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Silvering of Inert PET-Textile Materials by Means of One-Bath and Two-Bath Methods and their Characteristics

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Abstract

The metallised textile material available on the market is not suitable for several applications because of its uneven metal layer with imperfections on the fibre surface, which leads to a lack of adhesion and failures of the metal layer, impairing further processing as well as the functioning of the metallised textiles. Furthermore the wet-chemical metallisation of textile substrates has so far been limited to only a few polymers (polyamide). In the framework of this work, the scientific basis for the antimicrobial and electrical functionalisation as well as modification of inert textile material made of polyethylene terephthalate (PET) was acquired. Since textiles produced from PET have an inert and hydrophobic surface, which means they do not have functional groups, a wet-chemical one-bath and two-bath metallisation method was developed to permanently attach silver and silver compounds to the chemically inert fibre surface.

Key words: polyethylene terephthalate, wet-chemical metallization, silvering, one-bath method, two-bath method.

Introduction

Different methods have been used for the silvering of textile material, such as wet-chemical [1 - 3], Magnetron Sputter - [4], PVD - (physical vapour deposition) [5], CVD - (chemical vapour deposition) or galvanic ED - (electrolytic deposition of inorganic coatings), CD - methods (chemical deposition of inorganic coatings) [6] and plasma technology [7]. The main problem for the application of thin, flexible layers onto textiles is the realisation of a sufficient adhesion force. Especially the cross position of the yarns are the weak points for textiles for the deposition of a closed metal layer. On the one hand, a shadow area is formed through the curved fibre surface on the bottom side of each fibre, where only little or no metal particles are deposited. On the other hand, more or less large air gaps occur between conjoined threads in dependence on the yarn count and type of thread crossings [8].

Presently textile material is first galvanically and wet-chemically silvered as a knitted fabric to get silvered yarn through the knit-de-knit. The problem after the unstitching of the metallised knitted fabric is the crimping (loop effect, texturing) of the fibres. The production of textile fabrics and spacer fabrics with wavy fibres seems difficult or impossible and the productivity of the knitting process is reduced thereby. In order to reduce the crimping of the metallised fibres, an additional finishing treatment is needed in general [9].

Wet-chemical silvering methods for polyester have so far involved inhomogene-

ous and insufficient adhesion of the silver layer on the fibre surface. Oxidation agents such as persulfate with alkalimetalhydroxide, which can lead to damage to the textile material and binding, dispersing and/or thickening agents are used together, which are necessary for the binding and stabilisation of the silver particles in conventional methods [1 - 3].

Hitherto, natural fibres such as cotton and wool as well as chemical fibres such as polyamide have been metallised successfully. However, the demand for metallised, synthetic fibres such as polyethylene terephthalate (PET), polypropylene (PP) and polyetheretherketone (PEEK) for application in electronics, sensor technology, automotive engineering, lightweight constructions and water technology is increasing [10 - 13]. These fibres have a high strength and hydrolysis stability in contrast to natural fibre or polyamide. However, polyester possesses an inert, hydrophobic surface and does not have any functional groups which can be linked with silver.

With respect to this situation, the focus of the work is to develop a scientific basis for the functionalisation and modification of inert, textile material made of polyester. Technologies need to be developed to permanently immobilise the silver complex on the fibre surface without losing the basic properties of the textile material. The main challenge is to deposit possibly homogenous and defect-free metal layers from equally large silver particles with good adhesion on multi- and monofilament PET fibre surfaces. The newly developed method should be flexible and applicable for all polymer fibre material

in different forms (yarn, textile fabric und spacer fabric) so that a broader application field is opened up for metallised textile material in the future.

After the wet-chemical silvering, the silvered textile material, made of PET, after washing should prove to be a stable silver layer, with electrical conductivity and antibacterial effects. Spacer fabric, which consists of silvered yarn, was applied in water and other fluid containing systems to reduce the settlement and reproduction of microorganisms [13]. Therefore it is important to analyse the release of silver ions from the silvered PET-textile material in water.

Material

In close cooperation with the textile company St. Micheln GmbH & Co. Ltd. (Mülsen, Germany), different structures such as continuous filament yarns, textile fabrics and spacer fabrics made of polyester were used as a substrate for metalisation.

- PET continuous filament yarn ($T_{\text{tex}} = 48.3$ tex, 34 single filaments, without optical brightener, with circular filament cross-section) was used as yarn.
- A fine warp knitted fabric right/left, locknit, washed and fixed, $T = 50$ dtex, 24 single filaments, 12 stitch courses per cm was used as fabric.
- As spacer fabric: distance between two top surfaces is 16 mm.

Aminosilanes such as 3-aminopropyltrimethoxysilane (Fluka Chemie GmbH, Oberhaching, Germany) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Fluka Chemie GmbH, Oberhaching, Germany), synthetic amines such as Bis-(3-aminopropyl)-amine (Fluka Chemie GmbH, Oberhaching, Germany), tetraethylenpentine (Fluka Chemie GmbH, Oberhaching, Germany), lupamine® 9095 (Merck KGaA, Darmstadt, Germany) and natural amines such as chitosan (Sigma-Aldrich Chemie GmbH, Munich, Germany) were chosen for appropriate coating.

Method development for the metallisation of chemically inert fibre material

The key factor for the realisation of the silvering of chemically inert PET-textiles is the wet-chemical silvering method.

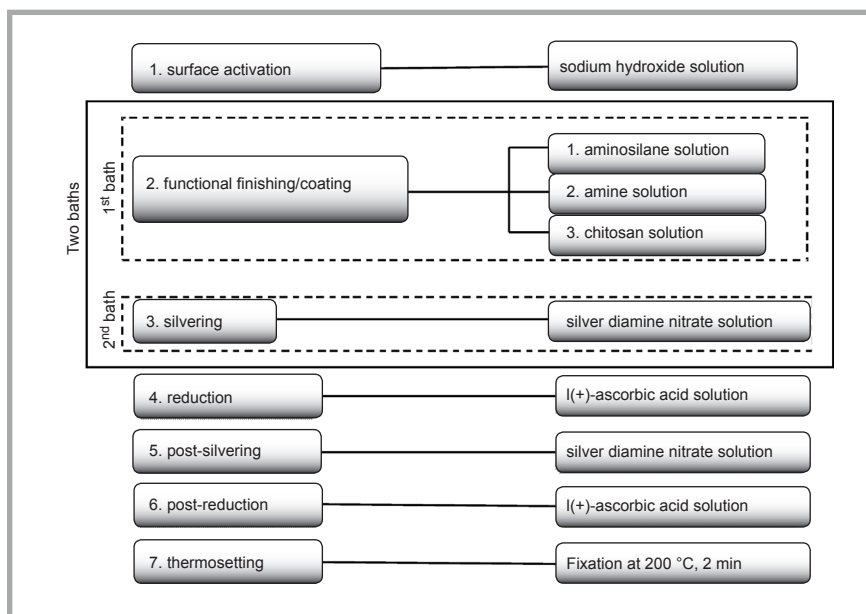


Figure 1. Process sequence for the wet-chemical silvering of inert PET-textile substrates with the two-bath-method (indirect).

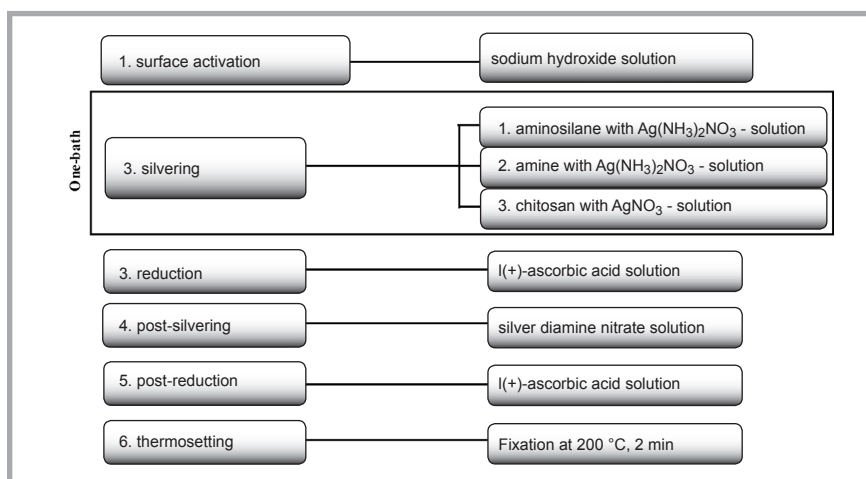


Figure 2. Process sequence for the wet-chemical silvering of inert PET-textile substrates with the one-bath method (direct).

The aliphatic amines, aminosilanes and chitosan have amino groups and have the ability to bond silver ions with their free electron pairs. In order to embed silver diamine complexes on the inert PET fibre surface, a wet-chemical one-bath (direct) or two-bath (indirect) silvering method was developed at the Institute of Textile Machinery and Textile High Performance Material Technology (ITM) of TU Dresden, Germany.

The process steps of silvering with the two-bath method are presented in Figure 1. In order to fix complex-forming materials (e.g. before-mentioned amino-compounds) on the polymer surface, the PET is pre-treated with a sodium hydroxide (NaOH) solution. Afterwards the pre-

treated textile material is impregnated in the chemical finishing agent/coating solution (aminosilane, aliphatic polyamines or chitosan). After the finishing, they are silvered either with silver diamine nitrate ($\text{Ag}(\text{NH}_3)_2\text{NO}_3$) solution or with silver nitrate (AgNO_3) solution. The silvered fibre surface is reduced with L(+)-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) solution, so that insoluble metallic silver stays permanently on the PET fibre surface. After the reduction, post-silvering with a silver diamine nitrate solution and post-reduction with an L(+)-ascorbic acid (AA) solution are carried out. The post-reduced test samples are cleansed with water, dried in air and then thermally fixed [14]. It is typical for the two-bath method that the function-



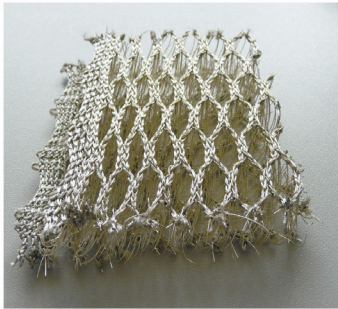


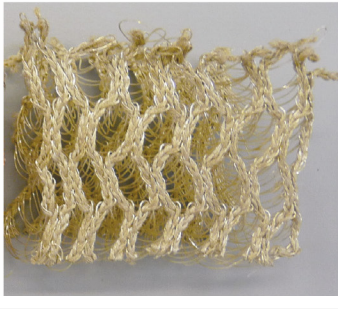
Materials		Continuous filament yarn	Warp knitted fabric	Spacer fabric
Method	Two-bath			
	One-bath			
Coating agent		TEPA	CTS	NAEPTMS

Figure 3. Wet-chemical silvered continuous filament yarn, warp knitted fabric and spacer fabric by means of one-bath and two-bath methods; TEPA - tetraethylenpantamine, CTS - chitosan, NAEPTMS - N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.

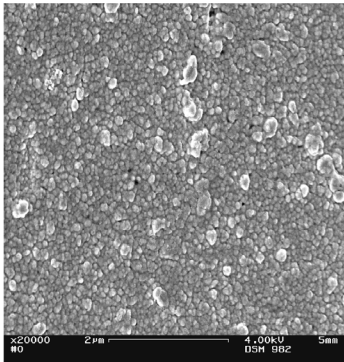
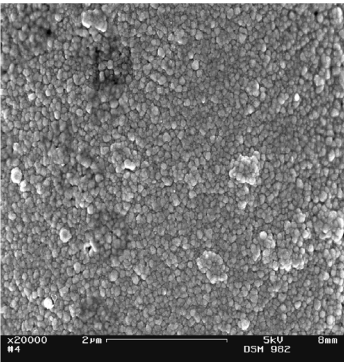
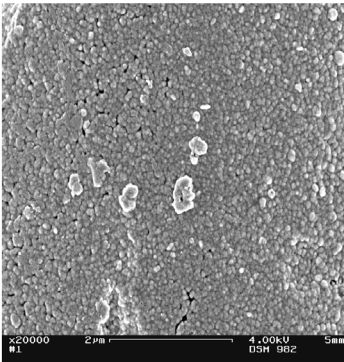
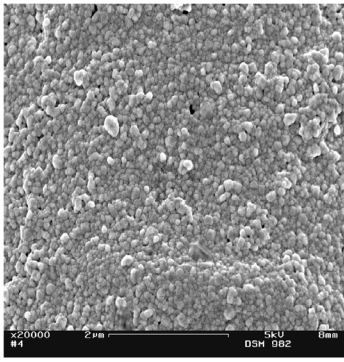
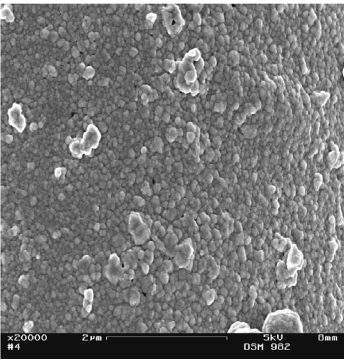
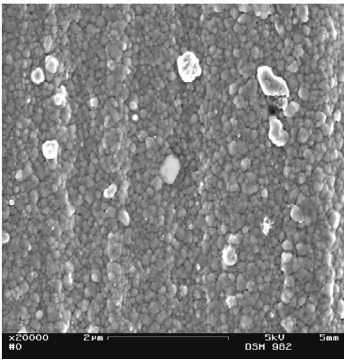
Materials		Continuous filament yarn	Warp knitted fabric	Spacer fabric
Method	Two-bath			
	One-bath			
Coating agent		TEPA	CTS	NAEPTMS

Figure 4. SEM-images (20 000 \times) of silvered continuous filament yarn, warp knitted fabric and spacer fabric made by the wet-chemical one-bath and two-bath methods: TEPA - tetraethylenpantamine, CTS - chitosan, NAEPTMS - N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.

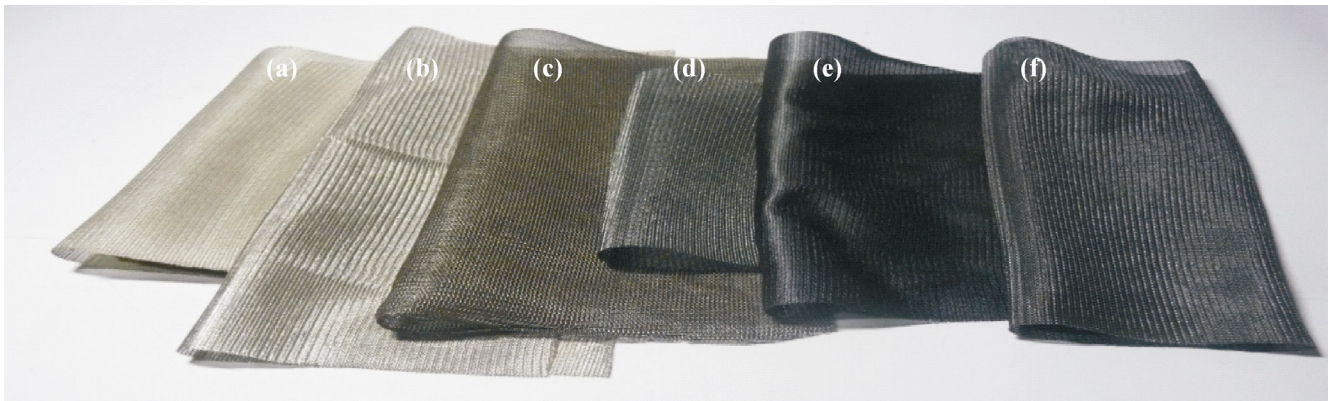


Figure 5. Optical characteristics of PET fabrics treated with the one-bath and two-bath methods: a) two-bath method with Chitosan (CTS), b) one-bath method with lupamine (LA) after 48 h ageing of the solution, c) one-bath method with lupamine (LA) after 384 h ageing of the solution, d) one-bath method with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, e) two-bath method with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (NAEAPTMS) and f) two-bath method with tetraethylenpentamine (TEPA).

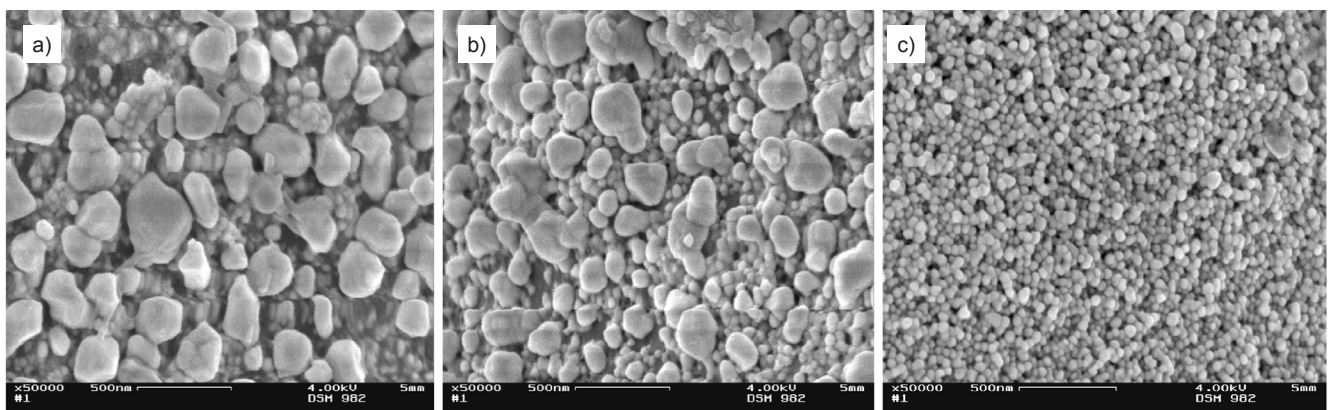


Figure 6. SEM-images (50 000 \times) of different silver particle sizes of silvered PET warp knitted fabrics.

alisation and silvering process are carried out separately in two baths.

A significant shortening of the process steps is achieved with the direct silvering in a one-bath method. Here it is possible to generate silver particles on the fibre, whose homogenous application leads to the realisation of a silver layer on the fibre surface. Transferred into refined method technology this means that the pre-treated PET textile material is silvered without preceding finishing or coating directly through dipping, stirring or impregnation (**Figure 2**). In the one-bath method, the silver salt solution (AgNO_3 or $\text{Ag}(\text{NH}_3)_2\text{NO}_3$) is added directly into the functional finishing/coating agent (aminosilane, aliphatic amine or chitosan). The PET textile materials pre-treated, are then silvered without coating directly with the silver-finishing/coating agent by means of dipping or padding. The silvered test samples are reduced afterwards wet-chemically, then post-silvered, post-reduced and thermally set.

When developing the wet-chemical silvering method, the use of oxidation agents such as persulfate in the presence of alkalimetallhydroxide is avoided as this leads to the damage of the textile materials. The addition of binding, dispersing and/or thickening agents, which are necessary for the binding and stabilisation of the silver particles, can also be omitted. The silvering process takes place at low temperatures ($35 \pm 3^\circ\text{C}$). Therefore the methods developed are more ecological and environment-friendly than the existing methods.

Results and discussion

The main challenge for the silvering of inert textile material is to achieve the following three main targets: good adhesion, an even size of the silver particles, and a completely covered fibre surface. To achieve the three targets mentioned, internal and external influential factors for the silvering were profoundly analysed changing their values. The internal and external influential factors are the following:

Internal influential factors:

- pH-value of silvering solution (pH 11),
- ageing of silvering solution (24 h),
- Ag-concentration (0.5%),
- AA-concentration (10%),
- Silvering time (1 h) as well as – temperature ($35 \pm 2^\circ\text{C}$) and
- Thermosetting time (2 min) as well as – temperature (200°C).

External influential factors:

- Type of filament (Multifil, Monofil)
- Pressure of padder roller (3×10^5 Pa) and
- Speed of padder roller (3 m/min).

Surface characteristics

Entire silver coatings with a uniform silver particle distribution on the PET-fibre surface by one-bath and two-bath methods in different forms (continuous filament yarn, warp knitted fabric and spacer fabric) could be achieved by a systematic analysis of all process parameters and their optimal adjustment (**Figure 3**).

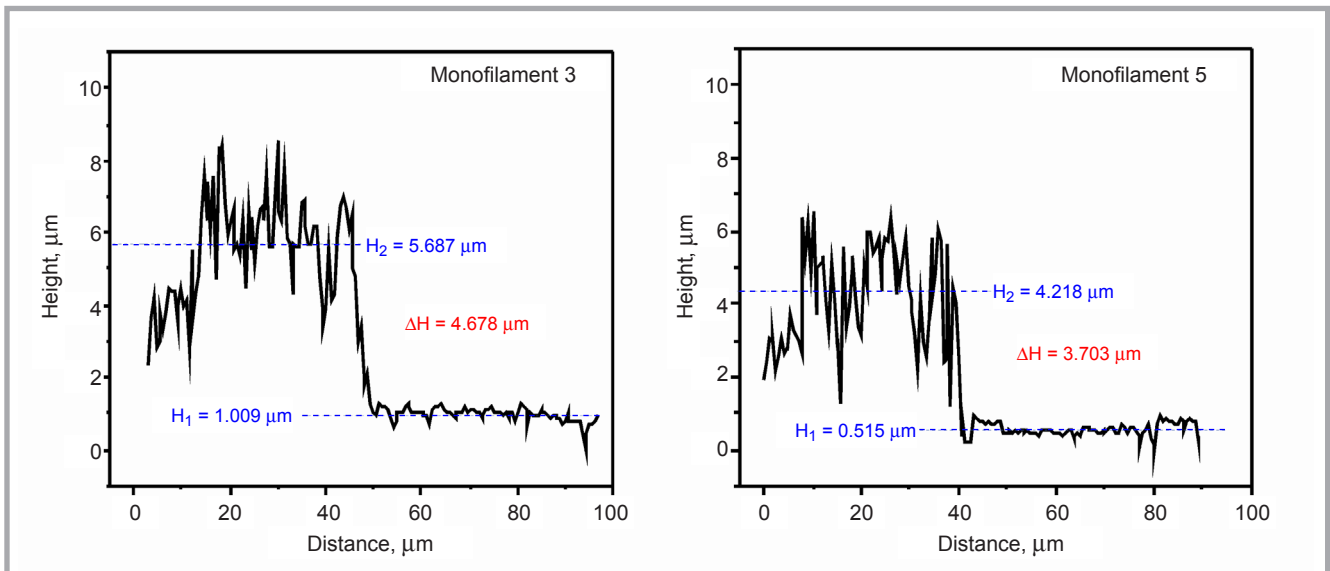


Figure 7. Layer thickness profile of post-silvered PET-monofilaments made of spacer fabric; (**Monofilament 3:** by means of one-bath method with TEPA and **Monofilament 5:** by means of two-bath method with NAEPTMS).

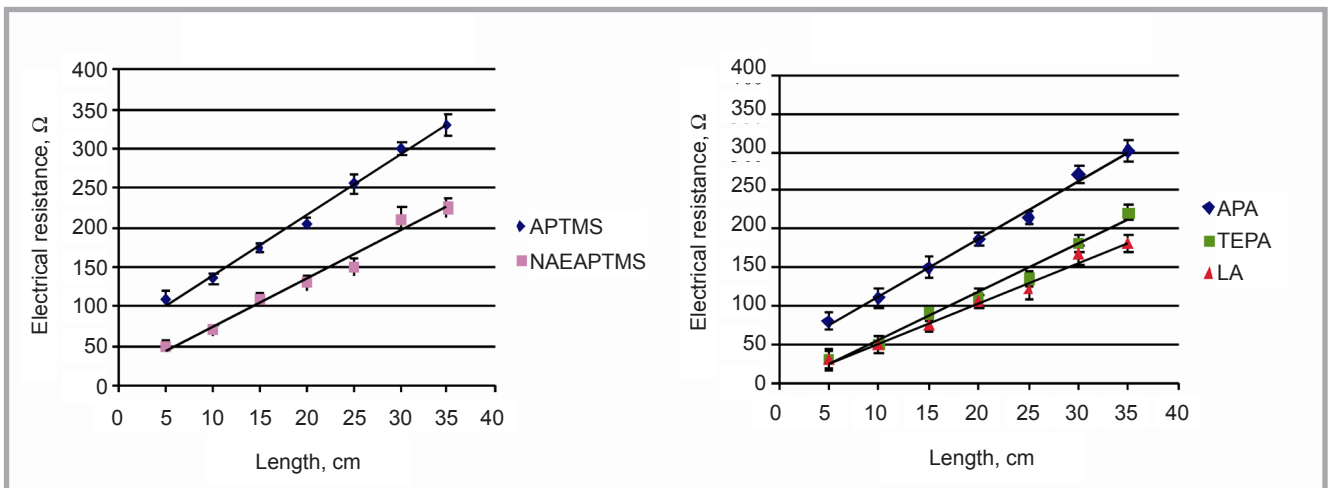


Figure 8. Influence of aminosilanes (left) and aliphatic amines (right) on the electric resistance in relation to the length, APTMS (3-aminopropyltrimethoxysilane), NAEPTMS (N-(2-aminoethyl)-3-aminopropyltri-methoxysilane, APA (Bis-(3-aminopropyl)-amine), TEPA (tetraethylenpentamine) and LA (lupamin® 9095).

The scanning electron microscopy (SEM) images (**Figure 4**) clearly show that the silvered yarns, warp knitted fabrics and spacer fabrics have a completely coated Ag-layer due to wet-chemical one-bath and two-bath methods.

Particle size A colour impression (**Figure 5**) after the silvering of the textiles is an important characteristic of the wet-chemical silvered PET material. The particle size has a significant influence on the colour of the silver liquor, which results in the covering of the fibre surface with a silver layer, which changes the optical properties of the silvered textile material after silvering (**Figure 5**). The test samples, which show different particle sizes, form a darker colour on the fibre surface and have various silver particle

sizes (**Figure 6.a**). The aliphatic amine- and aminosilane-silver diamine nitrate solutions are colourless at the beginning, but the colour changes from yellow to brown in dependence on the aging of the silvering solution. With the help of SEM-images (**Figure 6.c**) and the silver colour, it can be visually identified that from the yellow solution, a small, evenly distributed silver particle is on the PET fibre surface. With increasing concentration of ammonia in the amine-silver diamine nitrate solution and aminosilane-silver diamine nitrate solution, a shiny golden colour can be generated on the textile material.

The causes of the irregular sizes of the synthesized particles, the inhomogeneous distribution and coarse-grained

build-up of silver particles on the fibre surface are dependent on many factors. The size of the silver particles is controllably adjustable from nano- to micrometers by:

Smaller Ag-particle (50 ± 20 nm)

- Mixture of the finishing-/coating agent with silver salt solution (by means of one-bath method),
- the use of ammonia solution,
- exact time-phased ageing of the silver-containing solution and
- stirring for the attainment of even distribution of the silver particle in the solution.

Larger Ag-particle (160 ± 40 nm)

- longer silvering time,

- with no ageing of silver-containing solution,
- without stirring of silvering solution and
- thermosetting of silvered textiles.

Layer thickness

Another detailed analysis is dedicated to the coating formation or silver layer growth on the fibre surface. By mixing the finishing/coating agent with silver salt using ammonia solution, an evenly coated silver coating made of very small Ag-particles can be achieved on the fibre surface. By fixing the silver layer thermally, good adhesion and an even thickness of the silver layer on the PET-substrate can be achieved. The thickness of the silver layer is controllably adjustable, for example, the silver layer thickness of post-silvered PET-monofilaments made of spacer fabrics was determined using confocal microscopy - MicroSpy® FT, from the company Fries Research & Technology GmbH (Bergisch Gladbach, Germany). It was between 3.7 µm and 4.7 µm (*Figure 7*).

Textile-physical characteristics

Electrical conductivity

PET yarn has an elasticity property and the silver metal provides electrical conductivity. Silver has very good electrical conductivity. The advantages of silvered PET-yarn in contrast to wire are flexibility, large elasticity and deformation ability. Electrical conductivity of the non-conductive PET fibre surface was achieved through the formation of a completely closed silver layer on the fibre surface. If micro-scale silver particles are present on the fibre surface, it results in a free area between the individual silver particles, which reduce the electrical conductivity. Nano-scale silver particles compared to micro-scale silver particles covered completely the fibre surface. This has been achieved by a post-silvering, and therefore silver layer was thicker. The electrical resistance of silvered yarns produced with various finishing agents was different (*Figure 8*). The electrical resistance of the metalised yarns increase with an increase in the measuring length.

Gravimetric analysis

The percentage of silver immobilised on the PET fibre surface after the silvering was determined gravimetrically. It is be-

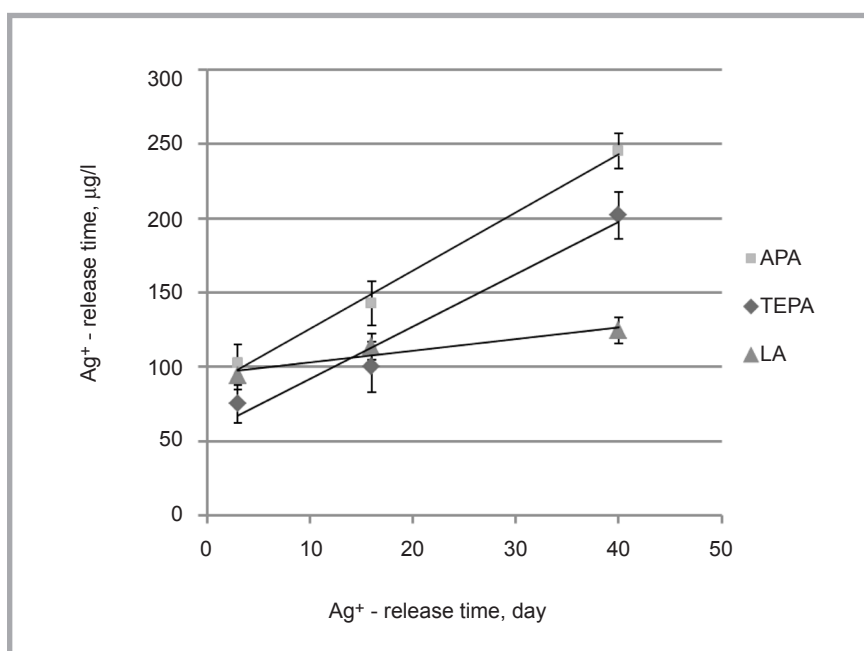


Figure 9. Influence of the applied finishing/coating agent on Ag⁺-release.

tween 2.5% and 7.0% for silvered PET textile material.

Textile-chemical characteristics

Wear property

Another area of analysis for the characterisation of silvered PET-textiles is thermal and hydrothermal behaviour, such as washing-fastness. In order to test the wear property, the silvered test samples underwent 20 washing cycles. After the first and second washing cycles, no significant loss of weight could be noticed. Here the silver particle was not bound on the surface and the residual reduction solution was dissolved. In order to prove the adhesion of the silver particle on the fibre surface, the silvered textiles were sown to adjacent fabrics, such as polyamide and wool, and then washed. After 20 washing cycles, the adjacent textiles had not absorbed any silver and no change in colour for the silvered PET textiles could be recorded. Thus it is proven that a good, wash stable silver layer on the inert PET fibre surface can be achieved. Defects of the silver layer as well as the cross positions of the threads were evaluated under a microscope after undergoing several washing cycles. No layer breaks nor crack formations on the fiber surface could be detected. The cross positions of the threads are fully covered with silver particles.

Elution

Detailed, time-resolved analyses of the elution behaviour of silvered textile material made of PET are of practical inter-

est. The World Health Organization allows a maximum silver concentration of 100 µg/l for drinking water and according to the Drinking Water Ordinance in Germany - 80 µg/l. The silver ion release (Ag⁺) of silvered textile material made of PET in water decreases in thicker, entirely reduced silver layers made of smaller, evenly distributed and firmly fixed silver particles on the fibre surface. *Figure 9* shows the Ag⁺-release in water after 5, 15 and 40 days under the influence of the finishing-/coating agent used, which was under the permitted standard after five days. The Ag⁺-release in water increases linearly to the increasing time. During this work, additional external influential factors such as the fluid temperature, water hardness and concentration of chlorine on the Ag⁺-release in water were analysed. Soft water with an increasing fluid temperature and chlorine concentration leads to a higher Ag⁺-release in water.

Textile-mechanical characteristics

Breaking force and elongation at break

Textile-physical characteristics such as the breaking force (BF) and elongation at break (BE) of silvered as well as post-silvered PET were investigated in relation to the variation in different process parameters. Alkaline pre-treatment results in a decrease in the BF and increase in the BE (*Figure 10*, see page 114). A longer silvering period, high amine- and ammonia-concentration in the silvering solution, as well as high silvering- and thermosetting temperatures yield low strength loss in the textiles.

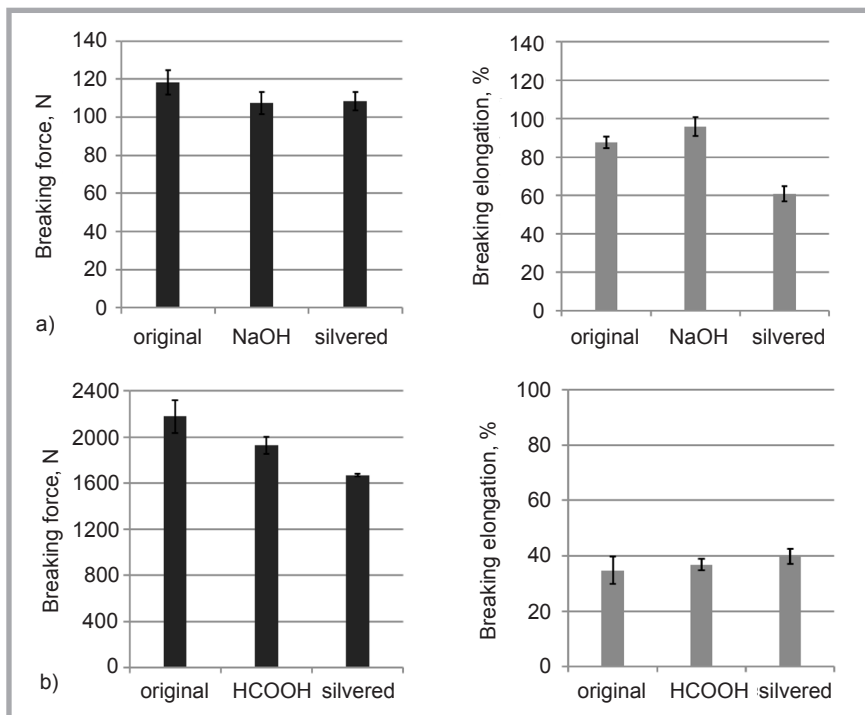


Figure 10. Influence of treatment processes (surface activation and silvering) on the BF (left) and BE (right) in the warp direction of original, pre-treated and silvered (a) warp knitted and (b) spacer fabrics.

Summary

By choosing suitable chemicals and by varying the internal and external process parameters for wet-chemical one-bath and two-bath silvering, a homogenous, completely covered silver layer with evenly distributed silver particles on the PET fibre surface in the forms of yarn, warp knitted fabric and spacer fabric was successfully silvered on a laboratory scale.

This was achieved by:

- precisely time-phased ageing of the silver-containing solutions (at least 24 h),
- specially chosen pH-value-areas of the silvering liquor (direct method and indirect method),
- relatively low process temperatures (35 ± 2 °C),
- minimised treatment times (1 h),
- defined reduction conditions (at room temperature, 10% ascorbic acid solution, 20 min) and
- optimal thermosetting (200 °C, 2 min).

The wet-chemical silvering method can be variably adjusted with different layer parameters (e.g. particle size and thickness of the layer) by mixing two or more different solutions.

Silvered textile material made of PET has the following properties:

- wash resistant silver layer,
- antibacterial effects,
- electrical conductivity.

Textile material made of post-silvered PET does not show a stiff grip. Furthermore the processability of silvered PET-yarns on a knitting machine is possible.

On the basis of successful laboratory results for the metallisation of yarns made of polyester and other textile material, industrially applicable methods need to be developed which can later be realised with existing technically well-engineered production equipment allowing the processing of functional textiles under very low-priced economical conditions.

Acknowledgement

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Elimination of Biological Contamination in Water Systems“.

References

1. Deutscher Patent DE 34 19 755 A1. Chemisches Versilberungsbad, 1985.
2. Deutsches Patent- und Markenamt DE 10 2005 020 889. Verfahren zur antimikrobiellen Ausrüstung von textilen Flächengebilden, 2006.
3. United States Patent US 6, 821, 936. Textiles having a wash-durable silverion based antimicrobial topical treatment, 2004.
4. Sant SB, Gill KS, Burrell RE. Nanostructure, dissolution and morphology characteristics of microcidal silver films deposited by magnetron sputtering. *Science Direct, Acta Biomaterialia* 2007; 3: 341-350.
5. Dietzel Y, Przyborowski W, Nocke G. Veredlung von textilen Flächengebilden mittels PVD-Technologien. Research Report, Projekt Nr. 4-755-70-5150-98/1; 4-7531.50-025150/01/1, Zittau, Germany, 2001.
6. Deutsches Patent DE 33 37856 A1. Verfahren zur Aktivierung von Substraten für die stromlose Metallisierung, 1985.
7. Hegemann D. Plasma-Metallisierung von Textilien unter industriellen Bedingungen. In: *1st Symposium-Smart-Text.* Weimar, Germany, 2008.
8. Dietzel Y. *Coating of knitted textile fabrics by means of PVD-technologies reactive vacuum arc evaporation and reactive magnetron sputtering.* Dissertation, TU Dresden, Dresden, Germany, 2004.
9. Onggar T. *Wet-chemical silvering of inert Polyester fiber surfaces. Materials - Techniques - Method - Properties.* Dissertation, TU Dresden, Dresden, Germany, 2012.
10. Lauterbach Ch. SensFloor®- mehr als nur Boden. Höhenkirchen-Siegersbrunn: Future-Shape GmbH, 2008.
11. Alexandrowicz A, Zimmermann N. Einsatzmöglichkeiten technischer Textilien im Fahrzeuginnenraum. In: *16th Aachen Colloquium Vehicle and Engine Technology.* Institut für Textiltechnik Aachen, Aachen, Germany, 2007.
12. Starke E, Landgraf J. Integrierte Sensornetzwerke in Faserverbundwerkstoffen. In: *13th ITG/GMA-Symposium Sensoren und Messsysteme.* Freiburg, Germany, 2006.
13. Hund RD, Rossbach V, Lück C, Rödel H, Militz D, Kreysig D. Silvered textile materials water-disinfection. In: *47 Man-Made Fibers Congress.* Dornbirn, Austria, 2008.
14. Onggar T, Hund RD, Rossbach V, Lück C, Rödel H, Militz D, Kreysig D. Silvered spacer fabrics as microbicidal actors. In: *3rd Europaen Technical Textiles Convention.* Lille, France, 2009.

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