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# Surface Modification of Polymer Powders by a Far Cold Remote Nitrogen Plasma in Fluidized Bed

Lynda. Aiche<sup>1,2</sup>, Hugues. Vergnes<sup>2</sup>, Bernard. Despax<sup>1</sup>, Brigitte. Caussat<sup>2</sup>, Hubert. Caquineau<sup>1</sup>

<sup>1</sup>Laboratoire des Plasmas et Conversion des Energies,  
118 Route de Narbonne, 31106 Toulouse  
E-mail: caquineau@laplace.univ-tlse.fr

<sup>2</sup>Laboratoire de Génie Chimique, UMR CNRS 5503, ENSIACET/INPT,  
5 rue Paulin Talabot, BP 1301, 31106 Toulouse Cedex 1, France  
E-mail: Brigitte.Caussat@ensiacet.fr

**Abstract:** In this work, nitrogen was grafted on the surface of polyethylene powders in a fluidized bed coupled to a nitrogen microwave post-discharge, at low pressure (10 Torr) and low temperature (<90°C). 50 g of powders have been treated per run. The influences of treatment-duration (1 to 9 h) and nitrogen flow rate have been studied on the XPS (X-ray Photoelectron Spectroscopy) N/C atomic ratio and on the powders wettability. These parameters increase with run duration and N<sub>2</sub> flow rate but reach a plateau after 3h of treatment.

## 1. Introduction

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.

To treat thermo-sensitive powders, some authors have coupled two technologies: a fluidized bed to promote gas-particles contact and a cold plasma to generate active species at low temperature [1-2]. Nitrogen cold remote plasmas allow to graft nitrogen on particle surface and then for instance, to increase the wettability of polymer powders [1-3]. For Vivien et al. [1], a maximum wettability was obtained at 600W, after 25 min of treatment, for 45 g of polyethylene (PE) powders at 1.4 Torr. Bretagnol et al. [3] observed an increase of the N/C atomic ratio with a treatment duration and the apparition of a plateau at 12% after 300 s at 0.4 Torr and 5 W for 3 g of PE powders.

## 2. Experimental

Experiments were carried out in a vertical cylindrical glass column, 50 mm in diameter and 0.9 m in height. Particles were supported by a polypropylene porous plate. The reactor was maintained under reduced pressure (fixed at 10 Torr) by means of a vacuum pump. The leak rate was always under 100 mTorr/min. The

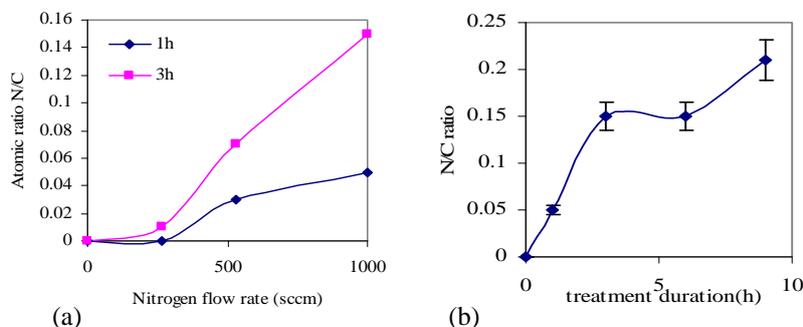
pressure at the top of the fluidized bed was controlled by a Pirani vacuum gauge. Entrained particles were captured by a particle filter.

Before entering the fluidizing column, nitrogen underwent a 2.45 GHz microwave discharge by passing through a microwave cavity (surfatron). The fluidized bed was 25 cm downstream of the plasma. The power was maintained at 300W.

A High Density polyethylene (PE) powder, 280  $\mu\text{m}$  in Sauter diameter and 930  $\text{kg/m}^3$  in grain density, was fluidized by nitrogen (N50 grade, Air Liquide), whose flow rate was regulated by a mass flow controller. 51g of particles have been treated per run, corresponding to a fixed bed height to diameter ratio of 1. The  $\text{N}_2$  flow rate was varied between 267 and 1000 sccm (standard  $\text{cm}^3/\text{min}$ ), corresponding to a fluidization ratio  $U/U_{\text{mf}}$  comprised between 3 and 11 where  $U$  and  $U_{\text{mf}}$  are the gas velocities respectively in the empty column and at the minimum of fluidization. The treatment duration was varied between 1 and 9 h.

### 3. Results and discussion

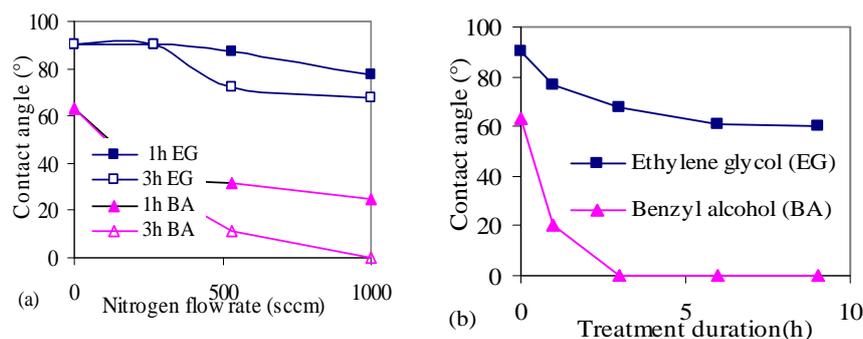
First, XPS analyses allowed to measure changes in the chemical state and composition of the PE surface induced by the plasma treatments. The as-received PE powder surface presents a single intense C 1s peak centred at 285 eV. After treatment, a N 1s peak appears at 401eV.



**Fig. 1.** (a) N/C atomic ratios versus  $\text{N}_2$  flow rate for 1 and 3 h of treatment. (b) N/C atomic ratios versus run duration for 1000 sccm of  $\text{N}_2$ .

It appears on fig. 1(a) that the N/C ratio increases both with the  $\text{N}_2$  flow rate and with run duration because of a concomitant increase of the amount of reactive species crossing the bed. By considering an error of measurement of 10% on measured values, fig. 1(b) shows that this ratio reaches a plateau after 3h of treatment, at a value close to 15-17%.

The wettability of the PE powder was evaluated in terms of contact angle by using the Washburn method [4] with benzyl alcohol (38.9 mN/m, 5.212 mPa.s) and ethylene glycol (48.3 mN/m, 16.1 mPa.s). Each contact angle value corresponds to the average of three measurements. The accuracy of the results is  $\pm 3^\circ$ .



**Fig. 2.** Influence of the N<sub>2</sub> flow rate and of treatment duration on the benzyl alcohol (BA) and on the ethylene glycol (EG) contact angles

Figure 2 shows that the contact angles decrease with the increase of N<sub>2</sub> flow rate and run duration. The best wettability (0°) is obtained with benzyl alcohol for 1000 sccm of N<sub>2</sub> and after 3 h. For the same operating conditions, the ethylene glycol contact angle is only 68°. This difference proceeds from the differences of viscosities and surface tensions between the two liquids used. As in XPS results, contact angles almost reach a plateau after 3h. This leveling corresponds to the competition between functionalization and degradation phenomena which is a well-known process observed in nitrogen plasma processing of polymers [3].

An additional run was performed adding 1 vol. % of O<sub>2</sub> to 1000 sccm of N<sub>2</sub> for 3h. It allowed reaching the best wettability of the whole runs.

#### 4. Conclusions

The N/C ratio and the wettability of polyethylene powder both increase with run duration and fluidization ratio till reaching a plateau after 3 h. Adding a small amount of oxygen allows reaching the best wettability. Studies are now in progress to characterize the plasma by OES (Optical Emission Spectroscopy), and to deposit continuous thin layer of silicon oxide from silane on the powders.

#### References

- 1 C. Vivien, C. Wartelle, B. Mutel, J. Grimblot, *Surf. Interface Anal.* 34, 575-579 (2002).
- 2 J. B. Leroy, N. Fatah, B. Mutel, J. Grimblot, *Plasmas and Polymers* 8, 13-29 (2003).
- 3 F. Bretagnol, M. Tatoulian, F. Arefi-Khonsari, G. Lorang, J. Amouroux, *Reactive Functional Pol.* 61, 221-232 (2004).
- 4 E.W. Washburn, *Phys. Rev. Ser.* 17 (3), 273-283 (1921)