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# SILICON OXIDE DEPOSITION FROM COLD REMOTE PLASMA ON POLYETHYLENE POWDERS IN FLUIDIZED BED

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## Abstract

In this work, a fluidized bed has been coupled to a far cold remote nitrogen/oxygen plasma to deposit silicon oxide  $\text{SiO}_x$  from silane  $\text{SiH}_4$  on the surface of a polyethylene powder. The influence on the characteristics of the silica-like deposit on powders, of several parameters such as the amount of oxygen injected in the plasma, the  $\text{SiH}_4$  flow rate and the treatment duration, has been studied. First, the particles wettability has been measured by contact angle (Washburn method), knowing that PE is hydrophobic and that silicon oxide would increase its hydrophilicity. The film chemical composition has been analysed by FT-IR spectroscopy. Its organization on the powder surface and its morphology have been studied by FEG SEM. Results indicate that the wettability of powders increases with the whole parameters studied. Deposition seems to occur under the form of nodules; its continuity is not ascertained. This is the reason why the increase of wettability could be due either to a better surface coverage of the deposition or to an increase of its thickness. Additional analyses are in progress to better understand the correlations between the deposition parameters, the plasma features and the deposition characteristics.

**Keywords:** Fluidized bed – Far Cold Remote Plasma – Polyethylene powders – Silane – Silicon oxide.

## 1. Introduction

The plasma technique is a dry process which can modify the surface properties of thermo-sensitive materials without changing their intrinsic bulk properties [1].

When coupled with a fluidized bed, a nitrogen cold remote plasma technology allows to modify the surface of thermo-sensitive powders either by grafting new functions (for instance hydroxyl OH groups) [2-4], or by depositing various materials, such as silicon nitride  $\text{Si}_3\text{N}_4$  from silane  $\text{SiH}_4$  and nitrogen [6]. The fluidized bed is a very efficient gas-solid contactor generating intense thermal and mass transfers between gas and particles, and then very uniform treatments. A very good contact between reactive species of the plasma discharge

and powder surface is obtained [4]. And the plasma reactivity is not destroyed by the fluidized bed [3]. The reactivity of nitrogen/oxygen cold plasma is used first to act on powders surface by creating active sites and then to dissociate the gaseous precursors, to form deposition [7]. The plasma assistance allows to operate at low temperature ( $< 90$  °C in our case).

This study concerns silicon oxide deposition on the surface of a high density polyethylene (PE) powder belonging to Geldart's group B, i.e. easy-to-fluidize. The reactive gases were nitrogen, oxygen and silane  $\text{SiH}_4$ . The influence of some key operating parameters such as the amount of oxygen injected in the plasma, the  $\text{SiH}_4$  flow rate and the treatment duration, has been studied on the characteristics of the deposition. First, the particles wettability has been measured by contact angle (Washburn method), knowing that PE is hydrophobic and that a  $\text{SiO}_x$  coating would increase its hydrophilicity. Its chemical composition has been analysed by Fourier Transform Infra-Red (FT-IR) spectroscopy. Its organization on the powder surface, and its morphology have been studied by Field Effect Gun Scanning Electron Microscopy (FEG SEM). First the experimental setup is described, before to present and discuss the main results obtained.

## **2. Experimental**

Experiments were carried out in a fluidization column in glass, 50mm in diameter and 0.9m high as shown in fig 1. High density polyethylene (PE) powders, 260  $\mu\text{m}$  in Sauter diameter and 930  $\text{kg}/\text{m}^3$  in grain density, have been studied. These particles were fluidized by a mixture of nitrogen and oxygen gases (respectively N50 and Alpha quality, Air Liquide). Gas flow rates were regulated by mass flow controllers. The particles were supported by a porous plate designed in our lab. The total pressure into the bed was maintained at 10 Torr by means of a vacuum pump. We ensured that the leak rate was less than 100mTorr/min. The bed pressure drop was measured by a MKS vacuum gauge. Elutriated particles were captured by a particle trap.

The gas flow mixture ( $\text{N}_2$  and  $\text{O}_2$ ) was excited by an electrodeless discharge by means of microwaves generator (2450MHz) that could deliver a transmitted power up to 300W. The quartz discharge tube (inner diameter 9 mm) was connected to the bottom of the fluidized bed reactor. The microwave cavity was positioned at 40cm from the reactor inlet.

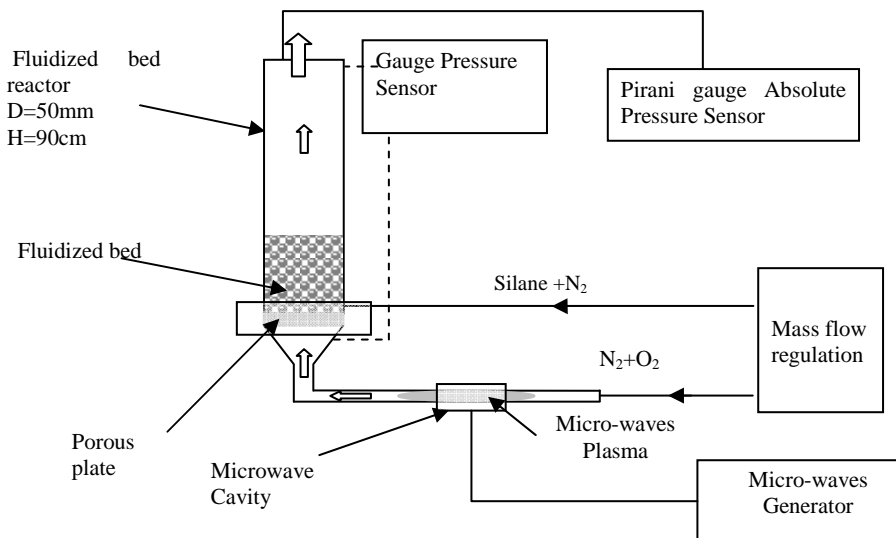
Silane  $\text{SiH}_4$  (max: 2.5 vol. % in nitrogen) was introduced directly in the fluidized bed through an annular injector located at 2.5 cm above the porous plate. We fixed this percentage in such a way that the calculated theoretical deposition thickness (corresponding to 100 % conversion

of silane and assuming that the deposition was continuous and uniform around each grain) is in the range between 50 and 200 nm for the conditions tested here.

The PE powder mass treated in this reactor was always 51g. Compared to similar works of the literature [1, 2], this represents an important amount of powders, for which the fixed bed height is of the order of the bed diameter.

The microwaves generator power was maintained at 300W. The total gas flow rate was fixed at 800 sccm ( $\text{cm}^3/\text{min STP}$ ) and the flow rate crossing the plasma was of 640 sccm.

In order to improve the silicon oxide film adhesion, the PE powder was always pre-treated by 0.3 vol. % of oxygen in nitrogen for 1hour before deposition. The pre-treatment conditions were determined after primary study based on our previous work [7]. Besides, the deposit duration was fixed to 2hours.



**Figure 1:** Experimental set up

The wettability of the treated PE powders was obtained by measuring the contact angle of liquids by means of the Washburn method [8], using a GBX Tensiometer. 500  $\mu\text{g}$  of PE powders is packed into a glass column (10mm ID); the bottom of the glass column is closed with a porous plate. In order to systematically have the same porosity, a system of vibration is used. The time and velocity of vibration are maintained at the same values. After this operation, the glass column is put in close contact with the chosen liquid (here, water) that penetrates up in the PE powders column by capillarity rising. The weight of penetrating liquid is measured as a function of time after contact of the porous glass plate with liquid. The contact angle of the PE powder surface is governed by the modified Washburn equation (1):

$$\frac{m^2}{t} = C \rho^2 \gamma_i \frac{\cos \theta}{\eta_i} \quad (1)$$

Where  $\eta_l$  (Pa.s),  $\rho_l$  (kg.m<sup>-3</sup>) and  $\sigma$  (mN/m) are respectively the viscosity, density and total surface tension of the chosen liquid. The water contact angle of the non treated PE powder is of 90°.

The attenuated total multiple reflection (ATR) technique was used to analyse the chemical modifications produced by plasma treatment. A *Nicolet 5700* spectrometer was used to obtain the IR spectra of the treated powders. A diamond prism was used and the incident angle of the IR radiation was 45°. One hundred scans with a resolution of 4 cm<sup>-1</sup> were obtained and averaged per sample.

The morphology of the treated powders surfaces was analyzed using a Jeol *JSM 6700F* FEG-SEM microscope. The samples were secured onto copper mounts using silver paint and gold coating in a Polar on high resolution sputter coater to obtain enough contrast in the FEG-SEM micrographs. The energy of the electron beam was 20 kV.

Optical Emission Spectroscopy (OES) measurements have been performed to study the plasma characteristics just below the porous plate, using a GetSpec 3648 set-up.

### 3. Results and discussion

#### 3.1 PE powders fluidization

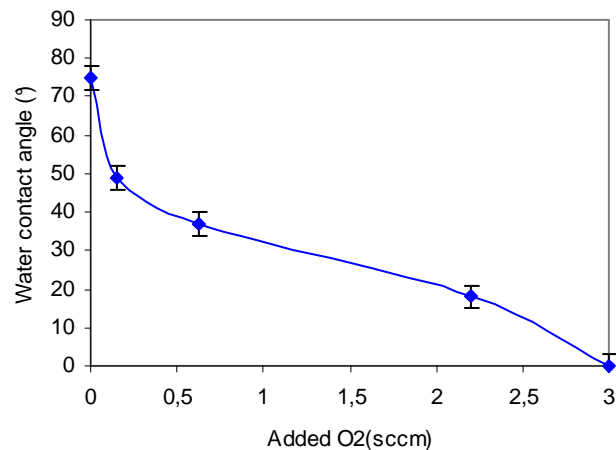
First, the choice to work under a total pressure of 10 Torr results from a compromise between the concentration of the active species responsible for creating active sites on powder surfaces and also for the dissociation of SiH<sub>4</sub> and the fluidization quality. The concentration of the active species increases when the pressure decreases and the fluidization quality is improved when the pressure increases.

Then, the minimum fluidization velocity at reduced pressure (10Torr) was deduced from the variation of the pressure drop through the fluidized bed versus the gas velocity. Harrison and Richardson method was adopted [6]. According to experimental data, the minimum fluidization velocity ( $U_{mf}$ ) was equal to 5.3 cm/s. This value agreed well with predicted value by Llop et al. correlation [9]. We chose to work at a fluidization ratio  $U/U_{mf}$  of 10 since it provides a convenient bed hydrodynamics and ensures an important active species concentration.

The granulometry of powders was lowly modified by the plasma treatment, as verified by laser granulometry measurements.

### 3.2 Effect of the oxygen flow rate

The influence of the oxygen flow rate on the contact angle with water for the treated PE powders is shown in figure 2.



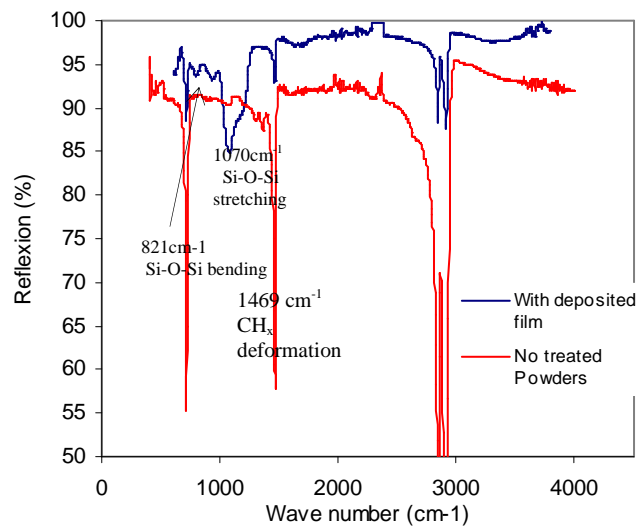
**Figure 2.** Variation of the water contact angle versus oxygen flow rate, 4sccm of SiH<sub>4</sub> diluted in 156 sccm of N<sub>2</sub> and 640 sccm of total plasma gas.

The increase of the oxygen percentage in the discharge enhances the powders wettability since the contact angle regularly decreases with the oxygen percentage, to reach 0° at 3 sccm of O<sub>2</sub>. In fact, the plasma treatment (only considering N<sub>2</sub> and O<sub>2</sub>) could create new chemical functions on the powder surface, which may change the surface chemical composition and roughness, affecting the polymer wettability [10]. Indeed, Arpagaus et al. [11] show in their works that the wettability effect is strongly influenced by the plasma gas composition and the degree of wettability increases with higher O<sub>2</sub> content in an O<sub>2</sub>/Ar mixture. The intensity of oxygen incorporation into the surface increases with the amount of O<sub>2</sub> in the plasma gas but levels off at a value higher than 30 vol. % O<sub>2</sub> [11].

In a previous work about surface treatment of these PE powders by a nitrogen cold remote plasma [7], we have shown that these new functions reduce the contact angle to 65° by adding 1% vol. oxygen in nitrogen in the cold plasma under 300W and microwave positioned at 20 cm far from the reactor. Consequently, it can be inferred that the reduction of the contact

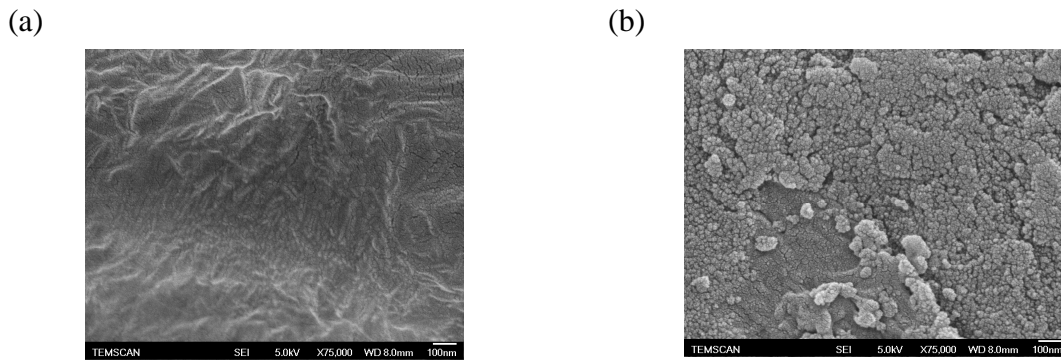
angle to  $0^\circ$  is not only due to these new functions grafted on the powders surface but mainly to the deposited material.

The chemical composition of the deposition has been analysed by FTIR-ATR as shown on Figure.7. Whatever the conditions tested, for all runs presented in this article, the spectra are very similar. The absorption at  $1070\text{ cm}^{-1}$  and  $820\text{ cm}^{-1}$  is due to stretching vibrational and bending mode of Si–O–Si group that mainly characterizes the deposition. The presence of carbonyl groups is also evident from the observation of the spectra since the deformation  $\text{CH}_x$  absorbs in the range  $1400\text{-}1500\text{ cm}^{-1}$ .



**Figure 3.** Normalized FTIR-ATR spectra of the PE powders before and after deposition.

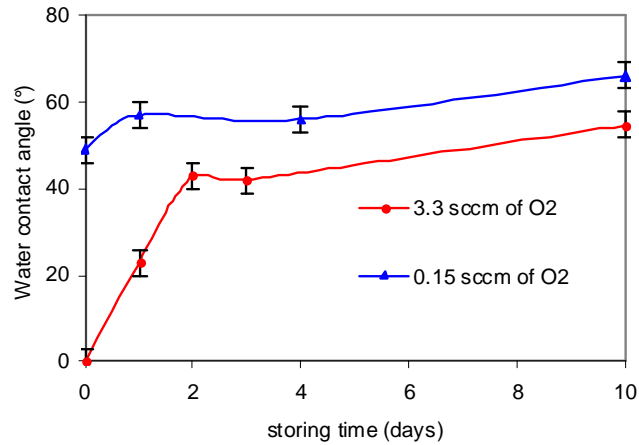
FEG-SEM analyses have confirmed the presence of the deposition on the powders, as shown below. The PE surface before deposition is quite smooth. The deposition is relatively rough; it seems to occur under the form of  $\text{SiO}_x$  nodules. Its continuity on the PE surface is not ascertained. As a consequence, the increase of wettability of the powders due to the increase of  $\text{O}_2$  flow rate could be due either to a better surface coverage or to an increase of the deposition thickness or even to a modification of the deposit chemical composition with more oxygen deposited. Some additional characterizations are in progress to elucidate these points.



**Figure 4.** FEG-SEM micrographs of the PE powders surface (a) before and (b) after plasma post discharge coating under 4 sccm of  $\text{SiH}_4$ , 0.63 sccm of  $\text{O}_2$  in 640 sccm of  $\text{N}_2$

The EOS investigations have revealed that in the deposition conditions without powders, the introduction of small amounts of oxygen strongly increases the concentration of the produced active species  $\text{N}(\text{^4S})$ . For more details, it is interesting to refer to the study of Boudam *et al.* [12]. Higher oxygen flow rate in the discharge promotes the production of silicon oxide by the combination of oxygen atoms with silicon coming from  $\text{SiH}_4$  decomposition. The produced  $\text{N}(\text{^4S})$  dissociates the  $\text{O}_2$  and  $\text{SiH}_4$  gaseous precursors and creates active sites on the powders surface.

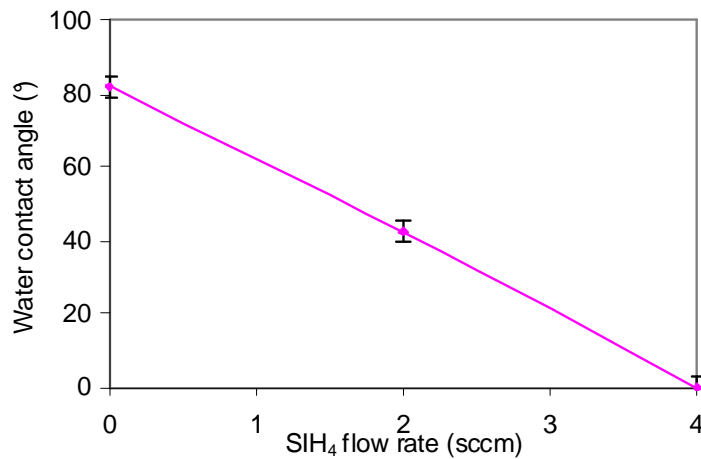
It can be seen on figure 5 that the surface modifications induced by the deposition are not permanent. The water contact angle increases rapidly to reach a plateau at proximally  $60^\circ$  after a few days when 3 sccm of  $\text{O}_2$  were added in the discharge, and after one day for 0.15 sccm. The increase of the coated PE powders wettability to  $60^\circ$  confirms our assumption regarding the wettability causes. In fact, when the hydrophilic character is induced by grafted functions, the PE powders become hydrophobic after a few days [4]. But in our case, the coated PE powders wettability stabilises at  $60^\circ$ . This indicates that water contact angle reduction to  $0^\circ$  is due to deposition. However, wettability evolution could be first the result of losing of the coated film by friction during handling. A second reason could be assigned to carbon contamination by the ambient atmosphere which would increase its hydrophobicity.



**Figure 5.** Variation of the water contact angle versus storing time, 4sccm of SiH<sub>4</sub> diluted in 156 sccm of N<sub>2</sub> and 640 sccm of total Plasma gas

### 3.3 Effect of silane flow rate

In this part, the oxygen flow rate was maintained at 3 sccm, which gave the best wettability, as previously shown. Figure 6 shows the evolution of the contact angle with water for various silane flow rates.



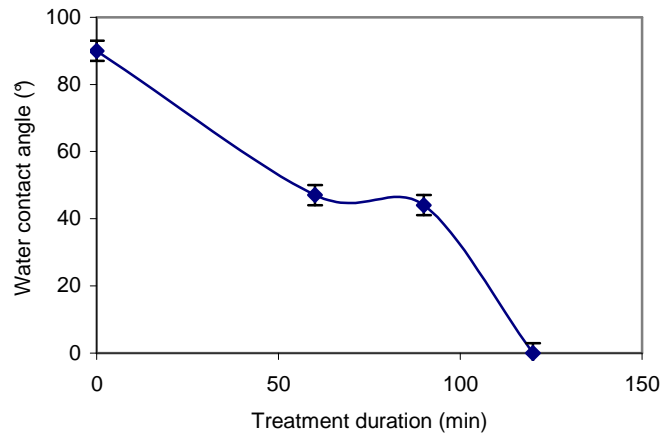
**Figure 6.** Variation of the contact angle versus SiH<sub>4</sub> flow rate, 3sccm of O<sub>2</sub> added in 640 sccm of total plasma gas.

It can be seen from figure.4 that an increase in SiH<sub>4</sub> flow rate linearly decreases the water contact angle; so the wettability is exalted. Increasing the silane flow rate increases the concentration of silicon atoms in the bed. So it appears that either the surface coverage or

the deposition thickness are enhanced by the presence of more silicon atoms in the bed for the conditions tested.

### 3.4 Effect of deposition duration

Figure 7 presents the influence of the deposition duration on the contact angle of the PE powders.



**Figure 7.** Variation of the water contact angle versus treatment duration, 3sccm of O<sub>2</sub> added in 640 sccm of total plasma gas and 4 sccm of SiH<sub>4</sub> flow rate.

By considering an error of  $\pm 3^\circ$  on experimental values on the water contact angles, the general trend is that increasing the coating duration decreases the contact angle, and so increases the powder wettability. By increasing the run duration, the theoretical deposition thickness also increases, since the amount of silicon injected is higher. So this parameter could explain the better wettability obtained here.

## 4. Conclusion

This work has demonstrated the feasibility to deposit silicon oxide on the surface of a polyethylene powder, using a far cold remote nitrogen/oxygen plasma and silane in a fluidized bed. This deposition occurs under the form of nodules and its continuity is not ascertained. It drastically increases the powder wettability. This hydrophilic character of the deposition is exalted by the oxygen concentration injected in the discharge, the SiH<sub>4</sub> flow rate and the treatment duration. Additional characterizations are in progress to understand if these parameters increase either the continuity of deposition, or its thickness or modify its chemical

composition. The surface properties induced by the deposition are not permanent, probably due to carbon contamination.

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