

Functionalization of HDPE Powder by CF₄ Plasma Surface Treatment in a Fluidized Bed Reactor

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Abstract—The surface of HDPE polymer powder was fluorinated by CF₄ plasma in a fluidized bed reactor. Plasma is generated by an inductively coupled electrode at 13.56 MHz (rf) frequency, connected to an auto matching network and an rf power generator. In plasma surface fluorination, the CF₄ gas is diluted with He gas. The experimental variables are treatment time and rf power. The chemical property of the modified powder has been determined by using ESCA and FTIR. Plasma surface fluorination with the powder in a fluidized bed reactor results from the formation of CHF-CH₂, CHF-CHF and CF₂ groups. These fluorine functionalities and the fluorine atomic ratio on the surface increase with the treatment time and rf power. It has been found that the composite parameter is a good measure for determining the effect of total energy input on the plasma surface treatment of polymer powder in a fluidized bed reactor.

Key words: Fluidized Bed, Polymer, Powder, Plasma, Functionalization

INTRODUCTION

Recently, new techniques have been developed for modifying surface layers to have different surface properties from its bulk materials, including chemical treatment, photochemical treatment, plasma treatment, and surface grafting [Nihlstran et al., 1997; Park, 1995; Park and Kim, 1994, 1997, 1998; Poncin-Epaillard et al., 1997]. There is growing interest in using "plasmas" to modify the surface structure and composition of solid materials. This interest has developed for two reasons. First, plasmas can produce a unique surface modification and, second, the extent of modification can be easily controlled. In particular, the most interesting technique among plasma surface treatments is glow discharge, in which free electrons gain energy from an imposed electrical field, and subsequently lose it through collisions with neutral molecules in the gas. The transfer of energy to gas molecules leads to the formation of a host of chemically reactive species, some of which become precursors to the plasma surface reaction.

The idea of using a plasma for altering surface properties of various polymeric and non-polymeric materials to generate specialty surfaces is well established, with potential applications in adhesive bonding of otherwise incompatible materials, biocompatible polymer surfaces, modifying barrier properties and other devices [Hayes and Dixon, 1979]. There is also interest in decreasing the polymer surface energy, e.g., to create a Teflon-like surface on a variety of polymer materials [Anand et al., 1981]. This interest arises from the fact that a Teflon-like surface has some unique properties, such as chemical inertness, low surface energy (non-wettable), excellent frictional properties, lower permeability, and relatively good thermal stability.

Plasma surface treatment has been especially successful with polymers, because the glow discharge or cold plasma is effective in modifying only surface properties, leaving the bulk properties unaltered. Apparently, the energetics of the active species in the plasma are such that the depth of penetration into most materials is only on the order of a few thousand Angstroms [Clark and Feast, 1978].

In general, the reactions of a plasma with polymers may be classified as follows. (1) Surface reactions: Both substitution and addition type reactions are included in this group. The number of carbon atoms in the polymer substrate does not change significantly. (2) Deposition/polymerization: In this process, substituted carbon atoms are added to the polymer surface. Polymer may be formed in the gas phase and then deposited on the substrate, or free radicals may be formed on the surface which then react with gaseous radicals. (3) Etching/ablation: Carbon atoms are removed from the polymer surface by physical etching and by chemical reaction at the surface to form volatile products. Which reactions predominate will depend on the gas mixture in the plasma and on the chemical structure of the polymer. Corbin [1985] and Loh et al. [1987] reported that the CF₄ plasma generally resulted in surface reaction and etching although deposition was possible in principle.

Previous studies were directed towards modifying films or fibers [Yasuda, 1984]. However, several application areas (including thermal energy storage materials, microcarrier for bioprocess and advanced composite materials for pigment, filler and bone cement) require materials in a powder form. Intimate mixing between the powder and the reactive gas phase should increase both the reaction rate and the homogeneity of the treated surface. Increasing mobility of the individual particles will promote mixing. For this reason, a plasma fluidized bed reactor was designed to modify powder materials [Inagaki et al., 1992; Park, 1995; Park and Kim, 1994, 1997, 1998].

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In a plasma system, the reactions consist of interactions of photons, electrons, ions, and metastables of neutral atoms and molecules with the substrate. The diffusion of reactants (ions, radicals, and neutrals) from the gas phase to the substrate surface is defined by the reactive parameters (pressure, gas flow rate and power input) and the interfacial surface area. Several reaction conditions that affect the fluorination process have been determined. The experimental variables are treatment time, power supplied to the plasma, flow rate of gases in the reactor, concentration of fluorine in the feed, location of plasma load, and reactor pressure. These parameters are known to influence the surface treatment of polymer films [Anand et al., 1981; Yasuda, 1984]. The importance of these parameters has been reconfirmed here on the powder materials. The effects of these parameters on the surface treatment of polymer powder have been determined in terms of high and low-resolutions of ESCA spectra.

The objective of this study is to modify the surface properties of fine powder in a fluidized bed reactor and to determine the effects of operating parameters on the surface functionalities of the polymer powder fluorinated by the reactions with active species in a glow discharge.

EXPERIMENTAL

Experiments for the plasma surface treatment of polymer powder were carried out in a fluidized bed reactor (34 mm-ID \times 0.8 m-high) made of Pyrex glass as shown in Fig. 1. High-density polyethylene (HDPE) powder with mean diameter of 231

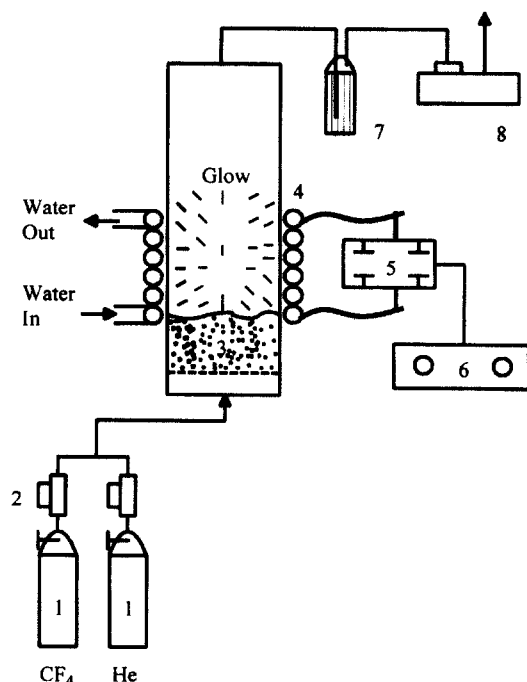


Fig. 1. Schematic diagram of plasma surface fluorination in a fluidized bed reactor.

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|--------------------------|---------------------------|
| 1. Gas cylinder | 5. rf matching network |
| 2. Mass flow controller | 6. Plasma power generator |
| 3. Fluidized bed reactor | 7. Particle trap |
| 4. Plasma load | 8. Vacuum pump |

μm was fluidized by CF_4 gas (5 sccm), which was diluted with He gas (20 sccm). An inductively coupled electrode (4.8 mm-OD copper tube, 6 turns) for glow discharge at 13.56 MHz (rf) frequency was placed at 60 mm from the gas distributor and connected to an auto matching network and an rf power generator. The pressure in the reactor, as monitored by the vacuum gauge, was 133 Pa. The details of the experimental procedures can be found elsewhere [Park, 1995; Park and Kim, 1994]. The ranges of experimental variables were treatment time (10 min-12 h), rf power (50-200 W) and the composite parameter (0-11,146 GJ-s/kg).

Fourier transform infrared spectroscopy (FTIR) was used to determine the functionality of polymer. Also, the functional groups and the primary source of atomic and molecular information within the surface region of polymer materials by plasma treatment can be determined from ESCA [Clark and Dicks, 1977]. The ESCA measurement utilizes monochromatic X-rays to photoionize core-type electrons [Boenig, 1982]. From the determination of kinetic energy of photoelectrons, the binding energy of that electron can be calculated. Binding energies of these photoelectrons are a characteristic of the element from which they emerge. Thus binding energy can be directly related to atomic species. ESCA is the surface sensitive analytical tool to characterize the surface chemical composition of HDPE powder treated by plasma in a fluidized bed reactor [Park and Kim, 1994, 1998]. The information that can be extracted from this technique includes quantitative elemental analysis (carbon, fluorine, and oxygen) and qualitative analysis of the carbon molecular environments through carbon 1s chemical shifts.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy was used for identification of chemical constituents of plasma treated polymer powder in a fluidized bed reactor. The IR bands for HDPE powder in the range of 600 to 1,300 cm^{-1} are shown in Fig. 2 where an obvious peak is not expected at 720 cm^{-1} due to CH_2 for untreated HDPE powder [Fig. 2(A)]. However, Fig. 2(B) is the spectrum of CF_4/He plasma treated HDPE powder under the given conditions of rf power (100 W), flow rate of feed gas

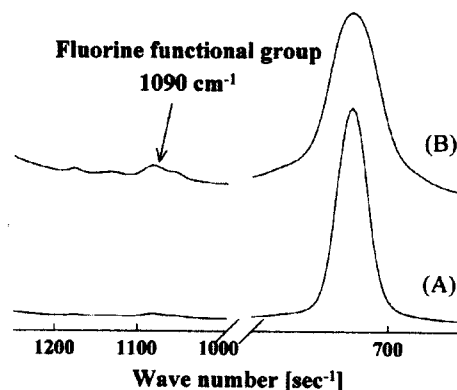


Fig. 2. Typical FTIR spectra of plasma-treated HDPE powder.

- (A) He plasma; 100 W, 25 sccm, 3 hr (B) CF_4/He plasma; 100 W, 25 sccm, 3 hr.

mixture (25 sccm) and treatment time (3 hr) in a fluidized bed reactor. The interpretation of the bands is quite straightforward based on the published data [Nielsen and Holland, 1961; Luongo, 1969].

In general, the region of IR bands from about 1,000 to 1,350 cm⁻¹ is assigned to various fluorine-carbon bonds. Polytetrafluoroethylene (PTFE) shows two very strong bands at 1,220 cm⁻¹ and 1,150 cm⁻¹ corresponding to CF₂ asymmetrical and symmetrical stretches, respectively [Das et al., 1994]. Giegengack and Hinze [1971] found a symmetric stretch band at 1,158 cm⁻¹ for plasma polymerized PTFE film. The region between 1,200-1,260 cm⁻¹ in the treated polymers could thus be assigned to -CF₂ groups. The strong broad band in the treated polymers is at 1,090 cm⁻¹. The CF₂ stretch is known to mix with FCF bending, CC stretch and CCC bend; this may result in a shift and broadening of the band especially rich in hydrocarbons in the present fluorinated systems. Also, CF saturates and unsaturates exhibit in the range 1,000 to 1,200 cm⁻¹. It is possible that some of these groups were being sampled in the depth since these groups are present especially if there is a gradient in the polymer composition from a completely -CH₂-CH₂- state in the bulk to a completely CF₂-CF₂ state on the surface. This indicates that the fluorine functionalities are produced at the surface of HDPE powder by CF₄/He plasma in a fluidized bed re-

actor. However, the fine structure of fluorine functionalities, such as CF, CF₂, and CF₃ groups, cannot be determined from the IR spectra. ESCA spectra yield information on the fine structure of the fluorine functionalities.

Many research workers have shown how ESCA as a spectroscopic tool could be used to investigate various aspects of the structure, bonding and reactivity of polymeric systems [Clark and Dilks, 1977]. Typical ESCA survey spectra (low resolution between 0 and 1,400 eV) are shown in Fig. 3. Fig. 3(A) is a survey spectrum for HDPE powder treated by He plasma under the given condition of rf power (100 W), He gas flow rate (25 sccm) and treatment time (3 h) in a fluidized bed reactor. Fig. 3(B) is one for the powder after CF₄/He plasma fluorination at rf power of 100 W, flow rate of feed gas mixture of 25 sccm and treatment time of 3 h. For plasma with no CF₄, the spectrum consists of C_{1s} peak (285 eV), N_{1s} peak (403 eV), O_{1s} peak (531 eV), O_{Au} peak (976 eV), N_{Au} peak (1,108 eV), and C_{Au} peak (1,226 eV). The peaks corresponding to fluorine element do not. However, for CF₄/He plasma, the large F_{1s} peak appears at about 684 eV and F_{Au} peak at about 832 eV. These results are similar to that of other investigations [Clark and Dilks, 1978; Anand et al., 1981]. This indicates that extensive fluorination occurs in the fluidized bed reactor.

ESCA spectra can also be acquired in a high-resolution mode. By measuring the area under the major photoelectron peaks of each element present, and using appropriate machine dependent correction factors [Wagner, 1980; Park, 1995; Park and Kim, 1998], atomic composition can be determined. Also, molecular information is also present in these spectra. Shifts in the exact position of the peaks result from a change in the chemical environment of the atom. These chemical shifts are on the order of 0.5 to 10 eV. Fluorine, due to its high electronegativity, tends to shift the observed carbon peak to higher binding energy.

Fig. 4 shows the spectra of high-resolution mode about carbon, oxygen and fluorine elements in previous survey spectra (Fig. 3). In Fig. 4(A), the F_{1s} spectrum almost disappears; the

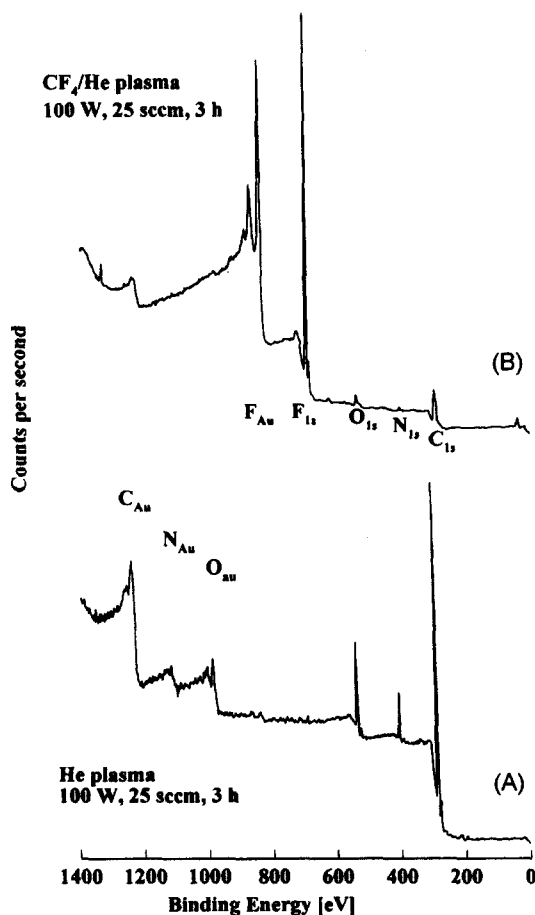


Fig. 3. Low resolution ESCA spectra of plasma-treated HDPE powder.
(A) He plasma, (B) CF₄/He plasma.

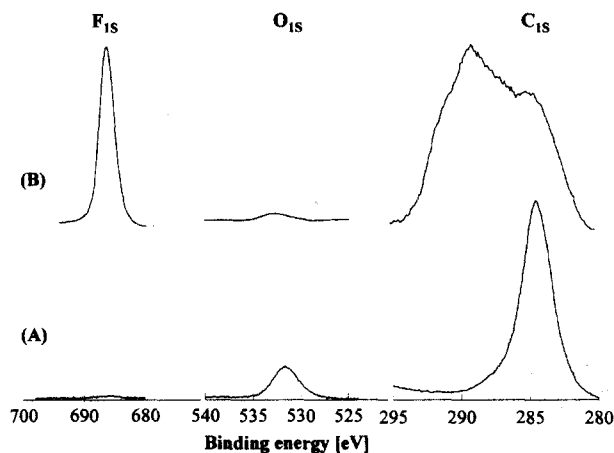


Fig. 4. Typical high resolution spectra of HDPE powders in a fluidized bed.
(A) He plasma; 100 W, 25 sccm, 3 hr, (B) CF₄/He plasma; 100 W, 25 sccm, 3 hr.

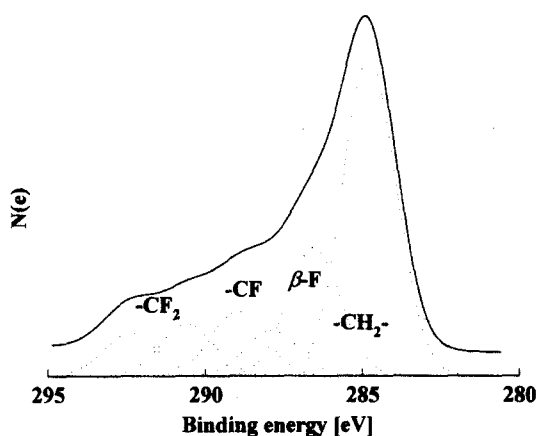


Fig. 5. Typical C_{1s} spectrum of high resolution mode with deconvolution of plasma-treated HDPE powders.

small O_{1s} spectrum is due to oxidation after He plasma treatment and then C_{1s} spectrum is symmetrical because of less change in the chemical environment of carbon atom. Due to the surface fluorination, however, the F_{1s} spectrum in Fig. 4(B) is sharp and the C_{1s} spectrum is asymmetrical. According to the experimental conditions, the peak areas of carbon, fluorine and oxygen elements are varied. From these data, the extent of fluorination can be obtained.

In the C_{1s} peaks resulting from changes in the chemical environment of the carbon atoms, a representative high resolution C_{1s} spectrum for the fluorinated HDPE powder in the fluidized bed reactor is shown in Fig. 5 from which six different peaks are identified [Park, 1995]. Four peak groups of these peaks can be labeled in Fig. 5 as $(-CF_2-)$, $(-CF- \text{ or } -CHF-)$, $(\beta-F: -CH_2-CFX-, \text{ or } -CO-)$ and $(-CH_2-)$. Inagaki et al. [1993] decomposed the C_{1s} spectra of HDPE powder by plasma polymerization into six C_{1s} components which appear at 285.0 (CH groups), 286-287.2 (CH-CF or C=O groups), 288.8-289.4 (CF groups), 291.0-291.8 (CF_2 groups), 292.1-292.8 (CF_2 -CF_n groups) and 293.3 eV (CF_3 groups). It has been reported that CF_4 plasma treatment of a polymer surface leads to the formation of CF, CF_2 , and CF_3 groups [Yasuda et al., 1988; Anand et al., 1981; Clark and Dilks, 1978]. Yagi et al. [1982] observed the following ESCA results: radicals of F and CF_3 would be expected to predominate and to react with the HDPE surface in a CF_4 discharge. According to Truesdale and Smoliusley [1979], a CF_4 discharge provides F, F_2 and mainly of CF_3 - CF_3 which further suggests the formation of CF_3 radicals. Based on chemical shifts in the C_{1s} spectra from ESCA measurements, an abundance of fluorine groups including $-CF_2$ group in the surface layers is found. According to the experimental conditions, the peaks of C_{1s} , F_{1s} and O_{1s} are changed. From these data, the effect of operation parameters, e.g., treatment time, rf power and composite parameter, on the extent of surface functionalities is determined.

The influence of treatment time on the extent of fluorination (F/C atomic ratio) and the percent of each functionality of the surface is presented in Table 1. At a given condition (100 W, 5 sccm CF_4 /20 sccm He), the F/C atomic ratio reaches a maximum at approximately 180 minutes of treatment time, but levels off at about F/C atomic ratio of 1.4. This is why degradation

Table 1. Summary of relative fluorinated carbon compositions of HDPE powder treated by CF_4 /He plasma in the fluidized bed reactor with treatment time

Experiment condition	F/C	Peak 1	Peak 2	Peak 3	Peak 4
100 W, 25 sccm					
10 min	0.48	66.1	13.8	11.3	8.8
20 min	0.61	59.0	18.8	12.5	9.5
30 min	0.85	44.9	19.5	21.8	13.4
60 min	1.39	29.2	22.0	27.3	21.4
180 min	1.71	19.1	18.3	37.7	24.9
360 min	1.46	32.2	13.5	20.4	33.9
720 min	1.28	36.5	10.5	19.3	33.7

Peak 1: CH_2 group (285 eV); Peak 2: β -F group (285.9-286.5 eV)
Peak 3: CF group (287.9-288.9 eV); Peak 4: CF_2 group (290.6-292.8 eV)

and fluorination occur simultaneously in a glow discharge environment [Anand et al., 1981; Corbin et al., 1983; Poncin-Epaillard et al., 1993]. The build-up of fluorine-containing species on the HDPE powder surface can be followed as the reaction proceeds towards completion. This table shows also the relative fluorinated carbon compositions of HDPE surfaces treated with the plasma at various treatment times. The surfaces of the plasma-fluorinated HDPE are mainly composed of CF and CF_2 groups, as well as CH groups. As the treatment time is increased, the fluorine functionalities increase up to 180 min, but level off. Although an F_2 /He gas feed system, the build-up of fluorine-containing groups with the treatment time is similar to that of Anand et al. [1981]. The hydrogen substitution reaction on the surface results in the replacement of hydrogen atoms by fluorine-containing groups, which can be conveniently monitored by ESCA. The important observation plots are: (a) reactions reach a level of maximum fluorination rapidly, and then level off, (b) fluorine contents are mainly composed of β -F, CF, and CF_2 functionalities so that the surface is made a Teflon-like surface.

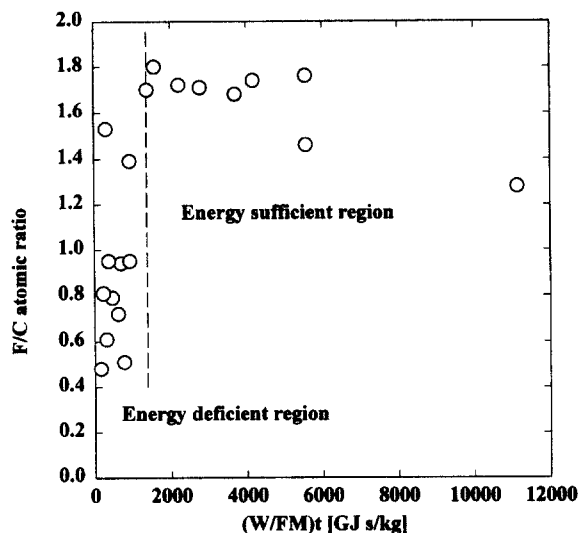
The reaction rate of fluorine species with HDPE powder is accelerated by using the cold plasma generated from a diluent mixture of CF_4 gas in helium. Fluorination may be expected to occur in this case due to the generation of active fluorine and diluent gas species in the plasma and the reactive species created on the surface of solid substrate (HDPE powder). The source of fluorine radicals (and ions) in the present study is CF_4 gas which dissociates readily into $F\cdot$, $CF\cdot$, $-CF_2$, etc. in a glow discharge [Park, 1995].

The effect of rf power on the type of fluorine-carbon bonds formed on plasma treated HDPE powder surfaces in the fluidized bed reactor can be seen in Table 2. As can be seen, fluorine functionality of the surface of HDPE powder increases with increasing rf power. The change of energy coupled with the plasma may result in changes of the energetic of the plasma species including electrons, ions, and radicals. An increase in rf power would accelerate the reactions and other plasma-substrate processes (e.g., ion-assisted etching). The overall change in energy of the active species slightly increases with power supply at the power range studied. It is found that CF_4 /He plasma-

Table 2. Summary of relative fluorinated carbon compositions of HDPE powder treated by CF₄/He plasma in the fluidized bed reactor with rf powder

Experiment condition	F/C	Peak 1	Peak 2	Peak 3	Peak 4
30 W, 25 sccm					
50 W	0.81	45.3	18.6	22.3	13.6
100 W	0.85	44.9	19.5	21.8	13.4
150 W	0.94	44.7	19.9	22.2	13.4
200 W	0.95	44.3	21.3	21.8	13.7
180 min, 25 sccm					
50 W	1.70	20.6	18.2	35.9	24.3
100 W	1.71	19.1	18.3	37.7	24.9
150 W	1.74	18.4	18.1	39.0	24.6
200 W	1.76	17.0	18.0	40.1	24.8

Peak 1: CH₂ group (285 eV); Peak 2: β -F group (285.9-286.5 eV)
 Peak 3: CF group (287.9-288.9 eV); Peak 4: CF₂ group (290.6-292.8 eV)

**Fig. 6. Effect of composite parameter of F/C atomic ratio of surface of plasma-treated HDPE powders.**

treated powder consists of functionality such as β -F, CF, and CF₂, and mainly CF functionality increases with rf power. This may account for hydrogen substitution for fluorine ion due to improving reactivity of the ion.

When the energy input is low (energy-deficient region), the reactions do not proceed fully for good modification of powder surface. When the energy input is too high (energy-sufficient region), etching/ablation or too many unnecessary reactions may take place [Iriyama et al., 1990]. Therefore, the composite parameter [(W/FM)t], which is the total energy input for all reactions occurring in the plasma [Iriyama et al., 1990], is an important parameter in controlling the plasma surface modification process.

Since the composite parameter is a good measure for determining the effect of total energy input on the surface modification, the obtained F/C atomic ratio is presented as a function of the composite parameter as shown in Fig. 6. The F/C atomic ratio

increases with increasing composite parameter [(W/FM)t] down to 1,300 GJ-s/kg; thereafter it remains essentially constant. Therefore, we can suggest that when the composite parameter is below the transition point the region is called an energy-deficient region because energy input is low for the reactions to proceed fully for good modification of the powder surface. Also, when the composite parameter is above that point, the region is an energy-sufficient region because energy input is so high for unnecessary reactions such as etching/ablation to proceed.

CONCLUSION

Fluorine contents in the surface of HDPE powder increase with the CF₄ plasma treatment in a fluidized bed reactor. The functionalities of plasma treated powder are found to be CHF-CH₂, CHF-CHF and CF₂ groups from the ESCA spectra and FTIR measurements. The intensity of fluorine functionalities on the plasma treated HDPE powder surface increases with increasing treatment time, but it remains constant with further treatment. The formation of fluorine functionalities of HDPE powder slightly increases with increasing rf power. According to the composite parameter, there are regions to modify the powder to the sufficient fluorinated surface of HDPE powder.

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