

Ludmila Černáková,  
R. Szabová,  
M. Wolfová,  
A. Buček<sup>1,2</sup>,  
M. Černák<sup>1,2</sup>

Institute of Polymer Material,  
Slovak University of Technology,  
Radlinského 9, Bratislava 812 37, Slovakia

<sup>1</sup> Department of Physical Electronics,  
Masaryk University,  
Kotlařská 2, Brno 611 37,  
Czech Republic

<sup>2</sup> Department of Experimental Physics,  
Comenius University,  
Mlynská dolina F2, Bratislava 842 48, Slovakia

# Surface Modification of Polypropylene Nonwoven after Plasma Activation at Atmospheric Pressure

## Abstract

*Polypropylene non-woven fabrics were activated by an atmospheric-pressure plasma treatment in ambient air using a novel plasma source. Subsequently, the plasma activated samples were coated by a nanostructured Fe<sub>2</sub>O<sub>3</sub> layer using surfactant-free water dispersion of Fe<sub>2</sub>O<sub>3</sub> nanostructured particles. The surface of the samples was characterised by scanning electron microscopy. The Fe<sub>2</sub>O<sub>3</sub> coating exhibited a remarkable wash resistance.*

**Key words:** polypropylene nonwovens, ambient air plasma, plasma activation, nano-powder immobilization.

of textiles were done at reduced pressures of 10<sup>-3</sup> - 10<sup>3</sup> Pa, where low-temperature plasma can easily be generated and brought into direct contact with the surfaces of fibres. However, the use of expensive vacuum systems that force batch processing has discouraged these applications, where on-line surface treatments of products with a low added value in large amounts are required [3, 4].

The surface treatment of textiles using atmospheric-pressure plasmas has the potential to replace costly and environmentally harmful conventional textile surface activation and finishing. Czech and Slovakian university teams have recently developed an innovative plasma source, the so-called Diffuse Coplanar Surface Barrier Discharge (DCSBD) [5 - 8], which has the potential to move a step closer to web finishing industry requirements. The idea is to generate a thin layer of plasma (of the order of 0.1 nm) with a high power density in the immediate vicinity of the treated surface and bring it into close contact with the treated fibre surfaces. Such a diffuse plasma layer is believed to provide substantial advantages in energy consumption, exposure time, and technical simplicity. Compared to other atmospheric-pressure plasma sources tested for textile treatment, DCSBD technology has the unique capability of generating diffuse "cold" plasma in ambient air, which eliminates the common need for expensive noble-gas containing a working-gas atmosphere. A narrow-web treater based on DCSBD technology is already commercially available for 21.5-cm wide fabrics and treatment speeds up to 50 m/min [8].

To exemplify the potential of our DCSBD atmospheric-pressure technique, the aim

of this work was to investigate the plasma activation of PPNW for subsequent immobilisation of Fe<sub>2</sub>O<sub>3</sub> nanopowders deposited from water dispersion without the use of surfactant. The preliminary results obtained using a small laboratory reactor confirm its potential to meet the required price and surface engineering requirements for this particular application.

## Experimental

### Diffuse Coplanar Surface Barrier Discharge

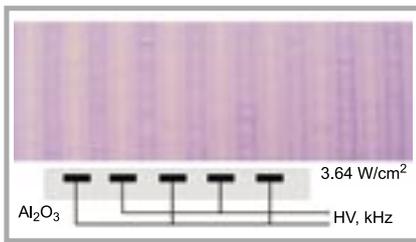
DCSBD is a type of dielectric barrier discharge generated on the surface of a dielectric barrier with embedded metallic electrodes. The primary feature that distinguishes DCSBD from the previous atmospheric-pressure coplanar barrier DBD studied in ambient air is its ability to create a thin layer of macroscopically uniform diffuse plasma due to the special design and optimisation of the electrode geometry.

DCSBD electrodes, consisting of 15 pairs of silver strip electrodes, were embedded 0.5 mm below the surface of 96% Al<sub>2</sub>O<sub>3</sub> ceramics. The electrodes were energised by 14 kHz sinusoidal voltage, supplied by a LIFETECH VF 700 HV generator. The mutual distance of the 220 mm long and 2 mm wide silver strip electrodes was 0.5 mm.

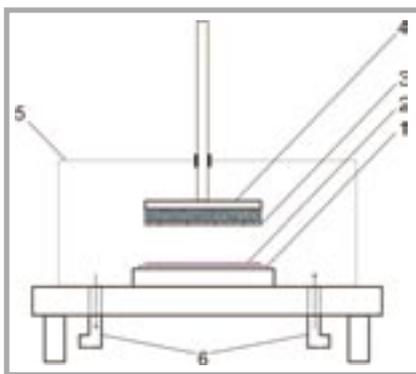
A schematic diagram of the discharge electrode system cross-section is shown in Figure 1 together with the space distribution of the light intensity emitted by the discharge in ambient air. A detailed description of the DCSBD electrode design is found in [5]. As illustrated in Figure 1, at a certain discharge electrode

## Introduction

Over the past two decades, the plasma surface treatment techniques of textile materials have been extensively reported in open as well as patent literature. Apparently, the most significant advantage of the non-thermal plasma surface treatments is that they are usually fast and affects about 10 nanometers of the outermost surface layer. Accordingly, using plasma surface activation, the surface functionalities and characteristics can conveniently be tailored on a nanometer scale. In a similar fashion, more exotic processes such as plasma grafting and plasma-assisted nanopowder coatings can produce totally new custom surfaces without loss of the desirable characteristics of the bulk polymer material [1, 2]. The aim of the plasma treatment of textiles has been, for example, to improve wettability, printability, adhesive properties at coating and lamination, mechanical and electrical properties, bioactivity, etc. The vast majority of plasma treatments



**Figure 1.** Schematics of the discharge electrode system cross-section. Visual appearance of the discharge in ambient air taken at a peak-to-peak gap voltage of 14 kV and frequency of 10 kHz from a view perpendicular to the electrode system surface, which is shown above the electrode system cross-section.



**Figure 2.** Laboratory DCSBD reactor: 1-DCSBD electrode system, 2-plasma layer, 4-treated fabric, 4 – sample holder coated by polyurethane foam, 5 – plexyglass reactor chamber, 6 – gas inlet.

arrangement it is possible to generate visually diffuse atmospheric-pressure plasma in ambient air without the use of helium. The planar electrode system was mounted inside a closed reactor chamber as illustrated in Figure 2.

#### Plasma activation and post-plasma immobilisation of Fe<sub>2</sub>O<sub>3</sub> nanopowder

An industrial spun-bounded polypropylene nonwoven (PPNW) fabric (50 g/m<sup>2</sup>, 272 ± 22 μm thick, an average fibre diameter of 26 ± 0.2 μm, an average pore diameter of 37 μm) supplied by PEGAS Company (Czech Republic), was used in the experiments.

The plasma activation was undertaken in ambient air atmosphere using the following procedure: A DCSBD discharge with a surface power density of 3.64 W/cm<sup>2</sup> was ignited, and after stabilisation of the discharge current (approximately 3s), the PPNW sample was brought into contact with the DCSBD electrode system surface using a sample carrier coated by a porous polyurethane foam layer. Treatment time was measured as the contact

time of the sample with the plasma using an electronic stopwatch. To ensure activation homogeneity the same plasma treatment was repeated for the other side of the fabric.

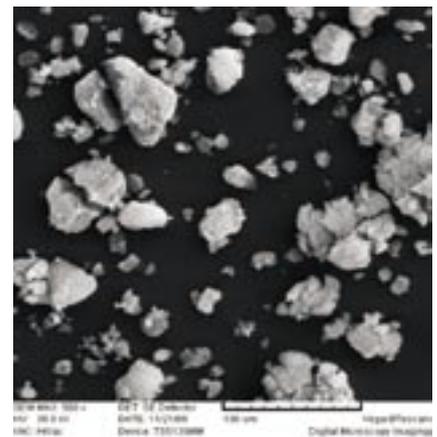
As a measure of the successful activation and hydrophilicity of the inner fiber surfaces of the treated nonwoven, the strike-through time of the test liquid was measured using a standard ETR 150.3-96 method. The tested sample was placed on the top of five layers of filter paper (ERT FF3 strike through/wetback filter paper supplied by Hollongsworth & Vose Ltd.) and weighted by a strike-through plate. Subsequently, the cylindrical hole in the strike-through plate was filled with a 5 ml water solution of NaCl (9 g/l) with a surface tension of 70.2 mN/m. The time required for permeating the liquid through the nonwoven fabric to the filter paper was measured with an accuracy of 0.05 s.

Based on our previous results for the air and nitrogen plasma activation of PPNW [1, 5 - 7], the samples were activated for 5 s on both sides. This was found to be the shortest plasma exposure time for making the samples hydrophilic with a strike time of 4.8 ± 0.4 s. and, consequently, made wettable by the nanopowder water dispersion immediately after the plasma activation.

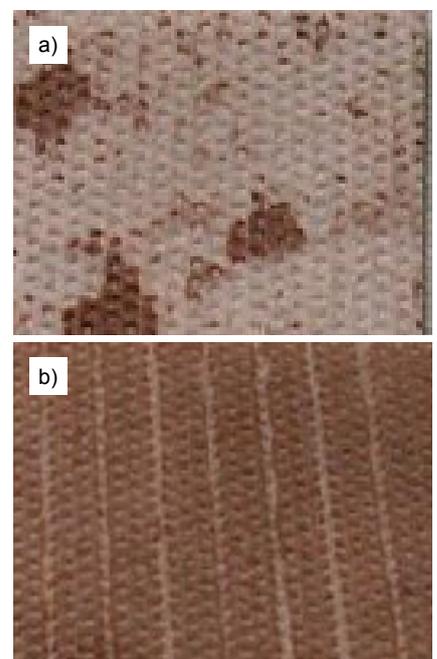
Nanoparticles of Fe<sub>2</sub>O<sub>3</sub> prepared using thermally induced solid-state synthesis [9, 10] at the University of Olomouc, Czech Republic were used in the experiment. As illustrated by the SEM image in Figure 3, the as-received nanoparticles created nanostructured aggregates of micrometer size.

To demonstrate the deposition of Fe<sub>2</sub>O<sub>3</sub> nanostructured particles onto the plasma-activated PPNW fibre surfaces without the use of surfactant or organic solvents, 1 g of the aggregated nanoparticles was mixed with 1 l of distilled water and subjected to a 30 min sonication in ultrasound bath. The plasma activated and nonactivated PPNW samples were dipped into the sonicated dispersion for 10 seconds, taken out and air dried for 24 hours. Finally, the samples were washed in distilled water in ultrasound for 30 min. and dried again. All processes were performed at room temperature.

Figure 4 compares the visual appearance of the samples prepared by the above

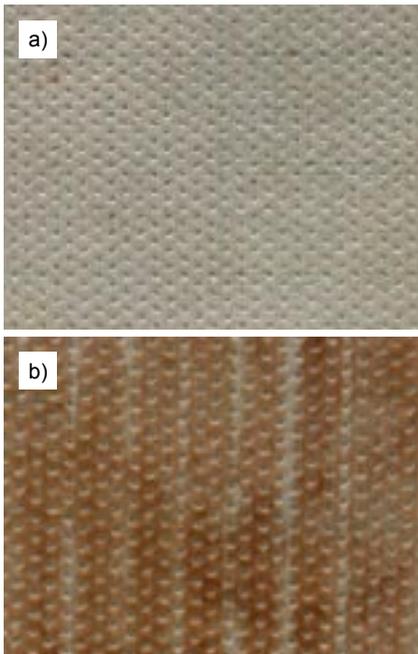


**Figure 3.** SEM image of the as-received aggregates of nanostructured Fe<sub>2</sub>O<sub>3</sub> particles.

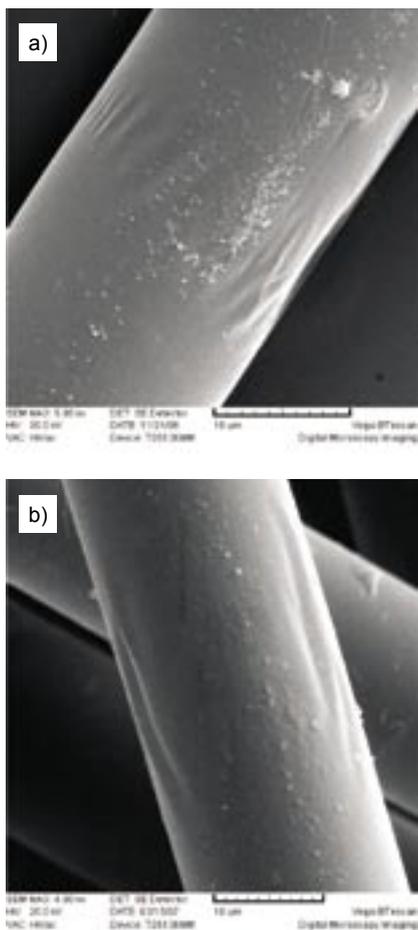


**Figure 4.** Comparison of the virgin (a) and ambient-air plasma activated PPNW samples (b) after the Fe<sub>2</sub>O<sub>3</sub> particle coating.

procedure using the plasma activated and nonactivated samples. It can be seen that the plasma-activated hydrophilic PPNW was coated quite uniformly by a Fe<sub>2</sub>O<sub>3</sub> layer with a strip pattern that follows the strip electrode structure. This is in contrast to the practically uncoated samples prepared without plasma activation, as shown in the same figure. When the sample was subjected to washing, a major part of the nanopowder coating was washed off. Nevertheless, a part of the immobilised Fe<sub>2</sub>O<sub>3</sub> exhibited good stability and was not easily washed off or removed by mechanical forces. This is illustrated in Figure 5, which compares a virgin PPNW sample with the plasma-activated sample coated by Fe<sub>2</sub>O<sub>3</sub> layer,



**Figure 5.** Comparison of the virgin PPNW sample (a) with the plasma-activated sample (b), both coated by  $\text{Fe}_2\text{O}_3$  layer and subsequently subjected to washing.



**Figure 6.** SEM images of the plasma-activated samples coated by iron oxide from water dispersion (a) and the plasma-activated sample coated by iron oxide from water dispersion (b) under sonication in ultrasound.

and subsequently subjected to a washing cycle. Figure 6 shows an SEM image of the sample after a washing cycle. It can be seen that  $\text{Fe}_2\text{O}_3$  particles were attached to the fibre surface as micrometer-size aggregates rather than nanoparticles. This is apparently due to their insufficient dispersion in water without the use of surfactants.

## Summary

The practical use of PPNW fabrics with immobilised nanoparticles is still at an early stage. However, the promising results obtained from the studies made so far indicate that such materials have potential for, e.g., permanent hydrophilisation [1], electric conductivity [11], and antimicrobial properties [12].  $\text{Fe}_2\text{O}_3$  particles of immobilised PPNW exhibit interesting and useful magnetic properties [13].

In this work we have presented some preliminary experiments of the immobilisation of  $\text{Fe}_2\text{O}_3$  nanostructures particles onto plasma activated PPNW. A lot of work still has to be done, for example, with regard to the nanoparticle dispersion process. Nevertheless, the results obtained indicate that simple and low-cost DCSBD ambient air plasma activation makes possible a wash-resistant immobilisation of  $\text{Fe}_2\text{O}_3$  particles onto a plasma activated PPNW fabric. Plasma activation improves wettability, and it is not necessary to treat the PPNW with a surfactant. This is of significant practical importance since it is known that the surfactants usually used tend to adversely affect nanoparticle adhesion as surfactants migrate to the interfaces and interfere with the microscopic intimate contact between the nanoparticles and polymer surfaces. As a consequence, surfactants tend to negatively affect the water sensitivity of immobilised nanoparticles.

## Conclusion

It is believed that the simple and cost-effective DCSBD activation technique described in this article can be used for the coating of PPNW, using a wide spectrum of nanoparticles, which will be the goal of our future research.

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## References

1. Cernakova L., Kovacic D., Zahoranova A., Cernak M., Mazur M.; *Plasma Chemistry and Plasma Processing*, Vol. 25(2005) pp. 427-437.
2. Ponomarenko E. A., Carter J. D., Cramer R. D., Schmidt M.: "Disposable absorbent article comprising a durable hydrophilic topsheet" US Patent Appl. 20040158214 (August 12, 2004).
3. "Plasma technologies for textiles" Edited by R Shishoo, Woodhead Publishing Limited, 2007.
4. Roth J. R.: *Industrial Plasma Engineering Vol II "Applications to Non-Thermal Plasma Processing"*. Institute of Physics Publishing 2001, Bristol and Philadelphia.
5. Šimor M., Ráhel J., Vojtek P., Brablec A., Černák M.: "Atmospheric-pressure diffuse coplanar surface discharge for surface treatments" *Appl. Phys. Lett.* Vol. 81(2002) pp. 2716-2718.
6. Černák M.: "Method and apparatus for treatment of textile materials", US Patent Appl. No. 2004/0194223.
7. Šimor, M. et al: *Generation of thin surface plasma layers for atmospheric-pressure surface treatments*, *Contributions to Plasma Physics* Vol. 44(2004) No. 5-6, pp. 492-495
8. <http://gimmel.ip.fmph.uniba.sk/treaters/>
9. Zboril R., Mashlan M., Petridis D.: *Iron(III) Oxides from Thermal Processes-Synthesis, Structural and Magnetic Properties, Mössbauer Spectroscopy Characterization, and Applications*, *Chem.Mater.* Vol. 14(2002) pp. 969-982.
10. Zboril R., Mashlan M., Barcova K., Vujtek M.: *Thermally induced solid-state syntheses of g- $\text{Fe}_2\text{O}_3$  nanoparticles and their transformation to a- $\text{Fe}_2\text{O}_3$  via e- $\text{Fe}_2\text{O}_3$* , *Hyperfine Interact.* Vol. 139(2002) pp. 597-606.
11. Avloni J.: "Electroconductive woven and non-woven fabric and method of manufacturing thereof" US Patent Appl. 20070054577 (March 8, 2007).
12. Sayre C. N., Feaster R. S., Villanueva J.: "Nonwoven webs containing bacteriostatic compositions and methods of making the same" US Patent Appl. 20070141934 (June 21, 2007).
13. "Roadmap Report Concerning the Use of Nanomaterials in the Automotive Sector" [http://www.nanoroad.net/download/roadmap\\_ai.pdf](http://www.nanoroad.net/download/roadmap_ai.pdf)



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