results, it is obvious that the surface properties of powders can be modified by the plasma polymerization in the fluidized-bed reactor.

CONCLUSION

This study is the first attempt to modify the surfaces of powders in the fluidization by the plasma-polymerization technique. Polyethylene and magnetite powders were fluidized in a plasma-polymerization reactor by the stream of the TFE/Ar mixture gas, and were modified by the plasma-polymerization of TFE. The surfaces of these modified powders were analyzed with FTIR and XPS. The static electrification properties of the plasma-polymer-coated magnetite powders were compared with those of the uncoated powder.

1. The surfaces of polyethylene and magnetite powders were coated with fluorine-containing polymers, deposited from the plasma polymerization of TFE. The plasma polymers were mainly composed of CH, CF, and CF₂ groups.
2. The elemental composition (F/C atomic ratio) and the composition of the fluorinated carbon component in the plasma polymers was dependent upon the W/FM parameter, as well as the TFE concentration in the TFE/Ar mixture. The W/FM parameter is a factor

to control the chemistry of the plasma polymerization reactions of TFE.

3. The triboelectric charge of the magnetite powders, when modified by the plasma polymerization of TFE, was higher by about two than the unmodified.

In conclusion, the plasma polymerization in a fluidized-bed reactor is a possible surface modification technique for powders. The plasma polymerization of TFE in the fluidized-bed reactor causes the surface of the magnetite powders to be negatively electrified.

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