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Surface modification of HDPE powders by oxygen plasma in a circulating fluidized bed reactor

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Summary

Surface modification of HDPE powders by oxygen plasma has been carried out in a circulating fluidized bed (CFB) reactor. The effects of solid holdup, treatment time and radio frequency (rf) power of oxygen plasma on the surface composition and hydrophilicity of HDPE powders have been determined. The solid holdup in the plasma reaction zone mainly governs the stability of plasma glow and surface property of the powders. The hydrophobic surface can be transformed to hydrophilic of HDPE powder and the oxygen functionalities are formed including C=O and C(O)O-, which reach 12% and 8% respectively of the total carbon elements by the oxygen plasma treatment. The CFB reactor outperforms 3.4 times to obtain the similar level of hydrophilicity compared to that in a bubbling fluidized bed based on the composite parameter [(W/FM)t]. The present CFB reactor can be utilized to modify the polymeric surface from hydrophobic to hydrophilic with high-energy efficiency.

Introduction

The possibility of altering the surface of polymer materials at room temperature and uniqueness of the modified surfaces are the particularly appreciated advantages of low-pressure plasma processing for the surface modification applications [1-3]. The macroscopic properties of powders are strongly influenced by their surface properties. Thus, surface modification is an important issue in materials that used in powder form [4]. However, most of the plasma processing has been directed towards films and flat materials. Since powder has a tendency to aggregate and large surface area per unit mass that makes it difficult to handle, research works on fine powder treatment are comparatively sparse [3-7].

The surface modification of the polymeric powders from hydrophobic to hydrophilic or vice versa has many potential applications such as adhesion improvement and biocompatibility [1, 5]. The most popular plasma gas for hydrophilic surface modification of polymers is oxygen. Essentials of the oxygen plasma treatment 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 surface with the plasma is important factor to modify efficiently the polymeric powder surface.

Behavior of powders in a plasma reactor can be classified into (1) Static bed: dense bed of solids in which only minor plasma can be generated [8]. (2) Moving bed: solid particles are slightly expanded state by either mechanical agitation or gravitational force. Rotary drums slightly expanded state by either mechanical agitation or gravitational force. Rotary drums can be used as a reactor with low energy plasma but powder dispersion is not satisfactory [9]. (3) Fluidized bed reactor: powders are suspended above the minimum fluidizing velocity and the plasma is generated in the upper part of a stationary bed [1, 2, 5-7]. In all cases there are possible uncertainties of gas reactivity gradients and resulting in inhomogeneous treatment of powders [4]. Therefore, we designed a CFB reactor for plasma surface modification of polymeric powders since the CFB reactor provides high gas-solid contact, less axial gas dispersion, easy control of solids circulation, smaller particle segregation and agglomeration [10] compared to a bubbling fluidized bed.

In the preset study, the effects of solid holdup, treatments time and rf power of oxygen plasma on hydrophilicity of HDPE powders have been determined in a circulating fluidized bed reactor (10 mm-ID x 850 mm-high, Pyrex glass).

Experimental

Reactor

The circulating fluidized bed reactor and accessory experimental facilities are shown schematically in **Figure 1**. It consists of CFB reactor, gas-supply section, vacuum pump and rf plasma matching section. The CFB reactor is composed of riser (10 mm-ID x 850 mm-high, Pyrex glass), cyclone, downcomer (22 mm-ID, Pyrex glass) and solids feeding system. In general, the solids feeding can be controlled by mechanical or non-mechanical valve. Typical mechanical valves are rotary, screw, butterfly and slide valves having moving parts for mechanical actuation to control solid flow rate. These valves cannot be easily employed under low-pressure conditions due to the sealing and mechanical problems. For applications for low-pressure system, the non-mechanical valves (loop-seal, L-, J-, and V-valve) are commonly employed [11]. The non-mechanical valves without moving parts can control solid flow by aeration. The present reactor adopted the loop-seal as a solid feeding system and controlled solid flow rate by adjusting the aeration rate at the bottom of the loop-seal. During the operation, solids particles were entrained by up-flowing gas and the particles leave the riser are separated in a cyclone and flow back to the riser through a downcomer and the loop-seal. The fluidizing gas was regulated and measured with a mass flow controller (Edward Inc., MFC-1605). The exit of cyclone was connected to a vacuum pump. The system pressure was measured

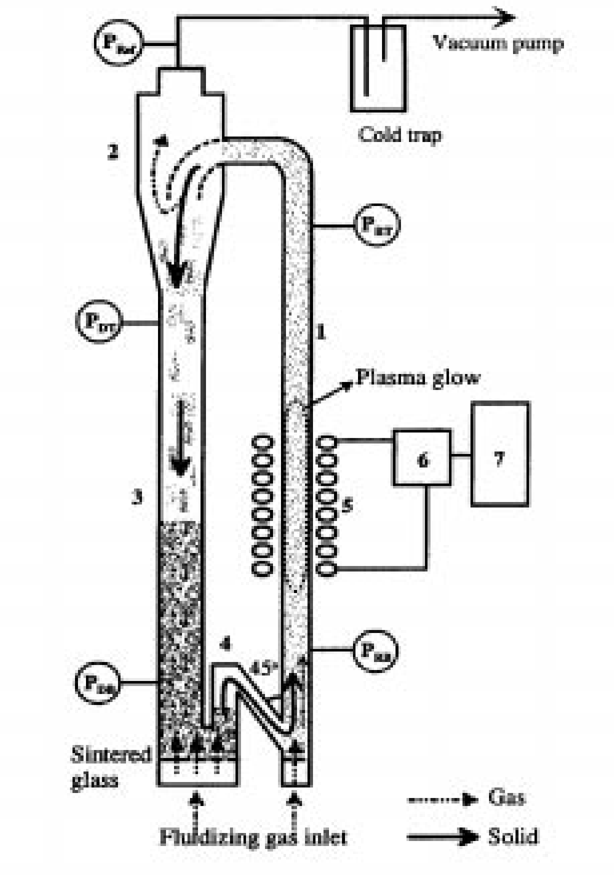

Figure 1. Schematic diagram of experimental apparatus: 1. Riser, 2. Cyclone, 3. Downcomer, 4. Loop-seal, 5. Inductively coupled electrode, 6. Rf matching network, 7. Power supply

The system pressure was maintained at 133 Pa during the plasma treatment. The plasma was generated at the upper region of the riser by coupling with a radio frequency (rf) of 13.56 MHz. An inductively coupled electrode (4.8 mm-OD copper tube, 12 turns) was connected to an auto-matching network and rf power supply (Eni power systems, ACG-5). To prevent overheating of the electrode, cooling water was supplied to the electrode.

Material

The high-density polyethylene (HDPE, d_p=231μm, ρ_s=956 kg/m^3) powder was used as a specimen to be modified since HDPE is a convenient substrate to determine hydrophilicity and to analyze the chemical composition of the modified surface. The solid inventory, I, was kept 45g. Oxygen gas (99.95%) as a reacting gas was used in the plasma surface modification.

Analysis

The surface properties of HDPE powders were measured by XPS, IR and contact angle, respectively. The XPS spectra of the plasma treated HDPE powder were determined by VG scientific ESCALAB MK spectrometer using Al Kα photon source. The quantitative atomic surface composition was deduced from the numerical fits of the different experimental peaks in the ESCA spectra. IR spectra of the plasma treated HDPE powders were recorded on Bomen FTIR spectrometer with a diffuse reflector. The contact angle of water on surface of HDPE powder was calculated by the method described elsewhere [1, 3]

RESULTS AND DISCUSSION

Solids behavior in the CFB

Particles in a CFB reactor have different age distribution over that in a bubbling fluidized bed. In case of a bubbling fluidized bed, particles spend substantial time in the main reactor with the continuous moving up and downward motions. There is a defined upper surface of dense bed and free board regions [10]. Plasma is generated above the dense bed; thus plasma treatment is restricted only on the top surface of dense bed with solids suspension in freeboard region. On the other hand, particles in a CFB are entrained by gas flow, collected by cyclone and pass through the reaction zone repeatedly via the solids re-circulating system. There is no distinguishable bed and plasma is generated in dilute phase of solids in the riser. The difference in static head in the reactor governs the driving force for solids circulation. The solids circulation rate (G_s, kg/m^{2}s) can be controlled by proper adjustment of the pressure balance. The effect of G_s on pressure balance in the CFB loop are shown in **Figure 2**. Pressure drop in the riser increases with increasing G_s at a given gas flow rate due to increment of solid concentration, namely solid holdup [12]. The pressure drops across the cyclone and the loop-seal somewhat increase with increasing G_s due to the increase of pressure loss with increasing G_s [11]. The increase of pressure drop in the downcomer is matched by a similar increase in pressure drop in the riser in order to balance the pressure in the CFB loop.

It has been found that the hydrodynamics under low-pressure condition exhibits similar fluidizing behavior to that of atmospheric pressure in the CFB. The effect of system pressure on the fluidization or hydrodynamic behavior of solids continues to be of considerable on the fluidization or hydrodynamic behavior of solids continues to be of considerable interest to researchers from both practical and theoretical points of view [13]. A limited number of investigations on the reduced pressure fluidization have been conducted respect to pressurized system, they all indicated that fluidization below atmospheric pressure is feasible to operate the system [14, 15].

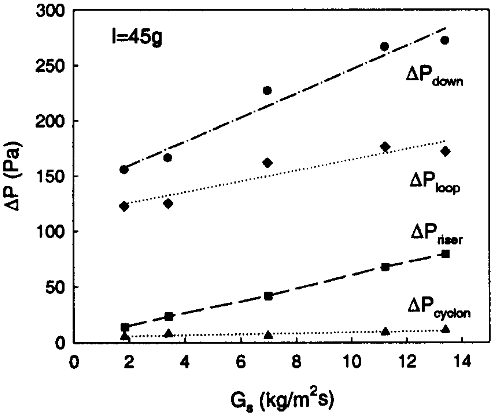

Figure 2. Effect of solid circulation rate on pressure balance in the CFB loop where, $\Delta P_{down} = P_{DB} - P_{DT}$, $\Delta P_{loop} = P_{DB} - P_{RB}$, $\Delta P_{riser} = P_{RB} - P_{RT}$ and $\Delta P_{cyclon} = P_{RT} - P_{DT}$

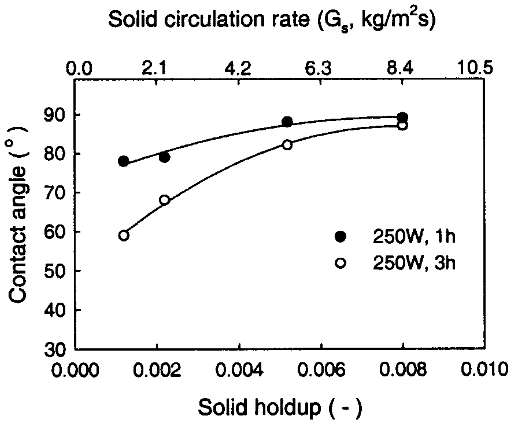

Figure 3. Effect of solid holdup in the riser on the contact angle of the plasma treated HDPE powders

Surface modification

Solid circulation rate, G_s, is a unique operating variable in the CFB system and it varies with pressure difference across loop-seal of the reactor and directly related to solid holdup in the riser where the plasma reaction occurs. Solid holdup, the volume fraction of solids, is defined as

$$\varepsilon_s = 1 - \varepsilon_g \qquad (1)$$

$$\frac{\Delta P_{riser}}{L} = (1-\varepsilon_g)(\rho_s - \rho_g)\frac{g}{g_c} \qquad (2)$$

where, ΔP_{riser}, L, ε_g, ρ_s, ρ_g are pressure difference across the riser ($P_{RB} - P_{RT}$), length of the measuring height, volume fraction of gas, solid density, gas density, respectively.

The effect of solid holdup on the contact angle of the oxygen plasma treated HDPE powder is shown in **Figure 3**. The stability of plasma can be negatively affected by interactions of particles and plasma. Particles may directly absorb rf energy or they could collide with excited gas species, namely reduce the number of electrons and its density. When solids concentration gets too high in the reactor, large parts of plasma volume can be eroded so that plasma could be extinguished [4]. As can be seen, the contact angle increases with increasing solid holdup. At a very dilute solid holdup ($\varepsilon_s = 0.0003$), the HDPE particles might be under the influence of electrostatic force. After a few minutes operation, particles clung to the riser wall and grew up rapidly and then the riser was clogged with the HDPE clusters and consequent increase in system pressure to lead the plasma glow extinguished. However, this phenomena did not observed with higher solid holdups greater than 0.001. When the solid holdup was 0.008, volumes of plasma glow were reduced apparently and contact angle of the treated HDPE powders changed slightly even with increasing the treatment time. Further increase in solid holdup in the riser, the plasma glow become unstable and results in the extinction.

The effect of treatment time on the contact angle of the plasma treated HDPE powder is shown in **Figure 4** where the contact angle decreases with increasing treatment time since the amount of oxygen functionalities at surface of the HDPE powder increases with increasing treatment time. The contact angle decreases initially with time and remains constant with a further treatment time. The reaction between the HDPE and the active species of oxygen plasma produces functional groups at the surface of HDPE powders. Thereby, the oxygen functionalities of HDPE surface increase with increasing the treatment time. It is well known that two processes take place simultaneously in the plasma surface modification process [3, 7, 16]. The first is surface reaction and deposition processes by combination of species from the plasma and atoms at surface of the polymer. The second is ablation and/or etching of the surface through reaction of atomic oxygen from the plasma with carbon atoms of the substrate surface. The balance between these parameters and processes reach steady state with reaction time. Therefore, the oxygen functionalities at the surface of a plasma-treated polymer increase and then levels off with increasing treatment time [3, 7].

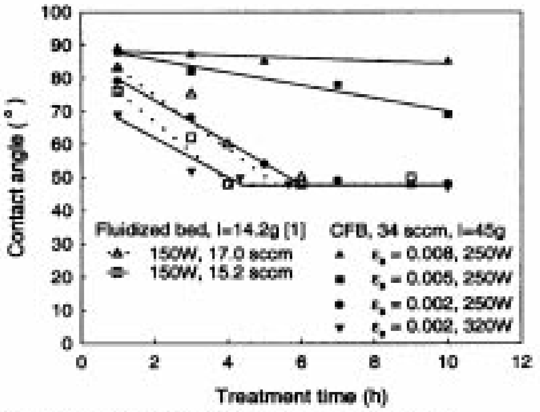

Figure 4. Effect of treatment time on the contact angle of the plasma treated HDPE powders

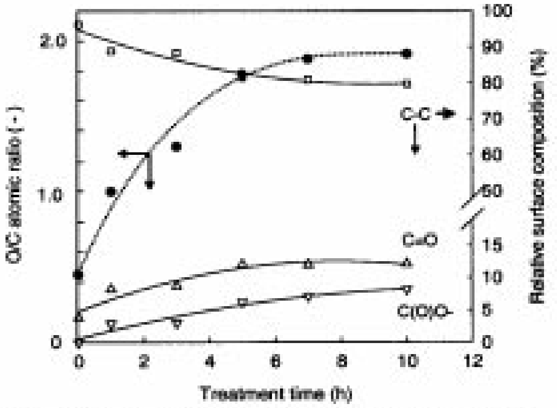

Figure 5. Effect of treatment time on the O/C atomic ratio and the oxygen functionalities (250W, ε_s= 0.002)

The effect of treatment time of plasma on the O/C atomic ratio and oxygen functionalities on the surface of HDPE powders is shown in **Figure 5**. The O/C atomic ratio and the oxygen functionalities increase with the treatment time at the given rf power and solid holdup and then reaches a steady value after 7 hours. The concentration of C=O functionality increases from 3.8 to 12.1 %. Also, C(O)O- functionality increase to 8.2 % of the total carbon elements in the XPS sampling depth.

The effect of rf power on the contact angle of the plasma treated HDPE powders is shown in **Figure 6** where the contact angle decreases with increasing rf power. For polymer surface modification proceeds by interaction with the reactive neutral species like oxygen in the plasma, the reactive dissociation products of the parent gas must weaken the polymer chemical bonds and change the surface chemical composition [15]. Although a large number of chemical reactions are possible in oxygen plasma, oxygen atoms are generally accepted as being the primary reactive species in initiating a modification reaction sequence [16]. Increase in oxygen atom concentration is a key factor to increase the modification rate [17]. Oxygen atom concentrations increase with electron energy and/or density in the plasma, or changes in gas phase chemistry that reduce the oxygen atom recombination reactions. Increase in electron energy and/or density can result from changes in power and frequency of the source. When the power is raised, both the electron energy and its density increase, and the reactive particles become more energetic [1, 18]. Thus, oxygen functionalities increase with the plasma treatment power.

The XPS spectra of the oxygen plasma treated HDPE powders with variation of rf power is shown in **Figure 7**. The C_{1s} spectrum of the untreated HDPE powder is symmetrical and contains a small amount of oxygen (O/C atomic ratio = 0.02). The C_{1s} spectra of the oxygen plasma treated HDPE powders are distinguished from that of the untreated powder. The spectra are asymmetric and decomposed into a main component at 284.6 (CH_2 groups) and two small components of which the peak lies, 286.8 (C=O groups) and 288.8 eV (C(O)O- groups), respectively. Under the given solid holdup, oxygen flow rate and treatment time, the C_{1s} spectra have thick tails with increasing rf power. The oxygen functionalities (C=O, C(O)O-) on the surface of treated HDPE powder increase with increasing rf power. The applied power can increase the mean energy of the electrons, which leads to an increase in the formation rate of chemically active species [3, 7, 18].

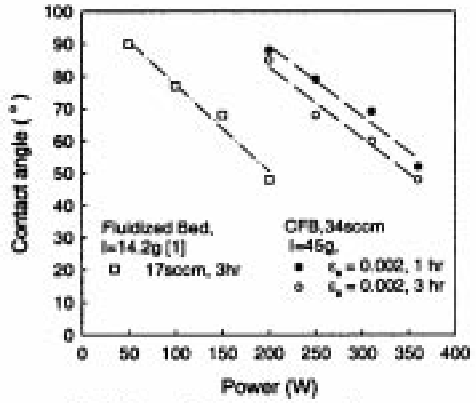

Figure 6. Effect of rf power on the contact angle of the plasma treated HDPE powders

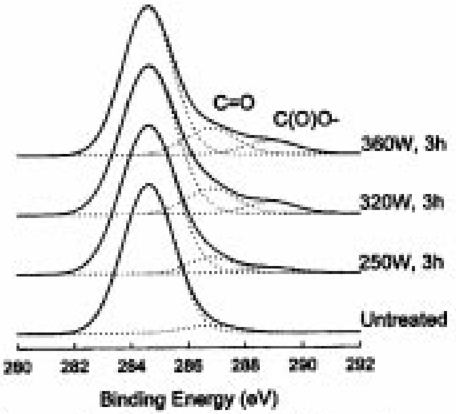

Figure 7. C_{1s} spectra of the plasma treated HDPE powders with rf power (ε_s= 0.002)

The composite parameter [(W/FM)t] represents the total energy per unit mass of gas which interpret surface properties of HDPE powder since most of the energy input is consumed by the reaction between oxygen and HDPE, where W, F, M and t are the input rf power, flow rate of oxygen gas, molecular weight of oxygen, treatment time, respectively [1, 2]. Relationship between the composite parameter [(W/FM)t] on the contact angle of the plasma treated HDPE under given condition is shown in **Figure 8(a)**. As can be seen, the contact angle decreases with increasing composite parameter down to 5300 GJs/(kg-O_2), thereafter it remains constant [1, 7]. The CFB reactor requires higher rf power compared to a bubbling fluidized bed because the plasma operation in CFB requires higher gas flow rate for circulation of powders. However, CFB provides the similar level of contact angle of plasma treated HDPE compared to that in a bubbling fluidized bed under the same composite parameter [(W/FM)t]. Also, the treatment capacities of the CFB and the bubbling fluidized bed are 45 and 14.5g, respectively at a given time.

Figure 8 (b) shows the comparison of the CFB and a bubbling fluidized bed with the composite parameter [(W/FM)t] per given solid inventory (I). As can be seen, the contact angle decreases with increasing the [(W/FM)t]/I down to 125 and 422 TJ s/(kg-O_2 kg-HDPE) respectively, thereafter it remains constant. The CFB reactor produces 3.4 times performance compared to a bubbling fluidized bed to modify the polymeric surface from hydrophobic to hydrophilic. The generated plasma provides high ion density during the volumetric contact of reactive species and solid in the dilute transport of solids in the CFB with low-pressure defined upper surface of dense bed where particles suspended in the freeboard and bubbles break the bed surface periodically with irregular pressure fluctuations of appreciable amplitude [10]. As can be expected, the CFB reactor can handle more solid inventory compared with a bubbling fluidized bed reactor for surface modification of polymeric powders.

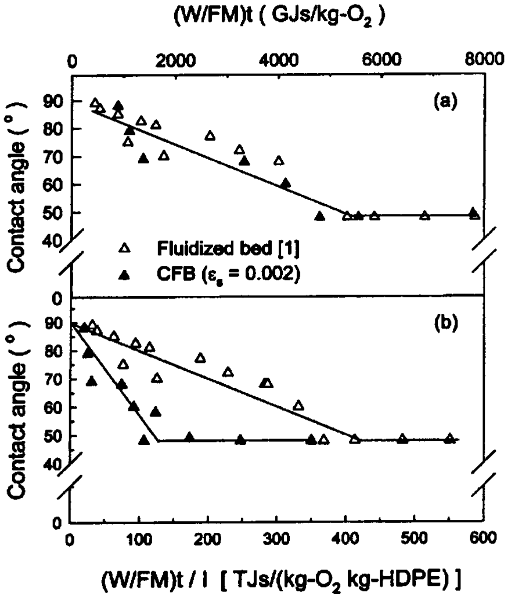

Figure 8. **(a) Relationship between the composite parameter (W/FM)t on the contact angle and (b) Relationship between the composite parameter per solid inventory, (W/FM)t / I and the contact angle of the plasma treated HDPE powders**

Conclusions

Fluidization behavior in the circulating fluidized bed under vacuum is similar to that of atmospheric pressure. The solid holdup in the plasma reaction zone mainly governs the stability of the plasma glow and surface property of the powders. The formation of oxygen functionalities including C=O and C(O)O functionalities reached 12 and 8% of the total carbon elements, respectively. The CFB reactor provides 3.4 times higher performance and obtain similar level of hydrophilicity compared to that in a bubbling fluidized bed under the same composite parameter [(W/FM)t]. The present CFB reactor can be utilized to modify the polymeric surface from hydrophobic to hydrophilic with higher energy efficiency.

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