유동층 반응기에서 산소 플라즈마 표면 처리에 의한 HDPE 입자의 기능화

박 성 희, 김 상 돈
한국과학기술원, 화학공학과

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

Soung Hee Park and Sang Done Kim
Department of Chemical Engineering, Korea Advanced Institute of Science and Technology

Introduction

Plasma surface treatment is the result of the interactions between the polymer surface and the plasma active species such that the first step consists of the formation of radicals on the surface layer by the elimination of hydrogen atoms. A oxygen plasma have been widely used to modify polymer surface properties such as wettability and adhesion without change of bulk property [1-3]. These active species are able to react with oxygen atoms or molecules to produce functional groups[4]. In the plasma surface treatment, good contact of the polymeric surface with plasma is an important factor. A 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].

In the plasma surface treatment, the operating parameters of rf power, gas flow rate and treatment time are known to affect the surface modification [8 - 11]. Usually the composite parameter [(W/FM)t] has been utilized to represent the total energy per unit mass of gas, where W, F, M and t are the rf power, the flow rate of gas, the molecular weight of the gas, and treatment time, respectively. The parameter can interpret surface properties of HDPE powder since most of the energy input is consumed by the reaction between O_2 and HDPE [12, 13]. Therefore, the parameter [(W/FM)t] is a main factor to control the plasma surface reactions.

The objective of this study is to determine the oxidation capability of HDPE powder by the reactions with active species in oxygen plasma in a fluidized bed reactor. The reaction chemistry of oxygen active species with HDPE powders in the plasma is also elucidated. Also, the effects of treatment time, rf power of plasma, O_2 flow rate and the composite parameter [(W/FM)t] on functionalization of plasma treated HDPE powders have been determined.

Experimental

Details of the apparatus and experimental procedures on plasma surface treatment of HDPE powder in fluidized bed reactor can be found elsewhere [14]. The IR technique is proved to be a simple and rapid method to determine the functionality

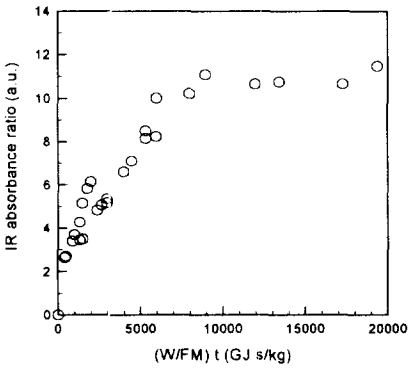

Fig. 1 Effect of composite parameter, (W/FM)t, on IR absorbance ratio of oxygen plasma treated HDPE powders.

of polymer [15]. In plasma polymerization, the effect of plasma parameters on the FTIR spectra have been studied by several investigators [16, 17]. An IR absorption ratio has been evaluated as a measure of functionality of plasma treated powder. This corresponds to use the absorbance band in the oxygen functionality as a measure of functionality of plasma treated powder with respect to the internal reference band. Also, the introduction of functional groups and modification of surface properties by plasma treatment can be monitored by ESCA. The quantitative composition information of atomic surface was deduced from the numerical fits of the different experimental peaks in the ESCA spectra. The fine structure of carbon peak, in particular, provides detailed information about the binding states of the different carbon atoms [18]. The C1s spectra were decomposed by fitting the Gaussian function to the experimental data using a nonlinear, least-squares curve-fitting program [1, 18].

Results and discussion

The oxygen plasma-treated HDPE powders exhibits similar IR absorption peaks to that of the untreated one, but new absorption peaks due to oxygen functionalities appear in the band at 1690 - 1750 cm^{-1} which can be attributed to ν(C=O) vibrations in carbonyl, carboxyl, and aldehyde groups [19-21]. Also, the intensity of absorbance peaks is changed with the different plasma parameters (treatment time, rf power, flow rate). Therefore, an absorbance ratio has been evaluated as a measure of functionality of plasma treated sample [21]. The effect of plasma parameters on surface chemistry can be determined by the ratio of IR absorbance. The absorbance peak at 720 cm^{-1}, which is attributed to CH_2, is used as a reference band in the absorbance ratio. The absorbance band at 1690 - 1750 cm^{-1} is used as a measure of oxygen functionalities of plasma treated powder with respect to an internal reference band of 720 cm^{-1}.

Since the surface is modified by the results of the combination of many reactions, the surface modification depends on how much of these reactions proceeds on the

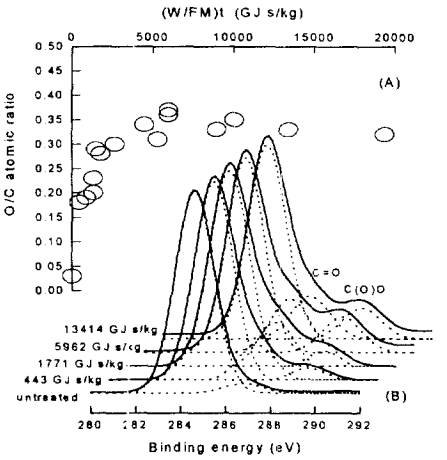

Fig. 2 (A) Effect of composite parameter on O/C atomic ratio (B) The C1s spectra of oxygen plasma-treated HDPE powders with variation of the composite parameter,(W/FM)t

surface. The composite parameter [(W/FM)t] is the total energy input for all the reactions occur in the plasma [13]. In the plasma process, the surface reaction (or deposition) and ablation (or etching) processes compete each other, and the treated samples resulted from the balance of the two processes. When plasma surface treatment is operated at lower composite parameters [(W/MF)t], the surface reaction (or deposition) process dominates rather than ablation (or etching) process and the reactions do not proceed fully for good modification of the surface. On the other hand, plasma surface treatment operates at higher composite parameters, the ablation process rather than the surface reaction/deposition process is predominant, and ablation/etching or too much unnecessary reactions may take place.

Since the composite parameter is a good measure to see the effect of total energy input on the surface treatment, the obtained IR absorbance ratio are presented as a function the composite parameter as shown in Figures 1. The IR absorbance ratio increase with increasing the composite parameter up to about 6,000 GJ s/kg, thereafter it remains constant.

The effect of composite parameter on O/C atomic ratio and the C1s spectra of oxygen plasma treated HDPE powders with variation of the composite parameter is shown Figure 2. The oxygen / carbon atomic ratio and oxygen functionalities increase with increasing the composite parameter up to about 6,000 GJ s/kg, thereafter it remains constant.

Conclusions

oxygen contents in the surface of HDPE powders increases by the oxygen plasma treatment in a fluidized bed reactor. The functionalities of plasma treated powder are found to be carbonyl and carboxyl acid (C=O, C(O)O-) from the ESCA spectra and IR absorbance measurements. The intensity of oxygen functionalities on the plasma treated HDPE powder surface increases with increasing treatment time but it remains constant with further treatment. The formation of oxygen functionalities of HDPE

powders and the IR absorbance ratio increase with increasing rf power. However, the oxygen functionalities decrease with increasing O_2 flow rate. The oxygen content on the surface of plasma treated HDPE powder increases up to about 6,000 GJ s/kg with increasing the composite parameter [(W/FM)t]. Also, a strong relation is found between the surface oxygen and the hydrophilicity of plasma treated powder.

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