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# Plasma Modified Polycarbonate Nonwovens as Filtering Material for Liquid Aerosols

**Abstract**
*The filter materials commonly used in filtration processes consist of nonwoven fabrics made by melt blowing. In order to improve filtration properties they are subjected to various modifications. This paper presents the treatment of polycarbonate nonwovens with low-pressure cold plasma generated by a 13.56 MHz RF discharge using process gases such as Ar and $O_2$. The effectiveness of such treatment was assessed on the basis of results of the penetration of nonwovens by paraffin oil mist as well as the air flow resistance. The effects of plasma on polycarbonate nonwovens, especially on their surface morphology and chemical structure, were evaluated by electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The results indicate that Ar plasma is a good tool for improving the filtration properties of polycarbonate filtering materials. According to these results, the surface roughness plays an important role in the high-efficiency filtration of liquid aerosols with a small increase in air flow resistance.*

**Key words:** *polycarbonate nonwovens; plasma treatment; liquid aerosols; filtration.*

## Introduction

Due to frequent use of hazardous liquid aerosol particles (mists) in manufacturing processes in such industries as pharmaceutics, textiles, plastic processing, cosmetics and food processing, workers are exposed to a considerably increased risk of respiratory disorders. This has prompted higher expectations concerning the efficiency of respiratory protective equipment used in the workplace. The basic materials used in respiratory protective equipment are systems of nonwovens consisting of several filter layers of varied porosity, which ensures homogeneous distribution of aerosol particles arrested in the filtering material during its use in the workplace [1]. At the same time, apart from requirements concerning high-efficiency filtration, additional expectations of the users concerning the safe working time of the protective devices are emerging. Therefore research work aimed at the improvement of air-filtering systems are oriented towards providing the possibility to create a filter material optimal from the point of view of both these criteria, also taking into account the energy efficiency of the technological process, as well as economic and environmental considerations. The demand for innovative filter materials meeting the above requirements has triggered intensive progress in the techniques of their production and modification [2].

The application of low-pressure cold plasma for the modification of a fibre surface can be a very interesting and environment-friendly method allowing to improve the filtration properties of polymer nonwovens [3]. It is associated with very extensive possibilities of surface modification by etching, the formation of functional groups with a complex chemical structure on the surface, and cross-linking processes [4, 5]. As a result, exposure to plasma allows to obtain the physical and chemical properties of the polymer fibre surface desired, i.e. increased porosity, charge accumulation potential, and formation of new chemical structures on the polymer surface. Research centres are currently conducting numerous studies indicating the possibility of the application of this technique in various industrial sectors, the textile industry in particular [6 - 8]. For example, it was established that the plasma treatment of polypropylene (PP) filtering nonwovens may influence filtration efficiency against solid particle aerosols (dusts) [9]. An improvement of filtration efficiency was obtained with no change in the air flow level. The above allows to conclude that the fibre surface modification method utilising cold plasma provides a realistic possibility to obtain high-efficiency and low-resistance materials for respiratory protective equipment against all aerosols, including liquid particle aerosols (mists). However, because of the different nature of phenomena associated with the deposition of liquid particles on fibres in comparison with that of solid particles [10, 11], further research in this field is necessary [12].

Filter materials used in the construction of respiratory protective equipment are most frequently produced from polypropylene (PP), utilising melt blown technology. Such common use of PP is due to its very good processing properties in melt blown technology. Additionally the correlation between cold plasma modification effects on the polymer surface and the polymer crystallinity was demonstrated [13]. PP with a higher crystallinity level was characterised by a lower wetting contact angle and higher oxygen concentration than PP with lower crystallinity. Considering such parameters as the tacticity (iso-, syndio- or atactic fractions), crystallinity and molecular weight of PP [14], it was necessary, in order to obtain satisfactory effects with respect to the improvement of the nonwovens' filtration efficiency against liquid aerosol particles, to test another polymer type with similar processing properties but of a lower crystallinity level than that of PP. Therefore investigations aimed at the development of a plasma modification technique for melt blown filtration nonwovens based on an amorphous polymer – polycarbonate (PC) were undertaken.

***Table 1.*** *Technological parameters of melt-blown production.*

| Process technological parameters | PC |
|---|---|
| Temperature, extruder zone 1, °C | 320 |
| Temperature, extruder zone 2, °C | 330 |
| Air temperature, °C | 325 |
| Nozzle temperature, °C | 330 |
| Air flow rate, $m^3/h$ | 3.5 |
| Polymer flow rate, g/min | 7.0 |
| Nozzles to collector distance, cm | 12 |
| Collector speed, m/s | 0.0055 |
| Voltage supply for fibre-forming head-heating elements, V | 185 |

***Table 2.*** *Structural parameters of polycarbonate filtering nonwoven.*

| | |
|---|---|
| Basis weight, $g/m^2$ | 90 ± 5 |
| Thickness, mm | 2.01 |
| Min fibre diameter, μm | 0.27 |
| Max fiber diameter, μm | 6.85 |
| Mean fiber diameter, μm | 1.18 |
| Standard deviation, μm | 1.10 |



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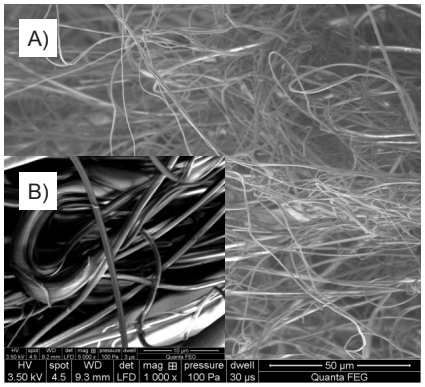


***Figure 1.*** *Polycarbonate (PC) nonwoven before plasma treatment.* ***Magnification****: A) 1000× and B) 5000×.*

In this paper, the low-pressure plasma treatment of PC filtration nonwovens manufactured by melt blowing, in order to obtain a material arresting liquid aerosol particles (mists) effectively, is presented.

## Experimental

### Material

LEXAN 144 Resin type non-crystalline polycarbonate with melt volume flow rate MVR 12.0 $cm^3$/10 min (manufacturer SABIC Innovative Plastics Europe, Netherlands) was the material used for production of filtering nonwovens.

### Preparation of filtrating nonwovens

The preparation of filtration of nonwovens was conducted using an experimental stand at the Central Institute for Labour Protection - National Research Institute (CIOP-PIB) [15 - 17]. The polycarbonate polymer (PC) in granular form was transferred from the hopper to the heated extruder zone. It was heated to obtain an appropriate viscosity before extrusion from the fibre-forming head. Compressed air passed from the flow controller to the heater, where it was dried and heated to an appropriate temperature. Then it was directed to the fibre-forming head. Leaving the head, air was blown through polymer streams extruded from the nozzles, forming elementary fibres, which were, in turn, deposited on the collector, forming a compact, porous fleece – the nonwoven material. The nonwoven-producing device is equipped with dome control points making it possible to change the technological parameters. The PC nonwovens were produced using the parameter settings presented in ***Table 1***. A characterisation of the structural parameters of the PC nonwoven obtained prior to the modification process is presented in ***Table 2***, whereas ***Figure 1*** shows an SEM image of the PC nonwovens surface before plasma treatment.

### Modification process

The plasma treatment was conducted in a two-electrode RF reactor (13.56 MHz) working under low pressure. A schematic diagram of the reactor is presented in ***Figure 2***. Polycarbonate filtration nonwovens in the form of disc-shaped samples 80 mm in diameter were placed on the powered (lower) electrode of the reactor. The pressure in the reactor chamber was decreased to 2 Pa, then an appropriate plasma gas - (Ar - 99.999% purity or $O_2$ - 99.95% purity) was introduced and a discharge initiated. The gas flow of Ar and $O_2$ was 2 and 1.5 sccm (standard cubic centimetres per minute), respectively. The power of the glow discharge was 80 W. The modification times ranged from 30 s to 6 min. Modification in Ar also included double-sided treatment. For this purpose, after the treatment of one side of the sample, e.g. for 30 s, the reactor was turned off and the modification process repeated for the other side.

### Testing methods

In the studies of chemical composition and surface morphology a scanning microscope manufactured by FEI Quanta

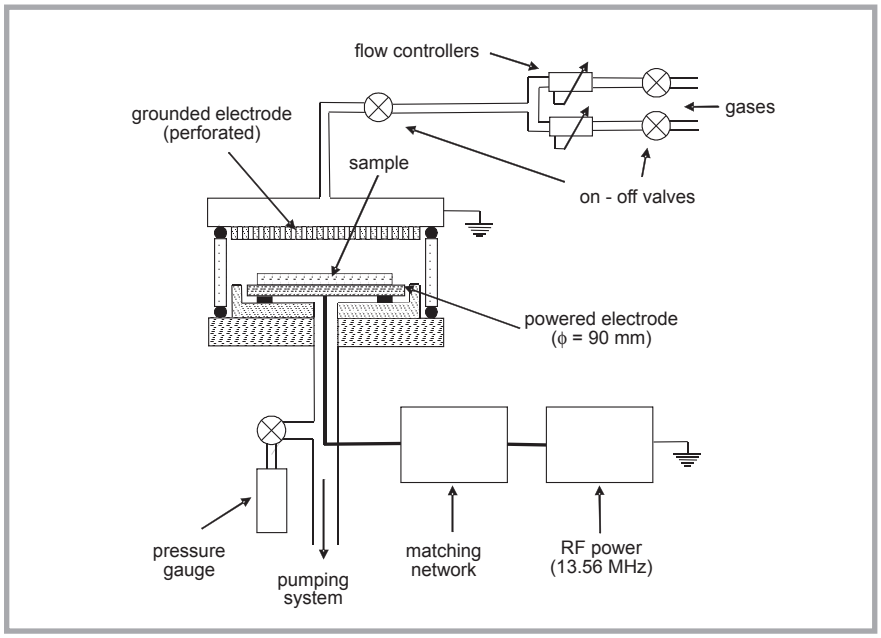


***Figure 2.*** *Schematic diagram of the RF plasma reactor.*

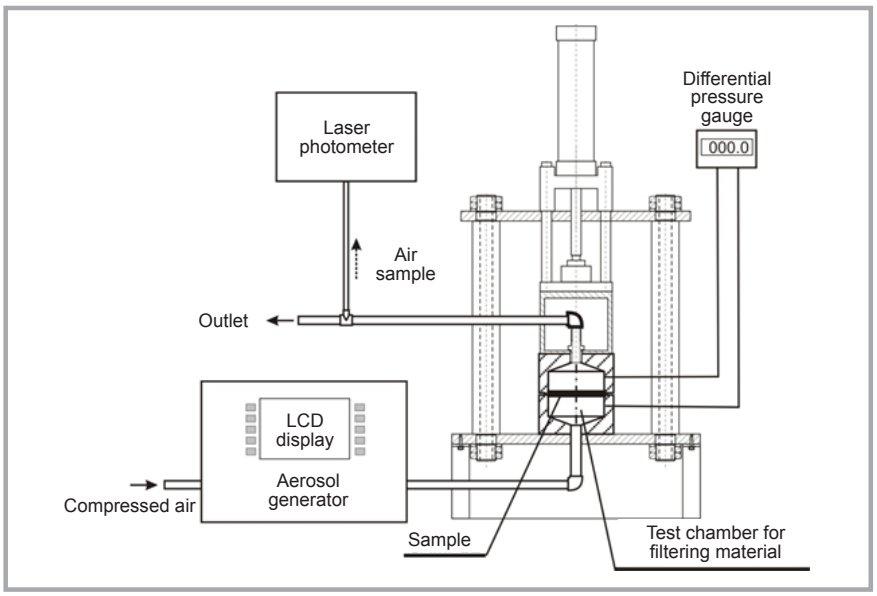


***Figure 3.*** *Schematic diagram of the paraffin oil mist penetration test stand.*

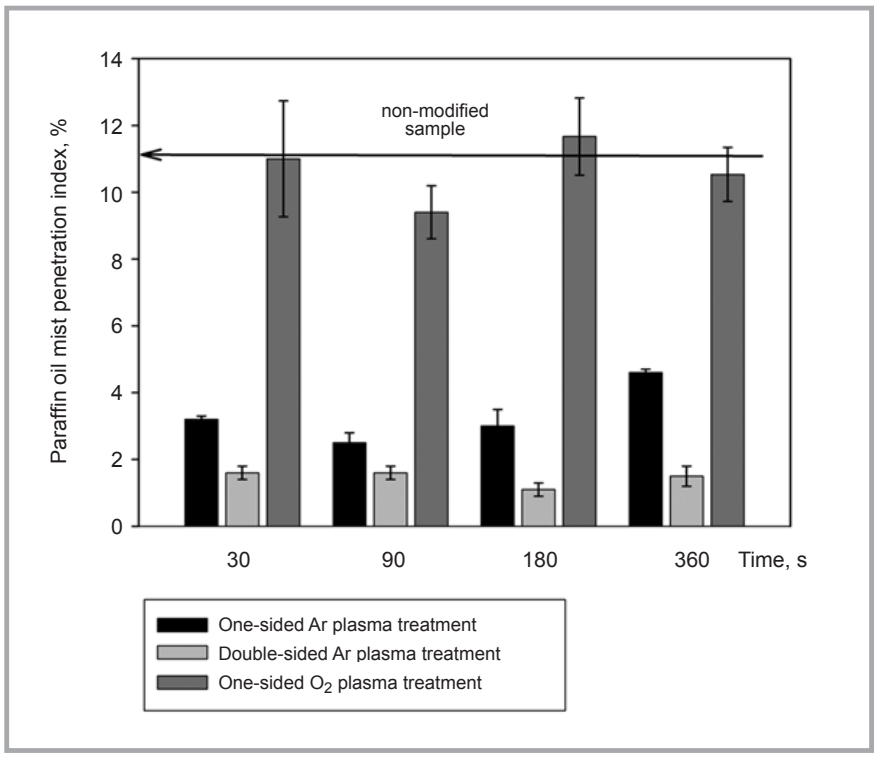


***Figure 4.*** *Paraffin oil mist penetration index for various treatment types.*

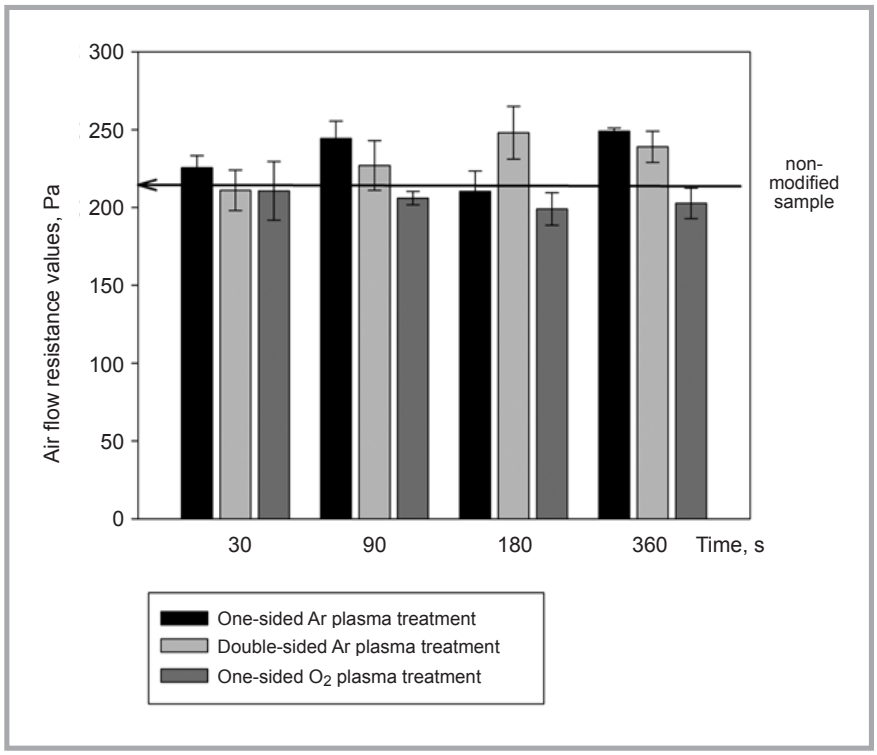


***Figure 5.*** *Air flow resistance for various treatment types.*

200F, equipped with an X-max model EDS (EDX) analyzer (Oxford Instruments), was used. The EDX spectra were obtained with shallow penetration of the electron beam (ca. 100 nm) using energy of 3.5 keV – corresponding to the elemental composition on the nonwoven surface. To determine the molecular structure of the fibre surface, X-ray photoelectron spectroscopy (XPS) was employed. Photoelectron spectra were recorded by a Thermo VG ESCALAB 250 spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) at a spot size of 500 μm. Binding energies were determined by attributing to the main C1s (C–C, C–H) peak a value of 284.9 eV. The spectra obtained were processed using background subtraction (Shirley-type) and a curve fitting procedure (mixed Gaussian 70% - Lorentzian 30% lines shape).

The selection of methods used to assess the filter nonwovens' performance and air flow resistance was determined by their designation for respiratory protective equipment. Currently respiratory protective equipment to be released for use in the workplace is subjected to tests conducted according to the appropriate procedures. In the European Union, tests of filters and filtering half-masks are conducted in compliance with the methodology described in the appropriate EN standards (EN 143:2000 and EN 149:2001+A1:2009) [18, 19] harmonised with Directive 89/686/EEC [20]. The performance of respiratory protective devices of this type is assessed with the penetration index using two model aerosols: non-neutralised polydisperse NaCl (solid particles) and paraffin oil particles (liquid particles) at a flow rate of 95 l/min. From the point of view of respiratory tract protection, the ability of filter nonwovens to arrest liquid particles is a stricter criterion than the arrest efficiency of solid particles. Therefore liquid aerosol was selected for tests in this study.

The filtering properties of PC filter nonwovens before and after plasma treatment were assessed on the basis of the paraffin oil mist penetration index and air flow resistance (breathing resistance) values according to test methodology specified in the appropriate EN standards [21, 22]. Determination of the penetration index using the paraffin oil mist penetration test was carried out on a test stand, presented schematically in ***Figure 3***.
The measurement involves generation of paraffin oil mist, which is then passed through the layer of filter material with a specified linear velocity of 0.15 m/s. Aerosol is produced in the generator (1) by spraying heated paraffin oil. It is then directed towards the filter material mounted in the grip (2) of definite diameter. The aerosol concentration before and after passing through the test material is measured with a Lorenz laser photometer (3). The penetration results are expressed as percentage values.

Air flow resistance is measured by passing air through the filter material at a con-

stant volume flow rate with determination of the pressure decrease on the other side of the material in comparison with the atmospheric pressure. The tests were conducted using a volume flow rate of 95 l/min, corresponding to the respiratory minute volume during intensive exertion. The pressures were read using a CMR-10A differential digital micromanometer coupled directly with the measurement chamber of the paraffin oil mist penetration test stand.

## Results and analysis

The results of measurements of the paraffin oil mist penetration index and air flow resistance are presented in ***Figures 4*** and ***5***, respectively.

Comparing the effects of modification by exposure to low-pressure cold plasma with either of the gases used, it should be emphasised that only Ar plasma treatment resulted in a considerable reduction in paraffin oil mist particles, which corresponds to an improvement in the PC nonwovens' performance. In view of the fact that Ar is an inert gas, its effect on the fibre surface primarily involves changes associated with the etching of the polymer surface, which consequently leads to the development of a nano-roughness surface. This fact has been confirmed by SEM images of the fibre surface modified by Ar plasma (***Figures 6.A*** and ***6.B***).

The micrographs clearly demonstrate that the nano-roughness of the fibre surface increases progressively with the duration of Ar plasma treatment, which can be associated with the development of the filtration capacity, and in consequence with the increasing potential of the PC nonwovens to arrest liquid aerosol particles.

The treatment by Ar plasma, in addition to the etching process, can also create oxygen functional groups on the fibre surface as a result of the reaction between plasma generated radical states and oxygen and water molecules from the atmosphere. To determine the role of oxygen groups in the immobilisation of oil particles, the concentration of oxygen on the fiber surface treated by Ar and $O_2$ plasmas as well as the type of oxygen groups created were investigated by EDX and XPS spectroscopies. The results of EDX analysis, presented in ***Table 3***, indicate that the oxygen content in the range of error is practically the same in the case of Ar and $O_2$ plasmas. However, some differences in the nature and concentration of the oxygen functional groups are shown.

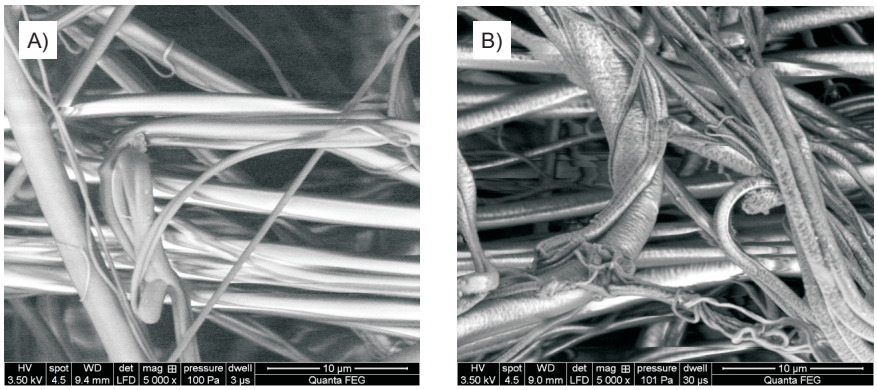


***Figure 6.*** *PC nonwoven after Ar plasma treatment. Time of treatment: A) 30 s, B) 360 s.*

***Table 3.*** *Elemental composition from EDX measurements.*

| Type of modification | Element at.% | Average from 10 measurements | Error (±) |
|---|---|---|---|
| plasma Ar 30 s | C | 88.01 | 0.26 |
| | O | 11.99 | 0.26 |
| plasma Ar 180 s | C | 89.13 | 0.40 |
| | O | 10.87 | 0.40 |
| plasma Ar 360 s | C | 89.07 | 0.32 |
| | O | 10.93 | 0.32 |
| plasma $O_2$ 30 s | C | 88.89 | 0.42 |
| | O | 11.11 | 0.42 |
| plasma $O_2$ 180 s | C | 88.65 | 0.38 |
| | O | 11.35 | 0.38 |
| plasma $O_2$ 360 s | C | 88.26 | 0.58 |
| | O | 11.74 | 0.58 |

***Table 4.*** *Concentration of oxygen functional groups on PC fibre surface after plasma treatments (determined from C1s band of XPS spectra).*

| Group | Plasma Ar 120 s | | Plasma $O_2$ 120 s | |
|---|---|---|---|---|
| | Binding energy, eV | at.% | Binding energy, eV | at.% |
| C–OH | 286.31 | 55.3 | 286.77 | 53.5 |
| C–O–C | 287.99 | 39.7 | 288.0 | 11.1 |
| C=O | 290.46 | 5.0 | 290.85 | 21.8 |
| COOR | – | 0 | 289.40 | 13.6 |

***Table 4*** presents the results obtained by analysis of the C1s band from XPS spectra for the nonwoven treated by Ar and $O_2$ plasmas. As one can see, the concentration of C–OH groups is similar in both cases, however, $O_2$ plasma treatment tends to form C=O groups at the expense of C–O–C groups created as a consequence of Ar plasma treatment.

Taking into account, however, the fact that $O_2$ plasma treatment does not improve the barrier properties of PC nonwovens against liquid aerosol particles (***Figure 4***), one can conclude that oxygen groups do not play a role in paraffin oil immobilisation on the PC fibre surface. On the other hand, in the case of $O_2$ plasma treatment, no changes in the fibre surface structure were observed, even with long-term exposures to plasma (***Figures 7.A*** and ***7.B*** see page 80). This clearly confirms that the nano-roughness of the fibre surface determines the filtration efficiency of the PC nonwovens.

In view of the fact that promising results consistent with the aim of this work were obtained with one-sided Ar plasma treatment, further improvement of the PC nonwoven's performance was tested with the use of double-sided Ar plasma treatment. The results presented in ***Figure 4*** confirm that double-sided Ar plasma treatment leads to more effective modification of the PC nonwoven samples, which is evidenced by a decrease in the paraffin oil mist penetration index

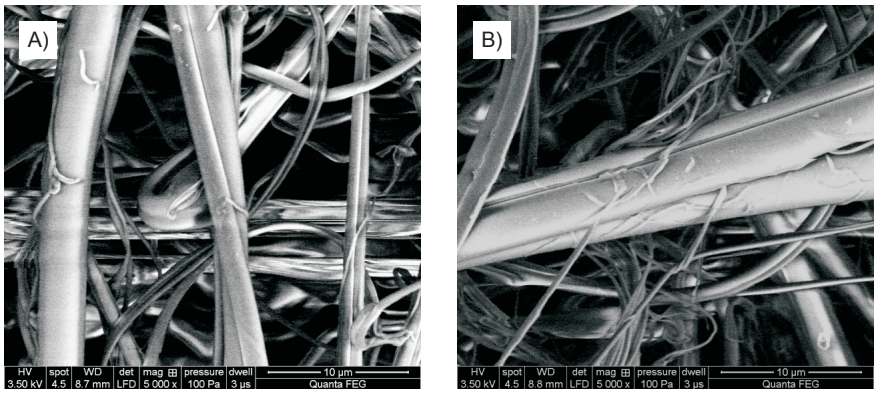


***Figure 7.*** *PC nonwoven after $O_2$ plasma treatment. Time of treatment: A) 30 s, B) 360 s.*

as compared with the nonwoven before plasma modification and those subjected to one-sided modification.

The air flow resistance values remained at similar levels irrespective of the plasma treatment type. The above results indicate that from the point of view of the construction of respiratory protective equipment, it is possible to maintain respiration comfort at the same level despite a significant improvement of protection efficiency using Ar plasma-treated PC nonwovens.

## Conclusions

It has been demonstrated that a considerable decrease in the paraffin oil mist penetration index can be attained by increasing the roughness of the PC fibre surface using Ar plasma treatment. In contrast, the formation of functional oxygen groups on the fibre surface is irrelevant in this case. The filtration effect of liquid aerosols can be enhanced by the use of double-sided Ar plasma treatment. It should also be emphasised that Ar plasma treatment does not change in practice the air flow resistance of PC nonwovens. The possibility of melt blown PC filtering nonwoven modification oriented towards improvement of their performance against liquid aerosol particles (reduction in the number of particles penetrating through the filtering nonwoven materials) by RF low-pressure cold plasma treatment in argon opens a new way for the application of this material for respiratory protective equipment.


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- *The XPS measurements were performed at Denis Diderot University - Paris 7 (CNRS, ITODYS). The authors would like to thank Professors M. Delamar and M.M. Chehimi for assistance in conducting this research.*


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