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# Plasma surface treatment of HDPE powder in a fluidized bed reactor

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## Summary

A plasma surface treatment of HDPE has been carried out in a fluidized bed. The effects of operation parameters on the surface composition and hydrophilicity have been determined. The oxygen functionalities are formed at the outermost layer of HDPE powder. The hydrophobic surface of HDPE powder has been transformed to hydrophilic surface by the oxygen-plasma treatment in a fluidized bed. The contact angle of the plasma treated HDPE powder decreases linearly with radio frequency (rf) power but increases with $O_2$ flow rate. Also, the angle decreases with increasing the composite parameter as the total plasma energy down to 6,000 [(W/FM)t]. The contact angle has been correlated with the composite parameter as: $\theta = 90 - 6.64 \times 10^{-3}$ [(W/FM)t].

## Introduction

The plasma treatment is a useful tool to modify the surface properties of the polymeric materials from hydrophobic to hydrophilic or inversely from hydrophilic to hydrophobic(1, 2). Low-temperature plasma has been utilized to improve polymer surface properties by introducing new functional groups without change of bulk property. A pure oxygen plasma is known to contain both positive and negative ions, atoms, ozone, and metastables of atomic and molecular oxygen, as well as electrons and a broad electromagnetic spectrum(3). Essentials of the plasma surface treatment technique are electrons, ions, 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 to form oxygen functionalities including OH, C=O, and COOH groups(4). Therefore, good contact of the polymeric surface with plasma is an important factor for surface modification.

In case of the plasma surface treatment of flat solid materials, such as polymer films, the intimate contact between plasma and solid surface are not critical and conventional plasma reactors, barrel- or jar-type, is good enough for practical use. However, such a conventional reactor cannot be used for powder materials due to the lack of solid mixing. Plasma fluidized bed reactor can provide intimate mixing between the powders and the reactive gas to improve both the reaction rate and the uniformity of the treated surface(5-7).

Experimental variables such as rf power, flow rate of gas and treatment time are known to influence the surface treatment of polymer films(8,9). Usually an external parameter, W/FM in Joules per unit mass of gas is used to express the plasma energy density, where W, F, and M are the rf power, the flow rate of gas, and the molecular weight of the gas. In polymer-forming gas, W/FM may represent properties of plasma polymer(10-12). In this study, the

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effects of oxygen flow rate, discharge power of plasma, and treatment time on hydrophilicity of plasma treated HDPE powders in terms of contact angle have been investigated in a fluidized bed reactor. Also, the parameter (W/FM)t is used to represent the total energy per unit mass of gas which can interpret surface properties of HDPE powder since most of the energy input is consumed by the reaction between oxygen and HDPE(13,14).

## Experimental

Experiments were carried out in a fluidized bed of 34 mm-ID x 0.8 m-high Pyrex glass column as shown in Fig. 1. High density polyethylene (HDPE-231 μm) powder was fluidized by oxygen gas. The gas flow rate was regulated and measured with a mass flow controller. The particles were supported on a sintered plate distributor which is situated between the main column and a distributor box. The reduced pressure in the bed was maintained by means of a vacuum pump. Entrained particles were captured by a particle trap.

An inductively coupled electrode (4.8 mm-OD, 6 turns) for glow discharge at 13.56 MHz (rf) frequency was placed at a distance of 90 mm from the gas distributor and was connected to an auto matching network and an rf power generator. To prevent overheating of the electrode, cooling water was supplied to the electrode.

Initially, HDPE powders were dried in vacuum oven at 60°C overnight. This dried HDPE powder of 14.2 g (apparent density; 956 kg/m$^3$; size; 60/70 mesh - 0.250/0.212 mm) loaded into the reactor and gas in the reactor was evacuated by a mechanical pump to 1.33 Pa. Oxygen gas was injected into the distributor box and the desired gas flow rate, pressure, and power were adjusted to start glow discharge. After the desired treatment time was over, plasma was cut-off, and the samples were kept in the reactor for more than 10 min at the given gas flow rate.

The high density polyethylene powders were treated by plasma in the fluidized bed at rf power of 50 to 200 W, oxygen flow rate of 15.2 to 28.4 sccm, and treatment time of 1 to 13 h at a pressure of 133 Pa.

IR spectra of the plasma-treated HDPE powders were recorded on a Bomem FTIR spectrometer with a diffuse reflector. The spectral resolution was 2 cm$^{-1}$, and 100 scans were

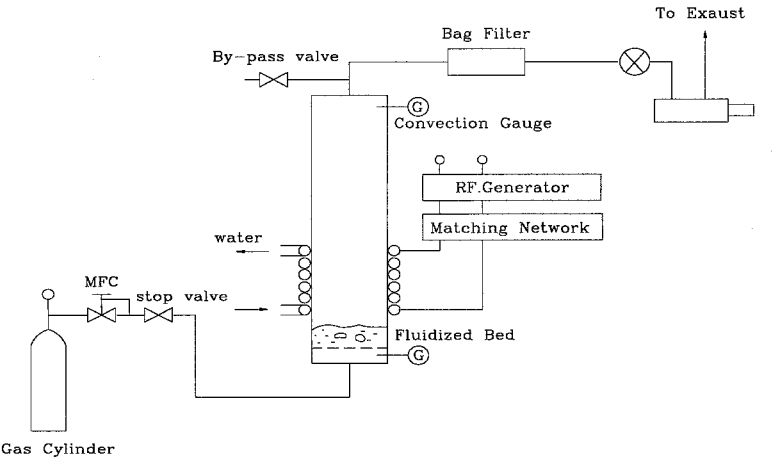


Fig. 1 Experimental apparatus of oxygen plasma treatment with fluidized bed reactor.

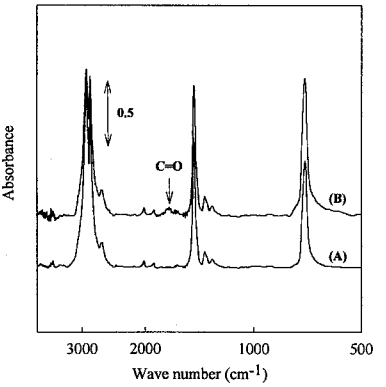


Fig. 2 Typical FTIR spectra of oxygen plasma-treated HDPE powders in the fluidized bed reactor (A) Untreated (B) treated for 200W, 28.4sccm, 3h.

recorded on each sample.

The introduction of functional groups and modification of surface properties by plasma treatment can be monitored by ESCA. ESCA spectra of the plasma-treated polyethylene powder which were obtained on a VG Scientific ESCALAB MKII spectrometer using Al Kα photon source. The anode voltage was 15 kV, the current 20 mA, and the background pressure in the analytical chamber 5 x $10^{-10}$ Pa. The sensitivity factors (S) for core levels were $S(C_{1s})$ = 1.00, $S(N_{1s})$ = 1.68, and $S(O_{1s})$ = 2.64. The quantitative atomic surface composition information was deduced from numerical fits of the different experimental peaks in the ESCA spectra. The atomic ratios were obtained by dividing the integral ESCA intensities of the oxygen ($O_{1s}$) core level emission by the integral intensity of the carbon ($C_{1s}$) emission after subtraction of a linear background. Thereby, any influences from possible variations in X-ray excitation intensities were eliminated. The fine structure of the carbon peak, in particular, provides detailed information about the binding states of the different carbon atoms. In principle, the curve fitting procedure yields an accurate determination of the binding energy and the integral intensity of a subpeak in case of a high peak intensity or in case of a steep intensity rise at the high- or low-energy side of the peak. The $C_{1s}$ spectra were decomposed by fitting Gaussian function to the experimental curve using a nonlinear, least-squares curve-fitting program supplied by VG Scientific LTD.

The dynamic wicking property of the plasma-treated polyethylene powders was determined as hydrophilicity of the powder surface using dynamic wicking meter and the details of the dynamic wicking measurement can be found elsewhere(5).

## Results and discussion

### *Surface properties of plasma treated HDPE powder*

Typical IR spectra of the oxygen-plasma-treated HDPE powders in a fluidized bed reactor is shown in Figure 2. On the IR spectrum for the untreated HDPE powder, strong absorption peaks appear at 2920, 2848, 1897, 1468, 1368, 1305, and 720 $cm^{-1}$ due to $CH_2$, $CH_3$, and terminal vinyl groups(5, 15). The oxygen-plasma-treated HDPE powders show similar IR absorption peaks to that of the untreated one, but new

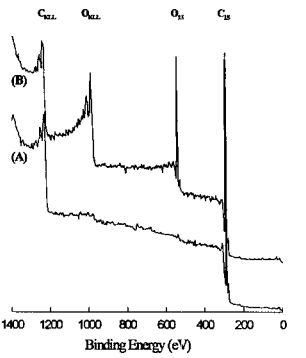


Fig. 3 Typical ESCA survey scan of oxygen plasma-treated HDPE powders in the fluidized bed reactor (A) Untreated (B) treated for 150 W, 15.2sccm, 1h.

Table 1 ESCA Spectra of oxygen plasma-treated HDPE powder in the fluidized bed reactor.

| Plasma Treatment Condition | W/FM t Parameter [GJ·s/kg] | O/C Atomic Ratio | C1s Component (Peak Position) Relative Peak Area | | |
|---|---|---|---|---|---|
| | | | C-C (284.6) | C=O (286.7) | C(O)O- (288.8) |
| HDPE (control) | 0 | 0.03 | 95.5 | 4.5 | |
| 50W, 17.0sccm, 1h | 443 | 0.18 | 79.6 | 14.8 | 5.6 |
| 100W, 17.0sccm, 1h | 886 | 0.19 | 78.3 | 16.4 | 5.3 |
| 150W, 17.0sccm, 1h | 1328 | 0.23 | 77.3 | 15.4 | 7.3 |
| 50W, 17.0sccm, 3h | 1328 | 0.20 | 77.9 | 15.8 | 6.4 |
| 150W, 15.2sccm, 1h | 1490 | 0.29 | 74.6 | 16.2 | 9.2 |
| 200W, 17.0sccm, 1h | 1771 | 0.28 | 74.0 | 16.1 | 9.9 |
| 100W, 17.0sccm, 3h | 2657 | 0.30 | 73.8 | 16.2 | 10.2 |
| 150W, 17.0sccm, 3h | 3985 | 0.28 | 75.0 | 15.9 | 9.1 |
| 150W, 15.2sccm, 3h | 4471 | 0.34 | 72.5 | 15.7 | 11.8 |
| 200W, 17.0sccm, 3h | 5314 | 0.31 | 73.0 | 16.1 | 10.9 |
| 150W, 15.2sccm, 4h | 5962 | 0.37 | 71.9 | 15.5 | 12.6 |
| 200W, 15.2sccm, 3h | 5962 | 0.36 | 73.0 | 16.1 | 10.9 |
| 150W, 15.2sccm, 6h | 8942 | 0.33 | 72.5 | 16.4 | 11.1 |
| 150W, 13.5sccm, 6h | 10044 | 0.35 | 71.4 | 16.1 | 12.5 |
| 150W, 15.2sccm, 9h | 13414 | 0.33 | 72.3 | 16.1 | 11.6 |
| 150W, 15.2sccm, 13h | 19375 | 0.32 | 72.1 | 16.7 | 11.2 |

absorption peaks due to oxygen functionalities appear in the range of 1700 ~ 1740 $cm^{-1}$ due to ν(C=O) vibrations in carbonyl, carboxyl, and aldehyde groups(15, 16). However, the peak attributing to C-O functional groups (1100 - 1400 $cm^{-1}$) does not appear as observed by Inagaki et al.(5). This indicates that the oxygen functionalities including C=O are produced at surface of HDPE powder by $O_2$ plasma in a fluidized bed reactor.

ESCA survey spectra (low resolutions between 0 and 1400 eV) for HDPE powder before and after plasma treatment are shown in Fig. 3. If carbon, nitrogen and oxygen atoms exist, the core level peaks of ESCA survey scan spectrum appear at 284.6, 403 and 532 eV, respectively and the Auger peaks of each element appear at 976, 1108 and 1228 eV, respectively(9). As shown in Fig. 3-a, for untreated HDPE powder, peaks of only carbon element appear since the surface is composed of only carbon element. However, new peaks at 532 and 1228 eV due to the oxygen atoms are found on plasma treated HDPE powder which may indicate the extensive oxidation takes place. The quantitative data of the surface elemental ratios on this plasma treated HDPE powders in the fluidized bed reactor are summarized in Table 1. The untreated HDPE powder contains a small amount of oxygen (the O/C atomic ratio is 0.03) but no nitrogen element present. The O/C atomic ratio increases from 0.03 to 0.37 with $O_2$ plasma treatment.

A representative high resolution of $C_{1s}$ spectrum for the $O_2$ plasma treated HDPE powders is shown in Figure 4. In the high resolution mode, the ESCA spectra reveal the shifts of $C_{1s}$ peaks resulting from the changes in chemical environment of carbon atoms. For the untreated HDPE powder, $C_{1s}$ spectrum is sharp and relatively symmetrical which is decomposed into a main component and a small component, which

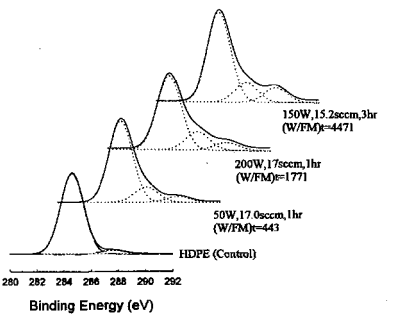


Fig. 4 Typical high resolution $C_{1s}$ spectrum of oxygen plasma-treated HDPE powders in fluidized bed reactor.

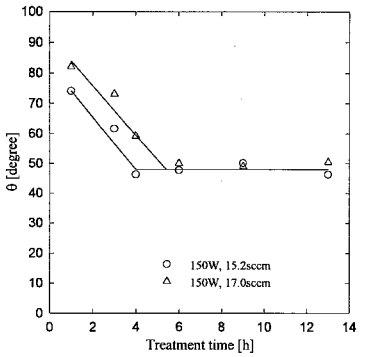


Fig. 5 Effect of treatment time on contact angle of water of oxygen plasma-treated HDPE powders in the fluidized bed reactor.

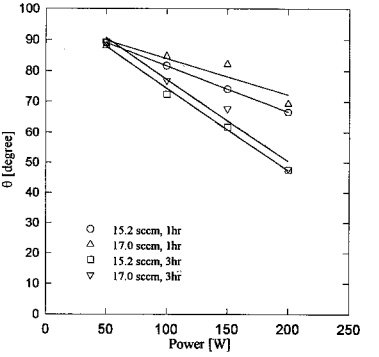


Fig. 6 Effect of rf power on contact angle of water of oxygen plasma-treated HDPE powders in the fluidized bed reactor.

are assigned $CH_2$ and C=O groups, respectively. The $C_{1s}$ spectra of $O_2$ plasma treated HDPE powders are decomposed into a main component and two small components of which the peak lies at 284.6 (-$CH_2$- groups), 286.7 (C=O groups), and 288.8 eV (C(O)-O- groups)(17). These decomposed peaks are assigned from the comparison data of Inagaki et al.(5) and the decomposition data is summarized in Table 1. For the polyethylene film exposed to $O_2$ plasma, the formation of oxygen functionalities including C-O (286.1-286.5 eV), C=O (287.6-287.8 eV), and C(O)-O- groups (289.2 eV) from the ESCA spectra were observed by Golub and Cormia(17). Similar ESCA spectra are obtained with the present $O_2$ plasma treated polyethylene powders in the fluidized bed reactor. It is obvious that the $O_2$ plasma treated HDPE powders in the fluidized bed leads to the formation of C=O and C(O)-O- functionalities at the outermost layer of the powder. The concentration of the C=O and C(O)-O- functionalities reaches 16 and 11% of the total carbon elements being in the ESCA sampling depth, respectively.

### *Effects of the operating parameters on plasma oxidation*

#### *Effect of treatment time*

The effect of treatment time on the contact angle of water for $O_2$ plasma treated powder is shown in Fig. 5. The contact angle of water is determined from dynamic wicking measurement. However, the contact angle of water for the untreated HDPE powder cannot be determined since water cannot penetrate through the powder column but it is expected to be more than 90°. The contact angle of water for the plasma treated powder decreases with increasing treatment time due to the formation of hydrophilic group including oxygen functionalties at the surface, but it levels-off with further treatment time. In a plasma process involving polymeric materials and oxygenated species, two processes take place simultaneously(12, 19): (1) Deposition and surface reaction processes by combination of species from the plasma and atoms at the surface of the sample, (2) Etching of the surface through reactions of atomic oxygen from the plasma phase with carbon atoms of the substrate surface giving volatile reaction products as:

$$XO\bullet + C \rightarrow CO_x$$

Ionic bombardment can also cause the etching of substrate surface through physical sputtering. The balance between these two processes depends on the experimental parameters and these two processes reach steady state with reaction time. Inagaki et al.(5) show that the contact angle of polyethylene powder decreases with the plasma treatment time but remains almost constant after 3 h. As can be seen in Table 1, the O/C atomic ratios increase with the plasma treatment time at given rf power and flow rate (150W, 15.2sccm) of $O_2$, and then reaches a maximum value at approximately 4 h. The oxygen functionalities on plasma treated HDPE powder surface decreases with increasing treatment time but it remains constant with further treatment time as the variation of contact angle of water for the treated powder with the treatment time.

### *Effect of plasma power*

The effect of rf power on the contact angle of water for plasma treated HDPE powder in the fluidized bed reactor is shown in Fig. 6. The contact angle decreases with increasing rf power that indicates the powder surface becomes more hydrophilic. When the power is raised, both the electron energy and its density increase, and the reactive particles become more energetic(18). The applied power can increase the mean energy of the electrons, which leads to an increase in the rate of formation of chemically active species through dissociation reaction as:

$$O_2 + e \rightarrow 2O\bullet$$

Clouet and Shi(21) reported that the degradation rates increase linearly with the applied power in the oxygen plasma since the reactive particles become more energetic. As shown in Table 1, under given flow rate of $O_2$ and treatment time, O/C atomic ratios and oxygen functionality (C=O, C(O)O-) increase with increasing rf power. Therefore, hydrophilicity of $O_2$ plasma treated HDPE powders linearly increases with increasing rf power in the fluidized bed reactor.

### *Effect of flow rate*

The effect of $O_2$ flow rate on the contact angle of water for plasma treated HDPE powder is

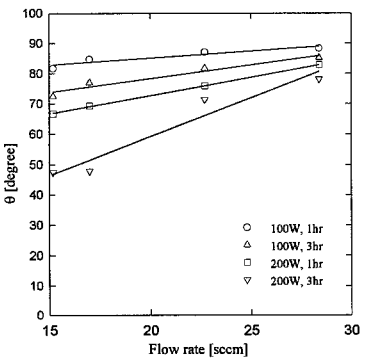


Fig. 7 Effect of flow rate on contact angle of water of oxygen plasma-treated HDPE powders in the fluidized bed reactor.

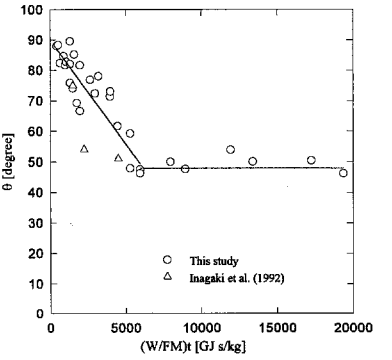


Fig. 8 Effect of composite parameter, [(W/FM)t], on contact angle of water of oxygen plasma-treated HDPE powders in the fluidized bed reactor.

shown in Fig. 7. The contact angle increase with increasing $O_2$ flow rate, that is, the HDPE powder becomes less hydrophilic. The flow rate of $O_2$ may modify not only the electron energy and its density but also the residence time of the active species. Thus, the residence time of reactive species in a plasma decreases with increasing gas flow rate that may result in rapid removal of the reactive species such as OH•(18, 20). Consequently, the surface reaction between the reactive species and polymer surface is less pronounced, and the surface of polymer has less oxygen functionalities as can be seen in the data of ESCA. Therefore, the hydrophilicity of $O_2$ plasma treated HDPE powder in the fluidized bed reactor decreases with increasing $O_2$ flow rate.

*Effect of the composite parameter*

The surface is modified by the results of the combination of many reactions. The factor of this surface modification depends on how much of this reactions proceeds on the surface. The composite parameter [(W/FM)t] which is the total energy input for all reactions occur in the plasma(13). When the energy input is low, the reactions do not proceed fully for good modification of the surface. When the energy input is too high, etching/ablation or too much unnecessary reactions may take place(13).

Since the composite parameter is a good measure to see the effect of total energy input on the surface modification, the obtained contact angle is presented as a function the composite parameter as shown in Fig. 8 with the data of Inagaki et al.(5). The contact angle decreases with increasing the composite parameter [(W/FM)t] down to 6,000 GJ·s/kg, thereafter it remains constant. Also, the O/C atomic ratios increase up to about 6,000 GJ·s/kg of (W/FM)t parameter as shown in Table 1. The obtained contact angles in the present and a previous study(5) have been correlated with the composite parameter as: $\theta = 90 - 6.64 \times 10^{-3}$ [(W/FM)t] with a correlation coefficient of 0.90.

## Conclusions

1. The surface property of HDPE powders has been changed from hydrophobic to hydrophilic by the oxygen plasma treatment in a fluidized bed.
2. The formation of oxygen functionalities and hydrophilicity of HDPE powders increase with the plasma treatment time and rf power.
3. The degree of surface oxygen content and hydrophilicity decrease with increasing flow rate of oxygen.
4. The contacting angle or hydrophobic property decreases down to about 6,000 GJ·s/kg with increasing the composite parameter as: $\theta = 90 - 6.64 \times 10^{-3}$ [(W/FM)t].

## References

1. Gao S, Zeng Y (1993) J. Appl. Polym. Sci. 47: 2065
2. Clark DT, Dilks A (1979) J. Polym. Sci. Polym. Chem. Ed. 17: 957
3. Hollahan JR and Bell AT (1974) Techniques and applications of plasma chemistry, John Wiley & Sons, New York
4. Boenig HV (1988) Fundamentals of plasma chemistry and technology, Technomic Pub., Lancaster
5. Inagaki N, Tasaka S, Abe H (1992) J. Appl. Polym. Sci. 46: 595
6. Inagaki N, Tasaka S, Ishii K (1993) J. Appl. Polym. Sci. 48: 1433
7. Morooka S, Okubo T, Kusakabe K (1990) Powder Technol. 63: 105
8. Wu S (1992) Polymer Interface and Adhesion, Marcel Dekker, New York

9. Clark DT, Feast WJ (1972) Polymer Surfaces, Chichester
10. Yasuda H, Hirotsu T (1978) J. Polym. Sci.: Polym. Chem. Ed. 16: 743
11. Gazicki M, H Yasuda (1984) J. Appl. Polym. Sci.: Appl. Polym. Symp. 38: 35
12. Yasuda H (1985) Plasma Polymerization, Academic Press, New York
13. Iriyama Y, Yasuda T, Cho DL, Yasuda H (1990) J. Appl. Polym. Sci. 39: 249
14. Iriyama Y, Yasuda H (1988) J. Appl. Polym. Sci.: Appl. Polym. Symp. 42: 97
15. Clark DT, Feast WJ, Musgrave WKR, Ritchie I (1975) J. Polym. Sci. Polym. Chem. Ed. 13: 857
16. Kondyurin AV (1993) J. Appl. Polym. Sci. 48: 1417
17. Golub MA, Cormia RD (1989) Polymer 30: 1576
18. Shi MK, Clouet F (1992) J. Appl. Polym. Sci. 46: 2063
19. Yasuda T, Gazicki M, Yasuda H (1984) J. Appl. Polym. Sci.: Appl. Polym. Symp. 38: 201
20. Lerner NR, Wydeven T (1988) J. Appl. Polym. Sci. 35: 1903
21. Clouet F, Shi MK (1992) J. Appl. Polym. Sci. 46: 1955

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