

Plasma treatment of textile fibers*

Hartwig Höcker

*Deutsches Wollforschungsinstitut an der RWTH Aachen e.V., Veltmanplatz 8,
D-52062 Aachen, Germany*

Abstract: Low-temperature plasma technology—both glow discharge under reduced pressure as well as barrier discharge under normal pressure—are well established in different industrial applications. Since recently, however, the plasma technology is being introduced in textile industry as well. Fields of application are desizing, functionalizing, and design of surface properties of textile fibers. Plasma technology is suitable to modify the chemical structure as well as the topography of the surface of the material.

Examples of natural as well as man-made fibers prove the enormous potential of plasma treatment of textile materials. It has proven to be successful in shrink-resist treatment of wool with a simultaneously positive effect on the dyeing and printing.

Not only the chemical structure of the surface is modified using different plasma gases but also the topography of the surface. A highly hydrophobic surface with a particular surface topography in contact with water is extremely dust- and dirt-repellent and hence should be also repellent to bacteria and fungi.

Man-made fibers to be used under chemical stress are modified with diffusion-barrier layers on their surfaces without modifying the bulk properties; hence, the stability of those fibers is significantly improved.

INTRODUCTION

The general reactions to be achieved by plasma treatment are the oxidation of the surface of a material, the generation of radicals, and the edging of the surface; when using special gases a plasma-induced deposition polymerization may occur.

For the treatment of textiles this means that hydrophilization as well as hydrophobization may be achieved; moreover, both the surface chemistry and the surface topography may be influenced to result in improved adhesion or repellency properties as well as in the confinement of functional groups to the surface.

Plasma treatment has to be controlled carefully to avoid detrimental action of the plasma onto the substrate.

PLASMA TREATMENT OF WOOL TO ACHIEVE SHRINK-RESISTANCE

The morphology of wool is highly complex; this is not confined to the fiber stem but extends to the surface as well. Cuticle cells are overlapping each other to create a directional frictional coefficient. Moreover, the very surface is highly hydrophobic. As a consequence, in aqueous medium, because of the hydrophobic effect, fibers aggregate and, under mechanical action, exclusively move to their root end. This is the reason for felting and shrinkage. Plasma treatment of wool has a two-fold effect on the

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surface. First, the hydrophobic lipid layer on the very surface is oxidized and partially removed; this applies both to the adhering external lipids as well as to the covalently bound 18-methyl-eicosanoic acid (Fig. 1).

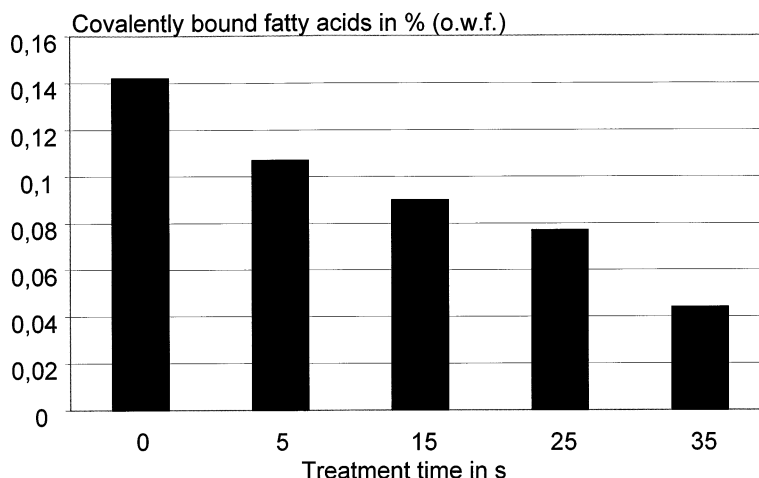


Fig. 1 Amount of covalently bound surface lipids in dependence on the treatment time in barrier discharges detected after isolation by transesterification and subsequent weight determination.

Since the exocuticle, that is, the layer below the fatty acid layer of the very surface (epicuticle), is highly cross-linked via disulfide bridges plasma treatment has a strong effect on oxidizing the disulfide bonds and reducing the cross-link density [1].

As the plasma treatment is surface-oriented the protein loss after treatment and extraction is very low (0.05 % o.w.f. for severe treatment). On the other hand, the specific surface area is significantly increased during plasma treatment from about $0.1 \text{ m}^2/\text{g}$ to ca. $0.35 \text{ m}^2/\text{g}$, which is clearly demonstrated by means of atomic force microscopy. Again, due to the surface-directed activity of the plasma, the tenacity of the fibers is hardly influenced.

As the surface is oxidized, the hydrophobic character is changed to become increasingly hydrophilic.

The chemical and physical surface modification results in decreased shrinkage behaviour of wool top; the felting density of wool top (before spinning) decreases from more than 0.2 g/cm^3 to less than 0.1 g/cm^3 .

With respect to shrink-resist treatment, this effect is too small as compared with the state-of-the-art treatment of wool top with acid aqueous chlorine solution, reduction with sulfite, and application of a thin resin (polyaminoamide) layer to the surface (Chlorine/Hercosett process). Therefore, an additional resin coverage of the fiber surface is required. This leads to a smooth surface with reduced scale height (Fig. 2) and an area shrinkage after 50 simulated washing cycles in a domestic washing machine (TM 31) in the range of the state of the art result, i.e., a little more than 1 % (Table 1). A top-treating, barrier-discharge machine on a pilot plant scale is running in industry to provide sufficient amounts of material to follow the textile chain.

It should be mentioned that the plasma treatment brings additional advantages, in particular, increasing dyeing kinetics, an enhanced depth of shade, and an improved bath exhaustion [2–5].

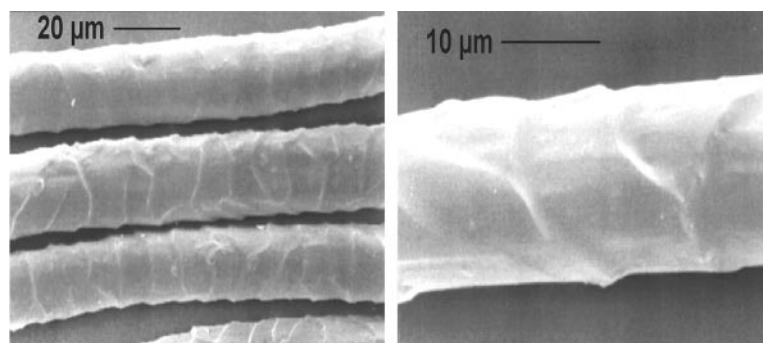


Fig. 2 SEM pictures of plasma-treated wool after resin application.

Table 1 Influence of the pretreatment on the area felting shrinkage of knitted fabrics after 50 simulated washing cycles in a domestic washing machine (TM 31).

Treatment	Area felting shrinkage (%)
Untreated	69
Plasma-treated	21
Plasma/resin-treated	1.3
Chlorine/Hercosett-treated	1

TREATMENT OF COTTON WITH DIFFERENT KINDS OF PLASMA GASES

As in the case of wool, the specific surface area of cotton after oxygen plasma treatment is increased. On the other hand, the treatment with a hexamethyldisiloxane (HMDSO) plasma leads to a smooth surface with increased contact angle of water (sessile drop method) up to a maximum of 130° . Thus, a strong effect of hydrophobization is achieved. Similarly, when a hexafluoroethane plasma is used instead of an HMDSO plasma the surface composition of the fibers clearly indicates the presence of fluorine and the material becomes highly hydrophobic. Still, the water vapor transmission is not influenced by the hydrophobization.

Hydrophobization in conjunction with increased specific surface area results in an effect generally known as Lotus effect: dirt particles are easily removed from the surface by water droplets (Fig. 3).

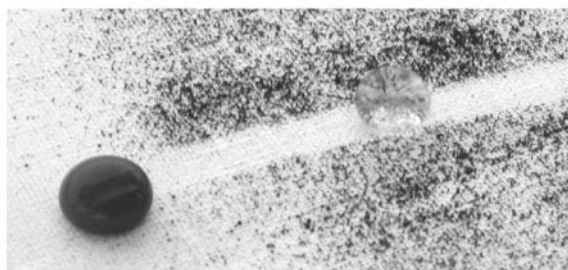


Fig. 3 Water drop-induced dye removal from an HMDSO-plasma-treated cotton fabric.

PLASMA TREATMENT OF SYNTHETIC FIBERS

The barrier discharge or corona treatment of polypropylene significantly increases the hydrophilicity of the surface, the contact angle of water being decreased from 90° to 55°. Even after two weeks a sustained effect is observed, the contact angle of water being 60°. Instead of the contact angle of water, the oxygen/carbon ratio of the atomic composition of the surface can be used to follow the influence of a plasma treatment, in particular for polypropylene fleeces with layered-structure. The oxygen/carbon ratio for the first layer is highest; but even at the tenth layer a significant effect is observed.

The uptake of oxygen at a polypropylene surface is even more significantly demonstrated when maleic acid anhydride (MAH) is used as an assisting reagent. The incorporation of oxygen is permanent and a contact angle with water of 42° can be achieved (Fig. 4).

When polyethyleneterephthalate (PET) fibers are used as an enforcing material for a polyethylene (PE) matrix, the hydrophobization of the PET fibers using an ethylene plasma is quite impressive since the adhesion strength can be increased from 1 to 2.5 N/mm. The fracture morphology of these composite materials clearly shows the tight adhesion of the matrix to the fiber (Fig. 5).

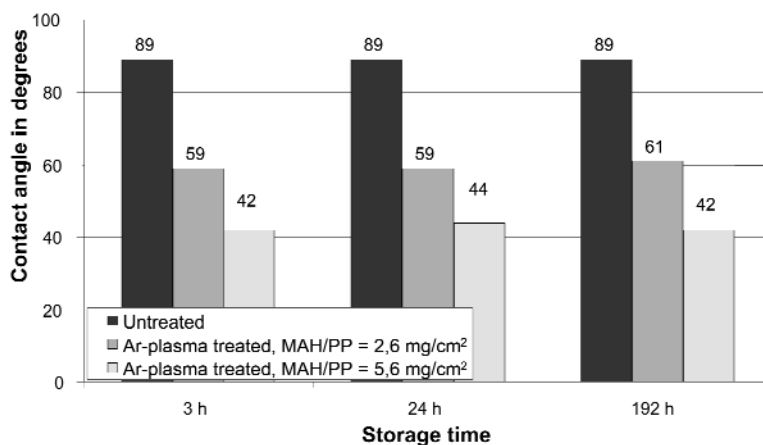


Fig. 4 Permanent hydrophilization of PP by plasma-induced grafting of MAH.

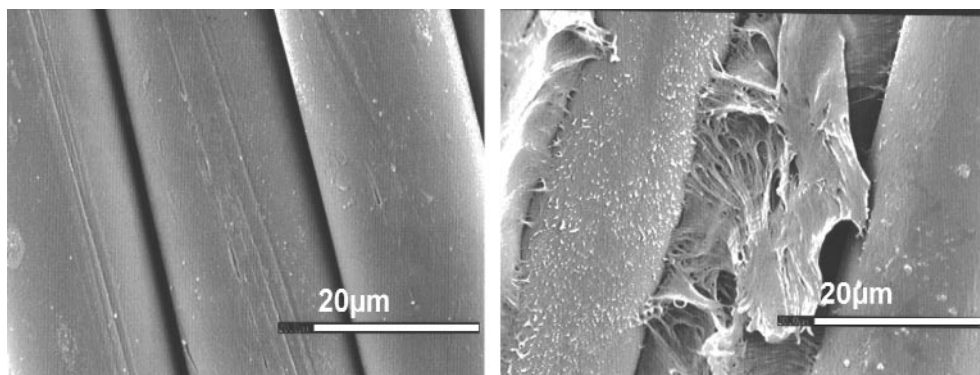


Fig. 5 Fracture morphology of PET/PE-composites prepared from untreated and C₂H₄-plasma-treated PET-fibers after application of the 180° peeling test (ASTM D903).

Polyaramid fibers such as Nomex[®] fibers are considered to be high-performance fibers; unfortunately, they are prone to hydrolysis. Thus, the application of a diffusion barrier to the surface should reduce the tendency to hydrolyze in respective media. A hexafluoroethane/hydrogen plasma is highly suitable to apply such a diffusion-barrier layer to the surface. The resistance to 85 % H₂SO₄ (20 h at room temperature) leaves the fibers completely intact while conventional fluorocarbon finishing under the given conditions produces significant shrinkage of the fibers in combination with loss of properties (Fig. 6).

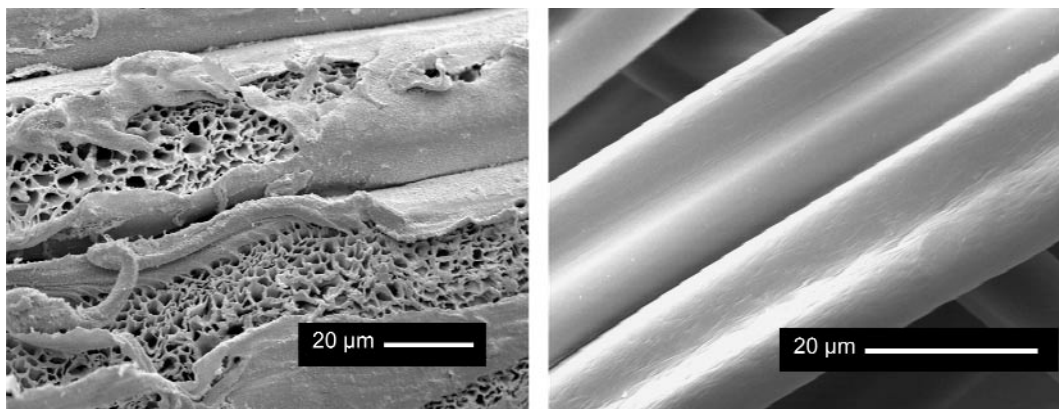


Fig. 6 SEM pictures of Nomex-fibers after exposition in diluted H₂SO₄.

CONCLUSIONS

The present examples show that plasma technology performed under atmospheric pressure or under reduced pressure (depending on the special needs) leads to a variety of processes to modify fiber or textile materials to fulfil additional highly desirable requirements. It is to be expected that this technology, which has been known for a long time and is being used in different branches of industry, in the near future will conquer textile industry as well.

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