유동층 반응기에서 HDPE 입자의 CF_4 플라즈마 표면처리

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CF_4 PLASMA SURFACE TREATMENT OF HDPE POWDERS IN A FLUIDIZED BED REACTOR

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Introduction

Recently, many materials having different surface properties from its bulk materials are used in high technology applications. In general, surface treatments are desirable, or may even be necessary, for a variety of reasons including economics, materials conservation, the unique properties obtained, and engineering and design flexibility by separating surface properties from their bulk properties. Therefore, new techniques have been developed within the past decade for modifying surface layers. Specially, many processes have been developed to modify polymer surfaces, including chemical treatment, photochemical treatment, plasma treatment, and surface grafting[1)].

A plasma is a partially ionized gas composed of ions, electrons and neutral species. The technique of most interest to plasma surface treatment is the glow discharge, in which free electrons gain energy from an imposed electrical field, and subsequently loses 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. There is growing interest in the use of "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.

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[2)], substrate cleaning in high vacuum systems (HVSs), biocompatible polymer surfaces, modifying barrier properties[3)] and other devices. 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 energetic 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[1,4)].

Polymer surfaces are often difficult to wet and bond, because of low surface energy, incompatibility, chemical inertness, or the presence of contaminants and weak boundary layers. Plasma surface treatments are used to change the chemical composition, increase the surface energy, modify the crystallity, morphology, and surface topography, or remove contaminants and weak boundary layers. On the other hand, there is also interest in decreasing the polymer surface energy, e.g. to create a teflon-like surface on a variety of polymer materials. This interest is due to the fact that a teflon-like surface has some unique properties, such as chemical inertness, low surface energy (non-wettable), excellent frictional properties, low permeability, and relatively good thermal stability. In a process developed by Air Products Inc.[3], a teflon-like surface is produced by direct reaction of a fluorine gas with a polymer.

Previous researches[4,5] were directed towards modifying films or fibers. However, several application areas (including thermal energy storage materials, microcarrier[6] and advanced composite materials) require materials in a powder form. Intimate mixing between the powder solids and the reactive gas phase should increase both the rate of reaction and the homogeneity of the treated surface. Increasing the mobility of the individual particles will promote mixing. For this reason, a plasma fluidized bed reactor was designed to modify powder materials[7].

The objective of this study is to modify the surface properties of fine powders in a fluidized bed reactor and investigate the capability of polymer powder to fluorinate by the reactions with active species in a glow discharge. The optimum reaction conditions for fluorination of polymer powders in a fluidized bed reactor have been identified under several different plasma conditions.

Experimental

The plasma surface treatment of powders were carried out in a fluidized bed reactor of 34 mm-ID x 0.8 m-high Pyrex glass column as shown in Fig. 1. High density polyethylene (HDPE) powders were fluidized by gas. 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. In plasma surface fluorination, the CF_4 gas is diluted with He gas. The

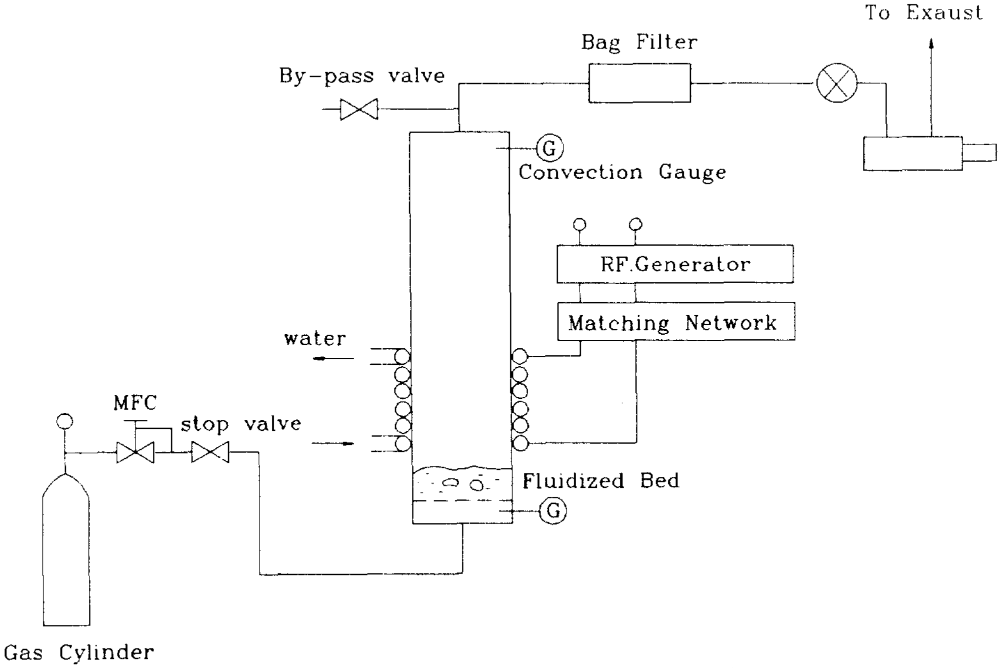

Fig. 1 Experimental apparatus of plasma treatment with fluidized bed reactor.

concentration of CF_4 in He gas was varied form 0 to 100 mol%. The ranges of experimental variables are treatment time (10 min ~ 12 h), flow rate of CF_4 and diluent He gas (15 ~ 38 sccm), rf power (50 ~ 200 W) and concentration of CF_4 gas in mixture (0 ~ 100 mol%)..

Results and Discussion

Typical ESCA survey spectra (low resolution between 0 and 1400 eV) are shown in Figure 2. Figure 2-(A) is 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). Figure 2-(B) is one for the powder after CF_4/He plasma fluorination in a fluidized bed reactor at rf power of 100 W, flow rate of feed gas mixture of 25 sccm and treatment time of 3 h.

For He plasma, 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 (1108 eV), and C_{Au} peak (1226 eV). The peaks corresponding to fluorine element are not. However, for CF_4/He plasma, the large F_{1s} peak appearing about 684 eV and F_{Au} peak at about 832 eV. These results are similar to one of other researchers[5,8]. It indicates that extensive fluorination has occurred in the fluidized bed reactor. 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 was found.

Several reaction conditions that affect the fluorination process have been investigated. These are 1) treatment time, 2) power supplied to the plasma, 3) flow rate of gases in the reactor, 4) concentration of fluorine in the feed, 5) location of plasma load, 6) reactor pressure. The influence of treatment time on the extent of fluorination and the atomic percent of each constituents is shown in Table 1. At a given condition (100 W, 5 sccm CF_4 / 20 sccm He), the extent of the fluorination (F/C atomic ratio from ESCA measurement) reaches a maximum at approximately 180 minutes of treatment time, but levels off at about F/C atomic ratio of 1.4. As as shown in Table 1, fluorine compound increases form 30 to 60.71 mol% during the time interval of 10 min to 3 h. This indicates that the CF_4 plasma makes HDPE powders rich in fluorine. Anand *et al.*[8] observed that in 5% F_2/He diluent plasma (under 40 cc/min, 2.0 mmHg, 50 W), atomic percent of fluorine increases from 25 to 60% as reaction proceeds (15 sec to 3 min), and levels off at 60% atomic percent. These results are similar to that of Anand *et al.*[8] although the

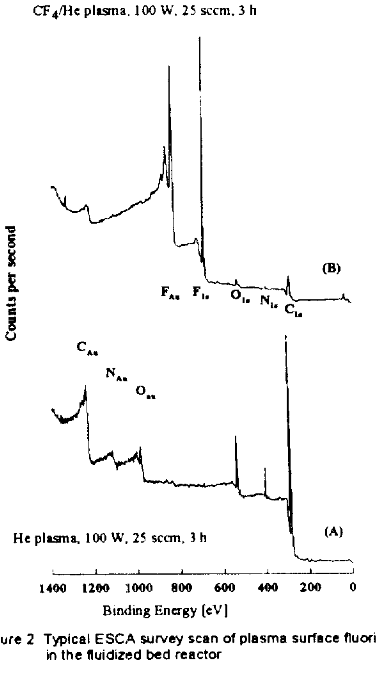

Figure 2 Typical ESCA survey scan of plasma surface fluorination in the fluidized bed reactor

Table 1 Effect of treatment time on plasma surface fluorination of HDPE powders in the fluidized bed reactor

Experiment condition	Element atomic ratio			Relative atomic percent		
	F/C	O/C	N/C	C	O	N
100 W, 5 sccm CF_4/20 sccm He						
10 min	0.48	0.07	0.01	64.25	4.32	0.81
20 min	0.61	0.08	0.01	58.87	4.77	0.70
30 min	0.85	0.06	0.03	53.15	3.39	1.33
1 h	1.39	0.07	0.03	40.12	2.97	1.25
3 h	1.71	0.08	0.03	35.15	2.73	1.05
6 h	1.46	0.07	0.02	41.09	2.79	0.90
12 h	1.28	0.06	0.02	42.40	2.49	0.86

plasma systems are different. The present system is CF_4/He plasma and the system of Anand *et al.*8) is F_2/He plasma.

It is known from previous study that ablation and reaction occur simultaneously in the glow environment 8,9). Also, Poncin-Epaillard *et al.*10) described plasma modification as a sum of two mechanisms: degradation and fluorination. These reaction seem to be competitive and parallel. The rates of degradation and fluorination are dependent on treatment time. These two parameters apparently reach a steady state after a certain reaction time since higher degrees of fluorination are not observed with longer reaction times.

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