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Nitrogen post-discharge assisted deposition from silane on polymer powders in a fluidized bed

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Abstract: Nowadays, powders represent about 75% of raw materials used in the industry. One of their main characteristics is their high surface to volume ratio. Therefore, modifying their surface properties is a great scientific and industrial challenge. In this work, a nitrogen/oxygen post-discharge is used to deposit silicon oxide from silane on polyethylene powders in a fluidized bed.

Keywords: cold plasma, fluidized bed, thermo-sensitive powders, silicon oxide layer

1. General

The nitrogen cold remote plasma technology coupled with a fluidized bed allows the surface of thermo-sensitive powders to be modified either by grafting new functions (for instance hydroxyl OH groups), or by depositing various materials. In this work, silicon oxide is deposited from silane and oxygen. The remote nitrogen/oxygen cold plasma creates active sites on the powders surface and also dissociates SiH_4 , inducing the silicon oxide deposition. The plasma assistance allows operating at low temperature ($< 90^\circ\text{C}$ in our case). The fluidized bed is a very efficient gas-solid contactor generating intense thermal and mass transfers between gas and particles, and so very uniform treatments.

2. Experimental set-up and analysis techniques

In this work, the powders are high density polyethylene (PE) particles, $260\ \mu\text{m}$ in Sauter diameter and $930\ \text{kg/m}^3$ in grain density. Several tens of grams of powders per run have been treated in a fluidization reactor (figure 1) of 5 cm in internal diameter and 90 cm in height, under a pressure of 10 Torr. Compared to similar works in 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 microwave power is transferred to a mixture of N_2 and O_2 through a surfatron. Silane SiH_4 is injected at the bottom of the fluidized bed in the post-discharge.

The nitrogen post-discharge was characterized using Optical Emission Spectroscopy (OES). The optical fiber was positioned upstream or downstream the porous plate. The powder contact angle was obtained using a GBX Tensiometer by means of the Washburn method [3] in order to study the powder wettability. A quantity of $500\ \mu\text{g}$ of PE powders was packed into a glass column (10mmID). The bottom of the glass column is closed with

a porous plate. In order to have the same porosity for each measurements, a vibrating device is used. The time and velocity of vibrations are kept at the same value. After this operation, the glass column is put in close contact with the chosen liquid which rises by capillarity in the PE powders column. The weight of the penetrating liquid is measured as a function of time after the contact of the porous glass plate with the liquid. The contact angle of the PE powder surface is governed by the modified Washburn's equation [1].

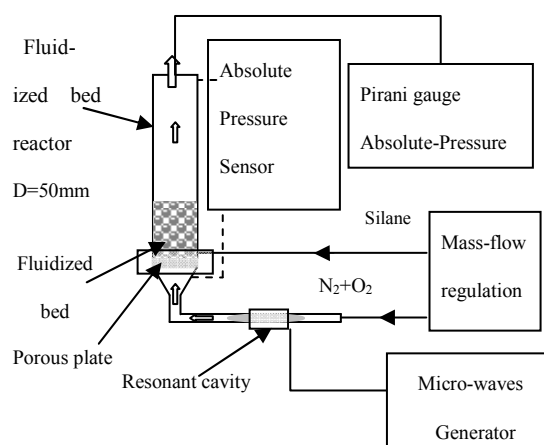
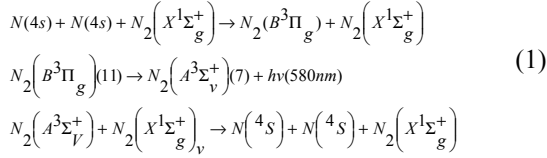


Fig.1 Experimental set up

3. Results and discussion

The occurrence of a flowing post-discharge in nitrogen is due to the transfer of the discharge electron energy to the numerous vibrational levels of nitrogen, which constitute the main energy reservoir of this kind of post-discharge. The post-discharge is mainly character-

ized by two distinct zones: the short-lived afterglow (SLA) and the far remote afterglow (FRA). While the N_2^+ cations and metastable species presence, high vibrational temperatures are signatures of the SLA, the FRA is characterized by its typical 580nm yellow emission which results from the following mechanism (1):



In this zone, the main reactive species is $N(^4S)$. The square of its concentration has been shown to be proportional to the intensity of the $N_2(B_3\Pi_g, v=11 \rightarrow A^3\Sigma_u^+, v=7)$ transition at 580 nm, in the FRA [4]. Hence, this band head intensity was followed by OES in order to evaluate the reactivity level of the post-discharge.

The intensity of the emission of $N_2(B_3\Pi_g, v=11)$ was monitored as a function of power, the position of the microwave cavity, and the amount of oxygen injected in the discharge. The emission spectra were recorded with and without the gas distributor which sustains the powders in the fluidized bed, allowing us to analyze the active species transmission through this important part of the experimental set-up.

When the microwave cavity is 20 cm upstream from the fluidised bed under 300W, the emission spectra indicates the presence of the nitrogen first negative transition $N_2^+(B\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ centered at 391.4 nm.

The decrease of power to 80 W permit avoiding the creation of these species but then the $N_2(B_3\Pi_g, v=11)$ intensity is very low. In order to increase the $N(^4S)$ creation and avoid $N_2^+(B\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ species, it is more interesting to keep the power at 300W and change the position of the resonance cavity. The influence of this parameter on the 580-nm emission was investigated.

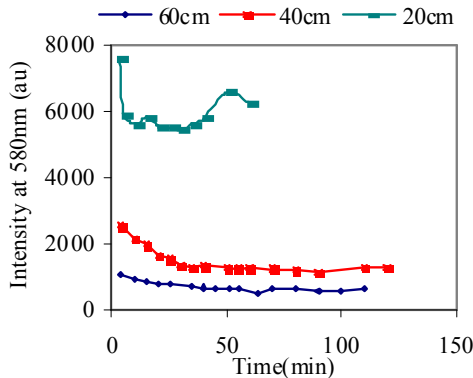


Fig.2: Temporal evolution of nitrogen first positive intensity versus treatment time, upstream the porous plate under 1 slm of N_2 , 10 Torr and 300W.

It can be seen in Fig 2. that the $N_2(B_3\Pi_g, v=11 \rightarrow A^3\Sigma_u^+, v=7)$ transition intensity versus treatment time is more important when the microwave cavity is placed at 40 cm from the reactor, than when it is placed at 60 cm. Besides, the intensity of the first negative system is then very low. The decrease of the nitrogen first positive system during the first 40 min is due probably to the desorption of the oxygen adsorbed on the internal walls [4]. This decrease of the 580-nm emission intensity draws our attention to the oxygen role in N_2 post-discharge.

In this context, small amounts of oxygen were injected in the discharge.

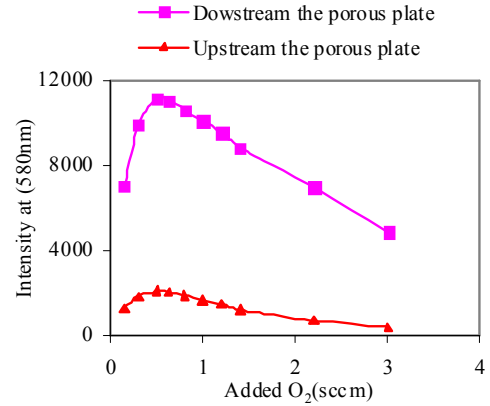
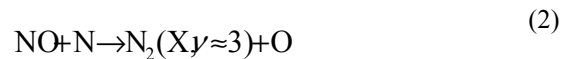


Fig.3 Influence of O_2 flow rate added on the $N_2(B_3\Pi_g, v=11)$ intensity upstream and downstream the porous plate.

Fig.3 shows that the intensity of the band at 580-nm reaches a maximum for a 0.63 sccm O_2 flow-rate (in 640 sccm N_2 though the discharge zone), before decreasing. Boudam et al. [5] showed that increasing the oxygen percentage in a N_2/O_2 mixture reduces the contribution from the early afterglow and increases that of the late afterglow. Vasin et al. [6] also brought to the fore that the addition of oxygen influences the degree of dissociation of nitrogen in the afterglow [6]. It was demonstrated by Nahorny et al [7] that the increase of $N(^4S)$ concentration is due to an increase of the dissociation degree of N_2 caused by an enhancement of the reduced electric field. In fact, the populations of vibrational levels $v>12$ and the concentration of metastable excited states decrease due to collisions with O, O_2 and NO. When the flow rate of O_2 is higher than 0.63 sccm, the $N(^4S)$ concentration decreases because NO destroys $N(^4S)$ following reaction (2):



The second part of this work is dedicated to the influence of the oxygen and silane flow-rates on the wettability and ageing characteristics of the treated PE powders, under the plasma conditions previously given ($Q_{N_2}= 640$ sccm, $P=10$ Torr, Power=300W and microwave cavity located 40cm upstream the fluidized bed.).

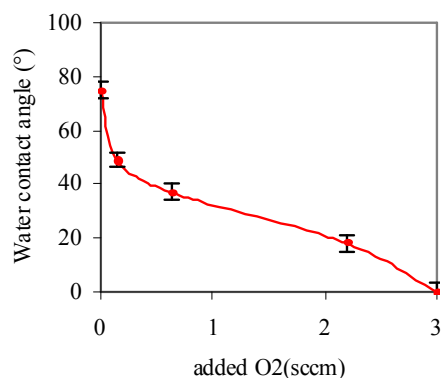


Fig.5 Variation of the water contact angle versus the oxygen flow-rate (4 sccm of SiH₄ diluted in 156 sccm of N₂ and 640 sccm of N₂/O₂ through the discharge).

The increase of the oxygen amount in the discharge has a great effect on the powder wettability (fig. 5): from an almost hydrophobic polymer powder, the contact angle decreases to zero for an O₂ flow-rate of 3 sccm. This change of the wettability presumably results from hydrophilic silicon oxide deposition on the powder. The hydrophilic nature of the powders depends on the quality of the deposited layer: its structure, its oxidation level and its surface coverage.

In a previous study [8], we have shown that the treatment of the same powder as in this work can lead to a water contact angle of 65° when a 1 % oxygen in nitrogen mixture is injected in the discharge without any supply of silane. Consequently, the reduction of the contact angle to 0° showed in fig.5 is not only due to the grafting of new functions on the powders surface but also to a deposited film.

It is interesting to note that the best treatment is not obtained for the optimal N(⁴S) production. This proves that the sole dissociation of silane by N(⁴S) is not the determinant step in obtaining a satisfying silica-like layer around the power. The oxidation of silicon-containing molecules in the gas phase or of the deposited layer also plays an important role. Moreover, as PE is etched by oxygen atoms, the oxygen flow-rate increase could also lead to an increase of the number of active sites on the powder surface.

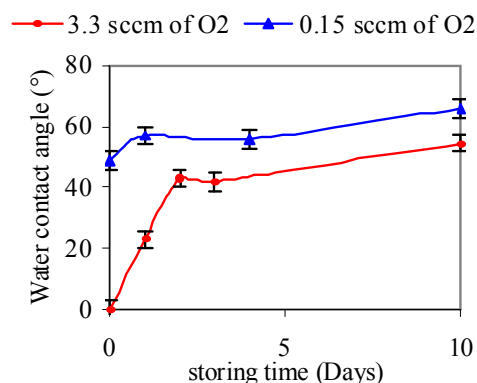


Fig.6 Variation of water contact angle versus ageing time (same conditions as for fig. 5).

It can be seen in fig. 6 that the treated powders suffer a non-negligible ageing. The water contact angle increases rapidly to reach a plateau at proximally 60° after a few days when 3 sccm of O₂ are added in the discharge and one day for 0.15 sccm. As the surface of the powders could be not completely covered by the silica film (scanning electron microscopy results not shown here), this ageing phenomenon could be due to several factors.

A first plausible reason for this ageing phenomenon can be assigned to the re-arrangement of the polar groups generated during plasma treatment on the uncovered surface. Indeed, the new created functions which improve the hydrophilic character tend to rotate and bury themselves below the surface [9, 10]. In that case, the hydrophobic characteristic of the surface is completely recovered [11]. In our case, the PE powder wettability reaches a plateau at 60°. This indicates that the observed wettability modification is also associated to the presence of the coated film. Two reasons can be cited to explain the contact angle increase of the covered part. First, the bad adhesion between PE and silicon oxide could lead to the wrenching of parts of the deposited layer and hence to an increase of the contact angle. Secondly, the carbon contamination could modify the contact angle of silica [12].

Fig.7 shows the evolution of the water contact angle versus silane flow-rate. The increase of the silicon precursor flow-rate appears as an important parameter in modifying the PE powder wettability. Once again, this could be due to several factors. Clean silica has a very low contact angle but sub-oxides do not. Nevertheless, this seems to be in contradiction with the recorded variation, since the O/Si ratio in the layer should be decreasing when the SiH₄ flow-rate increases, leading to an increase of the contact angle. The most plausible explanation is probably linked to the surface coverage which probably increases with the silane flow-rate. Silane appears here as a limiting factor.

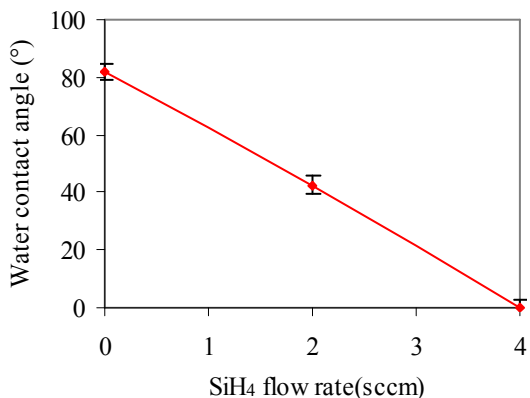


Fig.7 Variation of the water contact angle versus the SiH₄ flow-rate (3sccm of O₂ in 640 sccm of N₂ through the discharge).

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. Under the best plasma conditions, increasing the oxygen and silane flow rate enhances strongly the hydrophilic character of the PE powders. The surface modifications induced by the coated layer are not permanent, probably due to carbon contamination.

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