Nanoscale Silver Coatings on Polymer Fibers

M. Amberg*, E. Körner*, D. Hegemann* and M. Heuberger*

*Empa, Swiss Laboratories for Materials Testing and Research, *Advanced* **Fibers**
CH-9014 St. Gallen, Switzerland, manfred.heuberger@empa.ch

ABSTRACT

The low pressure plasma coating technology offers new possibilities when applied to fibers or textile fabrics. Two important strengths of plasma coatings are i) typically less than 200nm coating thickness, which does not affect the fiber mechanical properties, and, ii) the availability of a wide spectrum of different coating materials and morphologies.

This paper presents two different examples of plasma coatings, both are silver containing; we report some of their properties and sketch the respective application windows. The first coating is a homogeneous plasma silver metallization while the second example is a highly cross-linked plasma polymer containing variable amounts of silver nano particles.

Keywords: fibers, plasma, metallization, polymerization, nano-composite

1 PLASMA COATING OF FIBERS AND FABRICS

Nanometer thick metal coatings are widely used on different polymer substrates like foils; e.g. for anti-statics, optical effects, diffusion barriers and more [1]. The physical and chemical properties of such plain coatings are well understood.

We investigate the characteristics and properties of nanometer metal films and metal nano particle containing coatings on fibers and textiles. Fibers present a special geometrical challenge to the coating process, particularly if the process is a directed one [2]. For the same reason it is also difficult to reach shadowed areas of fiber material in a woven fabric.

A convenient way to produce homogeneous nanometer coatings on fibers and textiles is using a low-pressure plasma deposition [3]. In this type of plasma one ionizes a gas of selected chemical composition in an alternating electric field (i.e. RF or microwave). A reduced pressure in the process reactor is used to insure a useful diffusion length of the chemical radicals and control the extension of the plasma zone. The substrate temperature is moderately raised to 50-60°C, which represents a mild condition; thus not deteriorating the fiber mechanical properties.

Plasma coating reactors come in various shapes and geometries to accommodate different types of substrates. The here used reactors are of two types i) batch processing fabric stripes, or, ii) endless fiber or yarn coater, which delivers the substrate fiber from air to air via an orifice and a differential pumping configuration. Fig1 below shows the example of the cylindrical plasma zone inside an endless fiber coater.

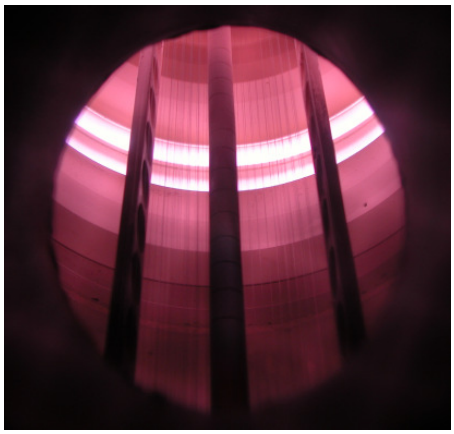

Fig1: Snapshot of synthetic fibers passing through a low-pressure plasma zone. A cylindrical target allows a homogeneous coating of the fibers.

The plasma deposition rates are limited to a typical range of 1-100nm per minute. Therefore, plasma coatings are well suited to produce thin coatings in a range 10-200nm. In order to increase the dwell time of the fiber inside the plasma zone, one can use configurations with multiple passes. The example shown in Fig1 provides a maximum of 64 passes.

It is important to note that the nanometer thickness of such coatings ensures that the "textile character" of a fiber or fabric remains intact. This is an important asset for the subsequent textile processing (e.g. weaving, stitching…) and also for the haptics of the final textile.

We present two different types of plasma processes to produce silver containing coatings on fibers. These are i) plasma sputter process to produce homogeneous metal films and ii) a combination of plasma sputter process with a plasma polymerization process to produce a cross linked polymer layer containing silver nano-particles (i.e. Ag nano-composite).

2 HOMOGENEOUS SILVER COATINGS

At a plasma base pressure of nominally 1Pa we introduced argon, which is ionized by irradiation of RF. The silver material is present inside the plasma reactor in form of a so-called silver target – a several mm thick plate of silver with magnets mounted in such a way that the ions are accelerated in circular trajectories towards the target surface (i.e. magnetron), where they sputter silver atoms and clusters into the adjacent space.

When a fiber is passed through the plasma zone a condensation of the metal clusters on the substrate surface takes place. There is a finite surface mobility of silver atoms on the fiber surface. A continuous rotation of the fiber along its axis is however needed to achieve a homogeneous metal coating all around, as the one shown in Fig2 below.

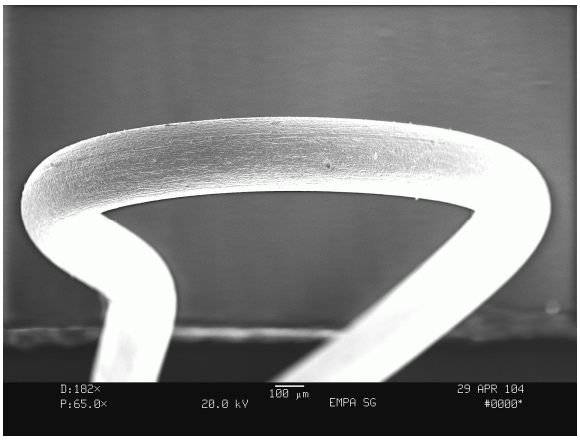

Fig2: SEM image of a polyester monofilament (PES 150f1) coated with a highly flexible, homogeneous silver coating of 250nm thickness.

It is important to note that the smoothness of such thin metal coating is directly dependent on the quality of surface cleaning prior to the silver deposition. An argon/oxygen plasma zone at the entrance of the plasma reactor is used to remove residual surface contaminations. A prominent source of fiber surface contamination stems from processing oils (~0.1 wt%) of so-called "avivage" or "appreture". These substances often contain a number of components that are used for fiber lubrication and anti-statics during and after the melt-spinning process [2].

The same plasma sputtering process can also be applied to a multifilament fiber or yarn. Again, a homogeneous coating can be achieved via spreading and long-axis rotation of individual filaments in the plasma zone. Fig3 below shows an example of a polyester multifilament fiber processed in a silver plasma sputtering process. The silver quantity (per length) is now distributed over a larger surface area, thus reducing the nominal film thickness by a factor of roughly 5x over the monofilament equivalent.

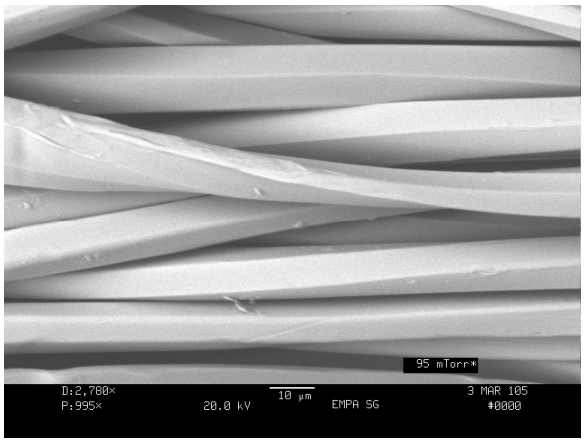

Fig3: SEM image of a polyester multifilament (PES 150f48) coated with a highly flexible, homogeneous silver coating of nominally 50nm thickness.

The electrical conductivity of such silver-coated fibers was investigated as a function of the silver quantity (per length) [4]. It was found that plasma metalized fibers can reliably cover a wide range of different conductivities and possible applications starting from EM-shielding or power supply (Z<1Ω/cm) to signal conduction (Z<100 Ω / cm), and anti-static applications (Z<10^8 Ω / cm). A comparision with the electrical properties of bulk silver is illustrative. Fig4 depicts how the specific resistance of silver coated fibers varies with the deposited amount of silver per unit length. For convenience, results are related to the theoretical limit (dotted line) of a silver wire with the same Ag quantity per length.

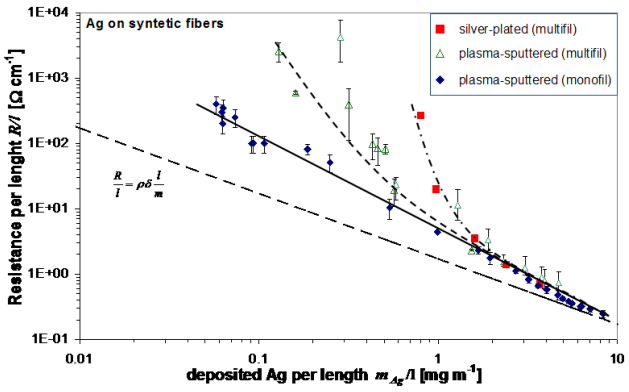

Fig4: Resistance of silver coated fibers versus the amount of silver deposited. The dashed line corresponds to the theoretical minimum, which would be reached for a film of ideal morphology (i.e. no defects).

All silver coated fibers have a resistance exceeding the theoretical minimum, which is indicative of small defects in the film. We note that at higher silver thickness these defects play a vanishingly smaller role, as expected. Furthermore, the monofilament outperforms the multifilament at lower silver quantities – again this is because defects play a more important role at the 5x smaller film thickness on the multifilament. For comparison, we have also plotted the resistivity of conventional electrochemically plated silver fibers that exhibit a much rougher silver film due to the different deposition technique [5]. At lower silver quantities, the plated silver fibers have therefore a comparably higher specific resistivity.

3 NANO-COMPOSITE SILVER/POLYMER COATINGS

A second type of silver containing plasma coating can be realized by the introduction of carbon containing monomer gases (e.g. ethylene) into the plasma chamber during the argon plasma sputtering process [6,7]. The pressure inside the reactor is thus raised to 10Pa. In order to accelerate argon ions towards the target under these conditions, an asymmetric electrode setup can be used as shown in Fig5 [8]. The different sizes of the electrodes effectively produces a dynamically induced DC bias voltage between the electrodes that is used to accelerate the ions towards the metal target. Simultaneously, the monomers fed into the reactor will be ionized and the produced hence chemical radicals in the plasma zone will deposit onto any substrate to form a highly cross-linked polymer coating. The Ag clusters that are simultaneously condensing on the substrate form silver nano particles according to the growth mode that is dictated by the local conditions (i.e. interfacial energies and surface diffusion kinetics).

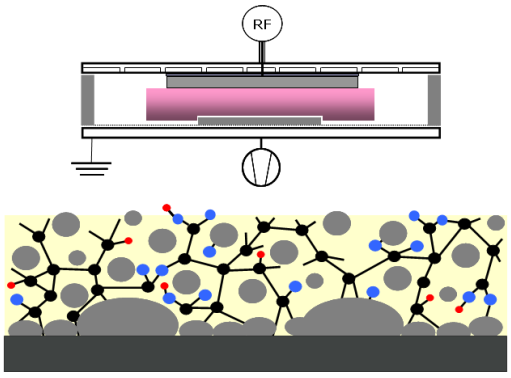

Fig5: An asymmetric plasma reactor setup can be used to simultaneously sputter silver metal and deposit a highly cross-linked polymer matrix. The growth mechanism of the silver nano-particles is governed by interface energetics and surface diffusion.

The number and size distribution of the thus produced nano-particles can be controlled by plasma input power and gas composition. It is to note that the silver contained in these coatings can be made in a highly oxidized form, exhibiting a very large specific surface area. These combined properties are responsible for a bust-like release of silver I ions from such coatings when exposed to an aqueous environment. As shown in Fig6 below, a fast initial silver ion release is a unique characteristic for this form of nano-composite.

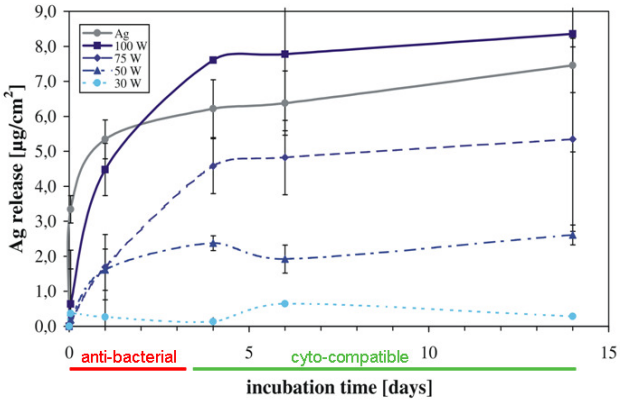

Fig6: The silver ion release kinetics of Ag nano-composite coatings depends on the size distribution of the silver nano-particles, their oxidation state as well as the water and proton conductivity of the polymer host matrix.

Furthermore, we have carried out bacterial colonialization tests with such surfaces that revealed a strong antibacterial effect for the first 24 hours. Once the silver containing supernatant was exchanged against fresh solution, it was found that these surfaces provide the grounds for cells to proliferate. The cell compatibility of these nano-composites was further enhanced by introducing nitrogen containing monomers into the plasma reactor, which led to the formation of amines and amides in the cross-linked polymer substrate. Such nitrogen rich coatings were found to promote cell growth comparable to a typical cell growth substrate [9].

4 DICUSSION AND CONCLUSIONS

We have presented two examples of silver containing nano-coatings on fibers and fabrics. These coatings are produced using the low-pressure plasma technology that allows control over chemistry and morphology of the coatings in ways that are hardly possible with other methods.

The example of homogeneous silver coatings has demonstrated that it is possible to coat literally any fiber

material with a flexible, well-adherent metal film. We have undertaken a number of chemical and mechanical tests with the coated fibers and fabrics to assure a high electro-mechanical quality. In addition to the electrical characterization mentioned in this paper we have also performed extensive tests for wash fastness and sweat fastness of these homogeneous silver coatings – in view of possible application of such fibers in wearable electronics. Future developments on the basis of the here presented fiber will include smart additional layers to add better chemical inertness or functional electronic coatings (e.g. insulation, organic semiconductors, sensors, and also multiple electrodes on a single fiber).

The silver nano-composite layers are now further explored as tunable antibacterial coatings on (textile) implants. Particularly the fact that we are able to install an application window with an initial anti-microbial burst, followed by a surface exhibiting cyto-compatible conditions is an interesting way to approach the common problem of post-implantation infection, which causes a significant amount of cost and patient discomfort.

REFERENCES

[1] J. Reece Roth, Industrial Plasma Engineering, Vol. **2**, IOP, Bristol, 2001, p451.

[2] M. Amberg et al, J. Adhesion Sci Technol, **24** 123-134, (2010).

[3] Plasma technologies for textiles, ed. R. Shishoo, Woodhead, Cambridge, (2007).

[4] M. Amberg et al., Plasma Process. Polym, **5**, 874-880, (2008).

[5] D. Hegemann et al., Mater. Technol., **24**, 41-45 (2009).

[6] H. Biederman et al., Pure Appl. Chem., **60**, 607-618 (1988).

[7] D. Hegemann et al., Progr. Organic Coat., **58**, 237-240 (2007).

[8] E. Körner et al., Plasma Process. Polym., **6**, 119-125 (2009).

[9] S. Lischer et al, Biomaterials, **submitted**, (2010).