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IN SITU DEPOSITION OF SILVER MICRO AND NANO PARTICLES ON POLYESTER FIBERS BY AQUEOUS IMPREGNATION

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ABSTRACT

The economical and technically simple impregnation process of aqueous solutions under different conditions of concentration, temperature and pressure was tested in this study for the In situ deposition of silver micro and nano particles on polyester fibers, commercial samples of polyester fiber were characterized by means of optical and electron transmission microscopy and X-Ray diffraction.

Keywords: silver particles, textile fibers, impregnation.

INTRODUCTION

Lately there has been a great interest into depositing micro and nano particles on textile material; it is estimated that 65% of the world's synthetic fibers production is used by the textile industry, approximately 70% of them are made from polyester. There have been several reports about the xxxx properties of silver containing textile fibers; silver has been extensively used due to its wide range of antibacterial activity while exhibiting low biological toxicity (Galeano *et al*., 2003; Gaonkar *et al*., 2003; Thomas and McCubbin, 2003). There are reports that exposure to silver nanoparticles over a long time are toxic to zebra fish, clams and rats. For example a high level of silver in the water of the San Francisco Bay led to the sterility of "macoma balthica" clams during the 1980`s (Marambio-Jones and Hoek, 2010).

On the other hand ionic silver is suitable for treating wounds by cleaning the tissue from bacteria like escherichia coli, staphylococcus aureus, klebsiella mobilis, klebsiella pneumonia and fungi like aspergillus niger, candida albicans, saccharomyces cerevisiae, trichophyton mentagrophytes and penicillium citrinum (Marambio-Jones and Hoek, 2010).

In contrast there is lack available information about the physical properties of the textile containing silver particles. Retrieving this information can lead to new applications of silver micro and nano particles on textiles. Some literature reports that the color of the textile has changed over a certain amount of time (Marambio-Jones and Hoek, 2010). The physical properties of silver indicate what could be achieved by the compound. Silver is an electrical and thermal conductor so it may be possible to transfer heat or electrical charges.

Several procedures has been proposed to deposit silver micro and nano particle on textile fibers; silver colloidal solution is widely use, but requires expensive reactants, other procedures could be cumbersome to applied at industrial scale as sonochemical deposition, inert gas condensation or inner gas co-condensation techniques (Durán *et al*., 2007; Perelshtein *et al*., 2008; Zhang *et al*., 2009). One of the most common approach to deposit micro and nano particles to fabrics is the Pad-dry procedure; where the textile is immersed in aqueous dispersions containing the source of the material to deposit and afterwards pressure is applied in order to define the amount of dispersion on the textile (Jeong *et al*., 2005; Ki *et al*., 2007). The economical and technically simple impregnation process of aqueous solutions under different conditions of concentration, temperature and pressure was tested in this study.

EXPERIMENTAL

Fiber characterization

The morphological characteristics of the polyester fiber were determinate by optical microscopy (Olympus BX41 with the camera Infinity 1 coupled with the Infinity software by Lumenera. In addition a freeware called J Micro Vision v 1.27 was used for further measuring) and scanning electron microscopy (SEM, JEOL NeoScope JCM-5000). Figure-1 shows an optical microscope photograph of the polyester fibers, the measurements indicate a fiber thickness of 9.7 micron for the polyester fiber; optical microscopic images were calibrated using a Neubauer grid.

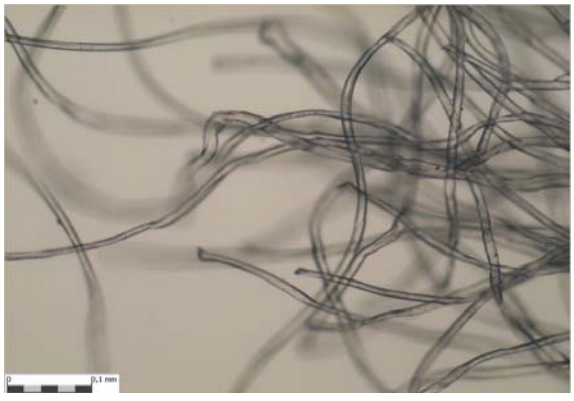

Figure-1. Optical microscopic image of polyester fiber.

Following, the textile properties were determined. While burning a sample of the textile it was degrading very fast and sooting heavily. The fabric was melting and after a short while a flame appeared. Determining the right size of the textile samples for further research was important. The shape and size of the following process has to be kept in mind while finding the right dimensions. Round samples were cut out with a diameter of 8.1 cm. In view of the changing weather conditions, air humidity and no possibility to climate the samples the dry weight of the fibers were measured using a Sartorius MA150C. The heating scale was certified according to ISO 9001.

The weight of a polyester sample under ambient humidity and temperature was measured. Following the sample was slowly heated up to 106 °C and put on hold until there was no change in weight due to water vaporizing, then the final weight was measured and denominated dry-weight.

Table-1. Dry weight determination of polyester.

Sample	**Weight** (mg)	**Dry weight** (mg)	**Humidity** (%)
1	620	614	0.997
2	633	631	0.317
3	617	615	9.325
4	616	614	0.326
5	614	611	0.491
6	627	625	0.320
7	604	601	0.499
8	614	611	0.491
9	608	604	0.662
10	624	623	0.161
Mean value	617.7	614.9	0.457
SD	8.7	9.3	0.2

Water absorption

The water absorption characteristic of the polyester textile was examined. Determination of water absorption was performed according to DIN 53923, using the current weight and the dry weight the water absorption and the absolute water absorption could be calculated with high accuracy. The water absorption can be calculated by dividing the wet sample weight with the dry sample weight.

Table-2. Water absorption of polyester.

Sample	**Water absorption** (%)	**Water absorption absolute** (%)
1	5.49	6.68
2	10.16	10.63
3	7.82	8.34
4	10.31	13.24
5	11.19	12.05
6	9.32	7.74
7	6.35	7.6
8	6.38	7.19
9	6.45	7.22
Mean Value	7.35	8.07
SD	22	2

Fiber pretreatment

It has been reported that polyester surface can be altered by dissolving the outer layers of the filament applying sodium hydroxide, this treatment creates gaps and cracks where micro and nano particles can deposit; it was stated that the weight loss and the treatment time are in a linear relation (Haghighatkish and Yousefi, 1992; Meyer *et al*., 2011). An aqueous solution of sodium hydroxide with a 10% concentration was used. Prior to the experiment a new batch of textiles was weighted using a scale: Sartorius MA 150C, certified according to ISO 9001 and their dry weight was noted in order to calculate the mass loss of the fiber. Immersed into the solution the textiles were put into an incubator oven (LIB 060M Labtech) at a temperature of 28°C. After 5 days in this solution a mass loss of 15% could be achieved. The fabric was rinsed with DI water several times in order to lower the pH-neutral values. With the sodium hydroxide solution the water repellant layer on the fiber was destroyed. Looking at the samples under the light microscope the surface showed small densely packed holes or in some cases lost its shape and showed an irregular surface, as shown in Figure-2. Furthermore the treated fiber feels rough and is not as brilliant as before.

By looking at the process time and the amount of weight dissolved, the type of fiber can be characterized. The used filaments are fully drawn yarn. In case of partially orientated yarn the treatment time would be halved (Haghighatkish and Yousefi, 1992).

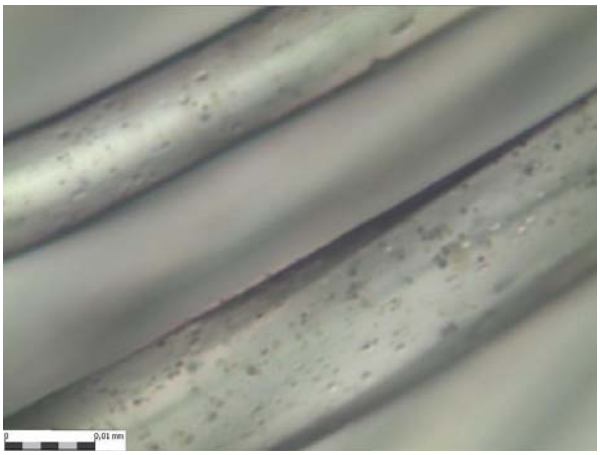

Figure-2. NaOH treated polyester fiber.

Silver particles deposition

The pretreated textile samples were impregnated with the silver nitrate dissolved in water in order to create silver particles at the surface of the textile; three different concentrations of aqueous silver nitrate solutions were used: 0.5%, 1% and 2% in weight.

Three different impregnation procedures were tested; in the first one, the fiber sample was place in intimated contact with the aqueous solution of silver nitrate and left to dry atmospheric pressure and room temperature. Due to the very slow water vaporization the equilibrium in the solution was slowly shifted until the limit of solubility of silver nitrate in water was reached and followed by the precipitation of small silver particles on the fiber. The fabrics were left for drying over 5 days. Precautions were taken in order not to contaminate the samples with the surroundings and vice versa.

In a second procedure the fiber immersed in the aqueous solution was heated up to the boiling point of the solution using a microwave oven (Daewoo KOR-6115, power input 0.92KW) at atmospheric pressure.

In the third procedure the fiber immersed in the aqueous solution was placed inside a sealed container connected to a vacuum pump which reduced the inner container pressure to 0.24 Bar and heated up to the boiling point; After 70 minutes there is no aqueous solution.

RESULTS AND DISCUSSIONS

Impregnation procedures

During the impregnation at atmospheric pressure and room temperature it could be noted that the aqueous solution in the sample with 0.5% turned red after a short while. The sample with 1% turned to a light red and the 2% sample showed no effect. One day later the red color of the samples turned to black but the sample which was impregnated with 2% Silver nitrate still did not show any effect. Five days after the initial impregnation the aqueous solution completely evaporates. The sample with 2% silver showed no effect at all. In comparison in the Petri dish of the 0.5 % sample appeared little crystals.

For the second type of impregnation procedure (ambient pressure and increased temperature), it was possible to observed small brown pigmented areas on the polyester surface; besides this subtle change in color the sample has stiffened, this could be this can be an indication of the formation of small particles or that the polyester has locally molten. Under the Transmission Light Microscope there are lots of particles visible. The fabric is changing its color very slowly. What should be noted is that the sample changed its color locally at the light spot of the Microscope.

In the third procedure (vacuum pressure and increased temperature), initially the system was heated to 52°C for 5 minutes. After applying the vacuum the aqueous solution instantly began to evaporate. The process took 25 minutes and after that the sample was dry. Therefore a shorter time could be achieved. Through the whole process the textile remained its white color. After exposing it to air at ambient pressure the sample started changing its color. All textile samples showed no color change as long as they were situated in the vacuum; right after exposing them to the ambient air the textiles started changing its color from white to brown.

Particle size

The particle size was measured using Transmission Light Microscope and the software JMicroVision v 1.27. The smallest detectable particle had the length 0.323 µm of and the width of 0.242 µm. Figure-3 shows the measured surface at a magnification of 40 times. When looking at the histogram below it shows that the mean width of the particle are 1.45 µm.

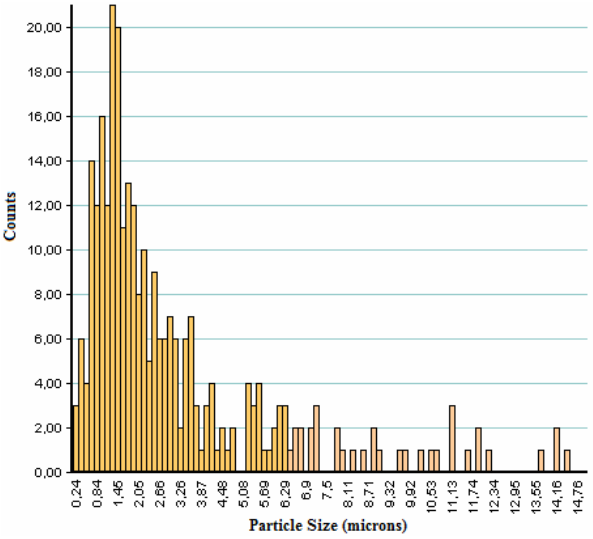

Figure-3. Histogram of particle width distribution of particles of the 0.5%, sample x-axis equals size.

The high standard derivation and variation coefficient can be explained by the limit of the smallest detectable particle for the light microscope. Utilizing a Scanning Electron Microscope, the detectable range is

extended and even particles in the range of Nano-millimeters can get visible. The SEM used was a transportable Unit from NeoScope with the indication JCM-5000 "JEOL". From 18 Samples three were further examined under the SEM.

Figure-4 shows the sodium hydroxide treated fiber and deposited silver particles. Clearly visible is the uneven shape of the fiber with little gaps and cracks on the surface where silver particles are concentrated in cluster; some other particles are observed on the surface with average particle diameter in the range of 50 to 100 nm.

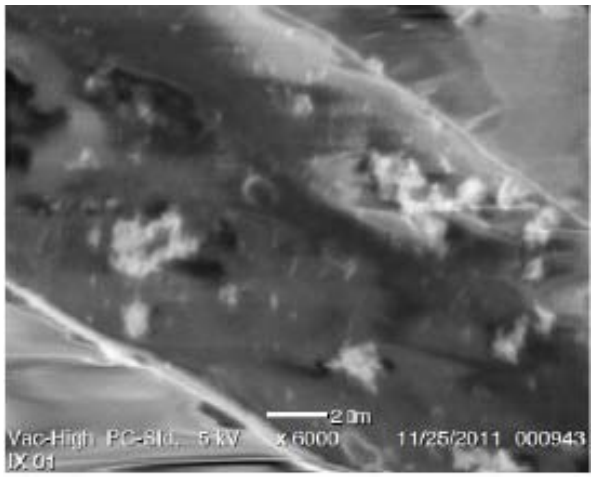

Figure-4. SEM Image 2% Ag + NaOH ambient pressure.

Figure-5 shows a not pretreated fiber which dried at ambient temperature and ambient pressure. Because the process of deposition of particles had more time to take place, the particles could form and cover the whole fiber.

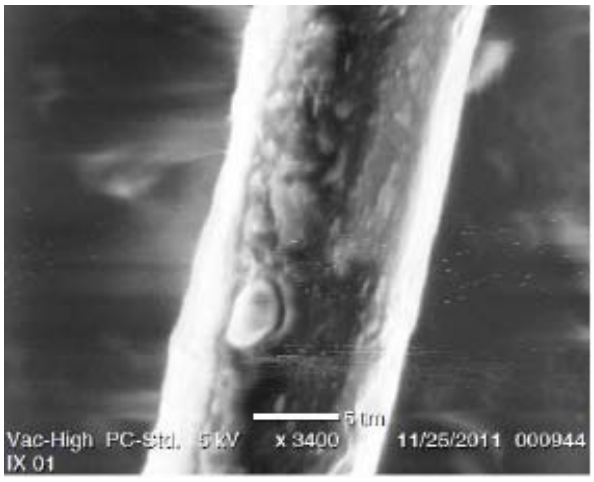

Figure-5. SEM Image 2% Ag ambient pressure.

In contrast to that in Figure-6 the particles had not that much time to react with the surface and as a result the particles are small and not densely packed. The fiber was hydrolyzed before; the uneven surface has holes.

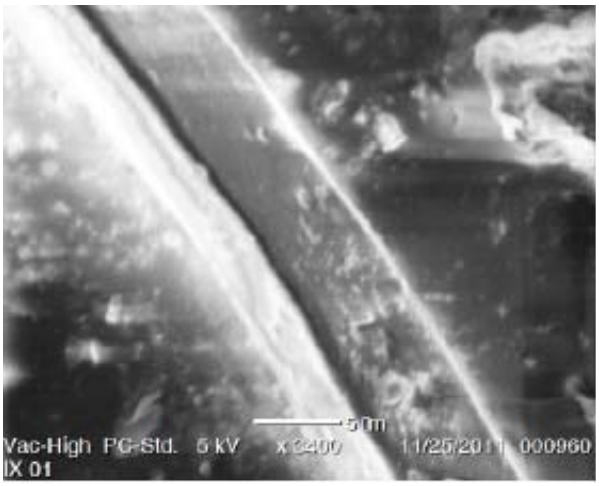

Figure-6. SEM Image 2% Ag + NaOH in vaccum.

Color change

During the impregnation experiments changes in color of the fibers to the textile was noticed in nearly most of the procedures, color change could described as turning from white to red-brown, dark brown or black. Under the microscope there are small particles visible with an amber or black color hue, as shown in Figure-7.

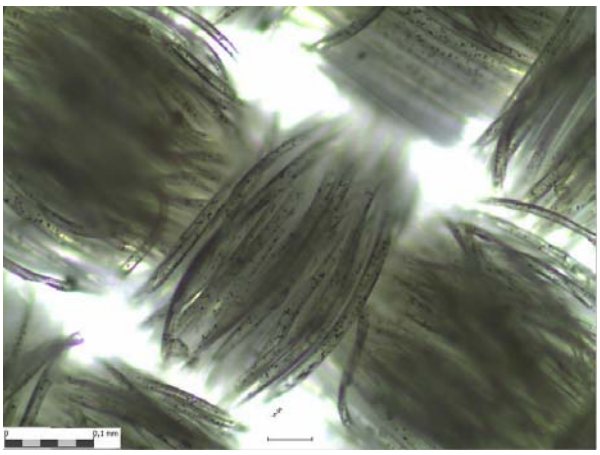

Figure-7. Polyester fabric with impregnated particles.

It should be noted that the textile drying at a pressure below ambient did not show the color change until the vacuum was released. Subsequently some textiles changed their color within 5 minutes. For every impregnation tests DI water and the same bottle containing the silver nitrate were used.

All samples were stored in dark environment in order to save them from sunlight. But still the samples changed their color in no-light (dark) conditions over days. Because some samples changed their color dramatically fast after the impregnation a set of recently processed textiles were taken to a workspace with a fluorescent lamp. Initially the samples were exposed for 5 minutes to a UV-lamp. The distance of the fabric from the lamp was 52

cm and the length of the light bulb was 41 cm. There was a slight color change visible so that the exposure time was extended to 15 minutes utilizing the same samples. The textiles were kept in a constant air volume using a foil covering the Petri dish. After this treatment the samples showed no accelerated darkening therefore UV radiation can be excluded. Nevertheless during examination of the same samples under the light microscope with a Halogen lamp and a focused beam on the textile surface the fabric changed its color within seconds. This effect was reproducible several times and therefore visible or infrared light or at least a higher temperature is involved in staining the fabric.

X-Ray fluorescence diffraction

Samples of impregnated and non impregnated fibers were examined utilizing an X-Ray difractometer (Magi XPro, Philips). Table-3 shows the elemental composition (% weight) of the samples; it can be observed a noticeable concentration of fluorine for the unprocessed sample and the one not treated with sodium hydroxide; this can be explained by the fact that most of the water repellent treatments done on textile fiber use fluorine compounds; X-Ray fluorescence diffraction shows that the impregnation procedures were successful in depositing silver particles on the textile fibers, the is a direct relationship between the concentration of silver in the aqueous solution and the amount of silver detected in the textile fiber after impregnation.

Table-3. Results X-Ray diffraction.

Weight percentage				
Element	**Blank**	**Silver nitrate** (0.5%)	**Silver nitrate** (1%)	**Silver nitrate** (1%)
F	0.253	0.252	0	0
Na	0	0	0.007	0
Mg	0.004	0.006	0.01	0
Al	0.008	0.041	0.126	0.123
Si	0.46	0.014	0.153	0.129
P	0.004	0.005	0.004	0.022
S	0.026	0.042	0.051	0.052
Cl	0.138	0.164	0.203	0.19
K	0.012	0.048	0.019	0.018
Ca	0.05	0.047	0.046	0.078
Ti	0.743	1.078	0.849	1.44
Fe	0.334	0.251	0.313	0.309
Cu	0.015	0.019	0.02	0
Zn	0.016	0.01	0.018	0.02
Ag	0	1.271	0.314	2.15

CONCLUSIONS

An economical and easy to set up impregnation process of aqueous solutions under different conditions of concentration, temperature and pressure was tested for de deposition of silver particles of polyester fibers; optical and electron transmission microscopy and X-Ray diffraction results allow concluding that the main particle average size deposited on the fiber is in the 1 to 2 microns, with a substantial particles population of particles below the 900 nm of average size. Clustering of particles was observed on gaps and indentations created on the fiber's surface by alkaline treatment.

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