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Silvering of three-dimensional polyethylene terephthalate textile material by means of wet-chemical processes

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Abstract

The aim of this research is to develop a wet-chemical silvering method for a three-dimensional (3D) textile material made of polyethylene terephthalate (PET) to prevent and eliminate biological contaminants in drinking water and other liquid-containing systems. Three-dimensional textile fabrics are particularly well-suited as silvered disinfection materials in water systems, because they have 3D structures, pressure-elastic textile design, and provide large contact areas. Furthermore, water can easily be passed through the structure. The developed wet-chemical procedures are based on aminosilane, which consists of at least two amine groups and is well-suited to form a silver diamine complex. The silvered textile material was coated with cationic silver. After the chemical reduction, the cationic silver turns into metallic silver on the surface of PET spacer fabrics.

The surface morphology of silver-coated spacer fabrics was analyzed and the uniform silver layer on the PET fiber surface was found. X-ray diffraction and energy-dispersive X-ray spectroscopy analysis spectrums showed that the silver was immobilized on the PET fiber surface. The layer thickness and the silver amount were also determined. The silvered spacer fabrics can be used in sealing and/or cooling water systems; therefore, the silver ion release in water was analyzed. Furthermore, textile physical tests for the measurement of breaking force and elongation were carried out. No significant change in breaking force and elongation was observed after silvering of PET spacer fabric.

Keywords

polyethylene terephthalate, spacer fabrics, silvering, wet-chemical process, biological contaminations

Nowadays, the most widely used disinfection methods are thermal, chemical, mechanical, and electrolytic disinfection, and disinfection by irradiation. The biofilms cannot be removed completely by most of the abovementioned physical cleaning methods (e.g. a high current condition, high-pressure cleaner, adaptable brushes for the management systems).^{1–3} The use of oxidizing agents (e.g. ozone, chlorine, and bromine) for chemical cleaning is ecologically questionable.⁴ These problems can be rectified by developing silver coating on textile surfaces. Functionally active silvered textiles can fight against dangerous bacteria and can save lives. The application of silvered three-dimensional (3D) textile materials will ensure higher process safety and reduction of the service cost

compared to conventional decontamination technologies.⁵ Reduced energy and chemical consumption of wet-chemical silvering is another advantage. The existing filter system consists of silvered polyamide (PA) yarns (functional) in the top surfaces, and unsilvered polyester yarn (structure-forming) in the

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pile. It has been applied for various purposes, such as sealing water circulation in paper pulp pumps, cooling water circulation systems for industry, and as a tempering device for an operating room. However, the life-cycle of silvered PA yarns in humid/wet environments is shortened by their low hydrolysis stability. Therefore, the 3D textile materials made of polyethylene terephthalate (PET) yarns need to be silvered to prevent and eliminate biological contaminants in drinking water and in other liquid-containing systems.

Silver has antimicrobial properties. PET has lower moisture absorption (0.4%) than PA 6.6 (3.8%) fiber, wool (35%), or cotton (8%) fibers. Therefore, the PET is well-suited for use with water and other liquid-containing systems. Spacer fabrics consist of three “layers” – two covering layers and a spacer layer. Three-dimensional textile fabrics are particularly well-suited as silvered disinfection materials in water systems because they have a 3D structure, pressure-elastic textile design, provide a large contact area, and allow water to pass through their structure easily. In addition, spacer fabrics have good drapeability and can thus also be used for lining pipes or irregular tank shapes (Figure 1).

The PET textile materials are metalized according to the current state of the art technology by separating the metal coatings from the vapor phase (Physical Vapor Deposition (PVD)^{6,7} and Chemical Vapor Deposition (CVD)), coating galvanical-electrolytically (Electrolytic Deposition of Inorganic Coatings) or galvanical-electroless (Chemical Deposition of Inorganic Coatings),^{8–10} or by plasma technology¹¹ and a wet-chemical method.^{12–16} PET textile materials or PET cotton blend fabric were silvered not as spacer fabrics, but as knitted and woven fabrics. In particular, the cross-position of the yarns are weak points in textiles for the deposition of a closed metal layer by means of PVD and CVD. Besides, a shadow area is formed through the curved fiber surface on the bottom side

of each fiber, where only few or no metal particles are deposited. On the other hand, air gaps of various sizes occur between conjoined threads, depending on the yarn count and type of thread crossings.⁶ Wet-chemical silvering by padding is not suitable for 3D construction of the spacer fabric.

The two covering layers and a spacer layer of 3D textile material are characterized by different yarn counts. Monofilament yarns are stiff and thick and have high tensile strength and low elongation compared to multifilament yarns. The surface of monofilament yarns is smooth. Such multi-component structures lead to many difficulties in the pretreatment, metallization, and thermo-setting process. For this reason wet-chemical dipping metallization was selected.

The PET spacer was not coated with nanosilver, but with a silver diamine complex solution, which was applied to the fiber surface in an ionic form by dipping and transferring with a reducing agent in metallic form. Nanosilver refers to silver in the form of particles of a diameter of up to 100 nm. As of yet, no consistent and experimentally/quantitatively substantiated research reports are available concerning the functional principle of nanosilver acting as an antimicrobial agent for disinfection or contamination protection in water or aqueous media. Currently there is no method for the quantitative analytical determination of the concentration of nanosilver in fluid media. The use of nanosilver is not allowed for disinfection of drinking water from contamination. The antimicrobial effect of these systems realized by the transfer of silver ions onto any microorganisms requires only a minimum release of silver. The Drinking Water Ordinance of the World Health Organization (WHO) allows a maximum silver concentration of 100 µg/l for drinking water.¹⁷ Our aim is to deposit approximately 7% silver on the fiber surface and to keep the silver ion release concentration lower than the values specified by the Drinking Water Ordinance of the WHO.

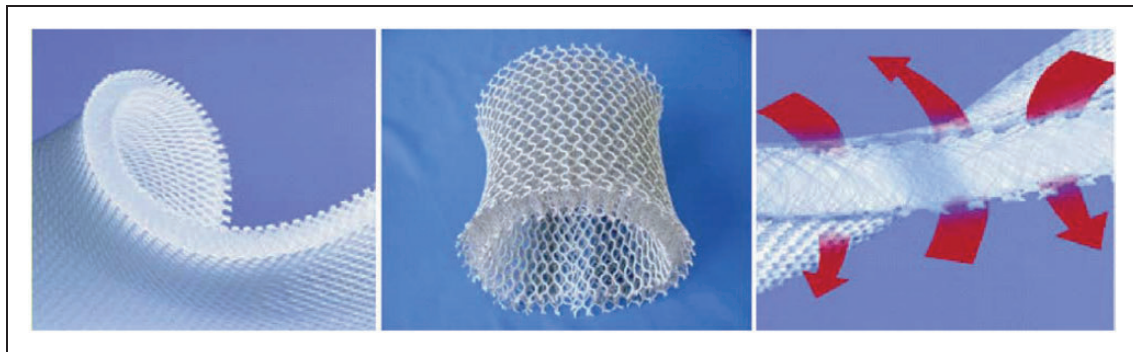


Figure 1. Optimum ductility, free air, and water circulation of spacer fabrics.

Materials and methods

Materials

Three-dimensional PET textile material (St. Micheln Co., Ltd, Mülten/Germany) was used as substrate for the metallization. The covering layers were produced from PET multifilament yarn (cover yarn) and the spacer layer was made of PET monofilament yarn (pile yarn). The multifilament yarns consist of 32 single filaments, have a yarn count $T_{tex}=33.4$ tex, and are double twisted. The diameter of the individual filaments is $d=0.012$ mm. The monofilament yarn consists of a single filament, has a yarn count of $T_{tex}=67.8$ tex, and a diameter $d=0.25$ mm. The distance between the two top surfaces in the spacer fabric is 16 mm.

Sodium hydroxide pellets and Invadin LUN were used for the surface activation of the textile materials. In order to increase the wettability of the fiber, Invadin LUN, 4-tert-octylphenyl (polyethylene glycol-[9/10]) ether surfactant, which acts as a universal wetting agent, was selected for textile treatment liquors. An amino silane, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (>96%), was chosen for the specific coating. The silver diamine complex was created from silver nitrate (99.5%) and ammonia (25%) solution. L(+)-ascorbic acid (powdered pure Ph. Eur., BP, USP) was used as the reduction agent. All chemicals were purchased from Germany.

The metallization process of 3D PET textile materials

Initially, the 3D PET textile material that needs to be metalized was pretreated with a 0.5 N sodium hydroxide solution and 0.5 g/l of the Invadin LUN wetting agent with a liquor ratio of 1:20 at 100°C for 30 min in a Labomat BFA-12 (Werner Mathis AG, Zurich, Switzerland) and afterwards rinsed with warm water until a pH value of 6.0–7.0 was achieved. The aim of the pretreatment was to activate the PET fiber surface. The aqueous silver diamine nitrate solution ($\text{Ag}(\text{NH}_3)_2\text{NO}_3$) was prepared from 5% aqueous silver nitrate solution (AgNO_3) and 25% of ammonia. It is typical for the dipping method that the finishing/coating agent (0.3 g/l *N*-2-aminoethylene-3-aminopropyltrimethoxysilane) is placed in one bath with an aqueous silver diamine nitrate solution. In order to attach the silver diamine complexes to the PET fiber surface, the pretreated fiber surface was then silvered with the newly developed wet-chemical dipping method in an aqueous silane-silver diamine complex solution with a liquor ratio of 1:20 at $35^\circ\text{C} \pm 2^\circ\text{C}$ for an hour. After fixing the ionic silver on the fiber surface the reduction was carried out with a 10% L(+)-ascorbic

acid solution with a liquor ratio of 1:20 at room temperature for 15 min to convert the ionic into metallic silver. The reduced specimens were rinsed in distilled water and air-dried. Finally, the metalized 3D PET textile fabric was fixed at 200°C for 2 min in a thermosetting process in a Mathis Labdryer TYP “LTE” (Werner Mathis AG, Zurich, Switzerland).

Analysis methods

Scanning electron microscopy. The morphological analysis of PET fiber surfaces was carried out using a DSM 982 Gemini scanning electron microscope (SEM) manufactured by Carl Zeiss AG (Jena, Germany).

Energy-dispersive X-ray spectroscopy. By combining the SEM with energy-dispersive X-ray spectroscopy (EDX), the percentage of the elements, such as carbon (C), oxygen (O), nitrogen (N), silicon (Si), and silver (Ag), was semi-quantitatively determined using point analysis, and the data was recorded.

X-ray diffraction. Phase formation and crystalline properties of the silver-coated textile materials were investigated by X-ray diffraction (XRD) using a PANalytical X'Pert PRO (Almelo, Netherland) analyzer with a $\text{Cu-K}\alpha$ radiation reflection geometry source. The scanning range of 2θ was set from zero to 80° at increments of 0.005 for silver.

Layer thickness. The silver layer was analyzed with a confocal MicroSpy[®] FRT microscope by Fries Research & Technology Company GmbH (Bergisch Gladbach, Germany).

Washing fastness. Specimens with a size of $7 \times 7 \text{ cm}^2$ were used. Wool and PA were selected to cover the specimen during washing. To determine the wash fastness, the DIN EN 20 105-C03 ($60^\circ\text{C} \pm 2^\circ\text{C}$, 30 min) standard for medium wash fastness was modified to match the experimental parameters and used to test the specimens. The specimens were washed in a laboratory beaker dyeing apparatus by Mathis (Zurich, Switzerland) with a liquor ratio of 1:20. Non-ionic detergent and wetting agent 0.5 g/l TISSOCYL CSB (alcohol ethoxylate) by Zschimmer & Schwarz (Germany) and 0.3 g/l sodium carbonate (Gruessing, Germany) were used for the washing processes. The weight loss of the silvered samples was calculated. The changes in color of the silvered specimens and the washing bath were visually evaluated.

Silver amount. The amount of silver taken up by the PET was determined after heating in a Controller B170 muffle furnace by Nabertherm GmbH (Lilienthal,

Germany) at $900^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 3 h. An average of 10 investigations was evaluated for each sample.

Silver ion release. The silver concentration in the eluate was detected by means of a ZENit 700 atomic absorption spectroscope (AAS) by Company Analytik Jena AG (Jena, Germany) DIN 38 406 part 18. To determine the content of ionic silver, 1 g of silvered PET spacer fabric, placed in a bottle of 100 ml distilled water, was shaken at room temperature and at different intervals at a frequency of 140 Hz, using a Promax 2020 platform shaker manufactured by Heidolph.

Breaking force and breaking elongation. The PET spacer fabric to be tested was conditioned in a standard climate according to DIN EN ISO 139 for 24 h. The breaking force and the breaking elongation of spacer fabrics were measured using a Z 100 tensile testing machine manufactured by Zwick GmbH & Co. KG (Ulm, Germany). The sample was held by clamps with polyvinyl chloride (PVC) surfaces and 3×10^7 Pa pressure.

Results and discussion

Optical properties

An untreated PET spacer fabric has a white color (Figure 2(a)). After dipping the PET textile materials during the wet-chemical silvering process, the fiber surface developed a brown coloring (Figure 2(b)). The brown colors represent the formation of the silver diamine complex on the fiber surface. A golden color (Figure 2(c)) on the fiber surface results from reducing the silvered spacer fabrics, as the ionic silver is transferred to the metallic silver by the reducing agent. No color change was observed after five months observation of the metalized PET spacer fabrics. So, the reduced spacer fabrics were not oxidized (Figure 2(d)).

The silver coating with a uniform silver layer distribution on the PET fiber surface was achieved by systematic analyses of all process parameters (pH of the solution, concentration of silver and L(+)-ascorbic acid, volume ratio of silane to silver, aging time of the silvering solution, silvering time and temperature, fixation time, and temperature) and their optimal adjustment. After the silvering of the PET spacer fabric using the wet-chemical dipping method, a golden color appeared on the fiber surface (Figure 3).

Completely silvered PET spacer fabrics and individual components are used in the application of silvered PET materials. The wet-chemical dipping method opens up many silvering possibilities (Figure 4), such as complete silvering (Figures 4(a) and (b)), one covering layer with the pile yarns (Figure 4(c)), only covering layers (Figure 4(d)), and the spacer fabric section (Figure 4(e)).

Surface characterization

The surface morphology (SM) of the untreated and the PET multifilament (Figure 5) and monofilament yarns (Figure 6) and their counterparts activated with sodium hydroxide solution was analyzed by means of scanning electron microscopy. The alkaline pretreatment of the PET yarn creates cavities or voids on the fiber surface. The silver (Ag) layer is deposited in these places.

The silvering of the activated PET spacer fabric was carried out using a $[\text{Ag}(\text{C}_8\text{H}_{22}\text{N}_2\text{O}_3\text{Si})_2]^+$ -complex solution (Scheme 1(a)). The *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane ($\text{C}_8\text{H}_{22}\text{N}_2\text{O}_3\text{Si}$) has two amino groups in the chain. Silanol is formed into an inorganic network on the fiber surface by the condensation of the amino silane and by the resulting hydrolysis (Schemes 1(b1) and (b2)). The nitrogen in the amino groups acts as the electron pair donor, giving an electron pair to the silver ions. The silver ions act as the electron acceptors, resulting in a coordination complex.

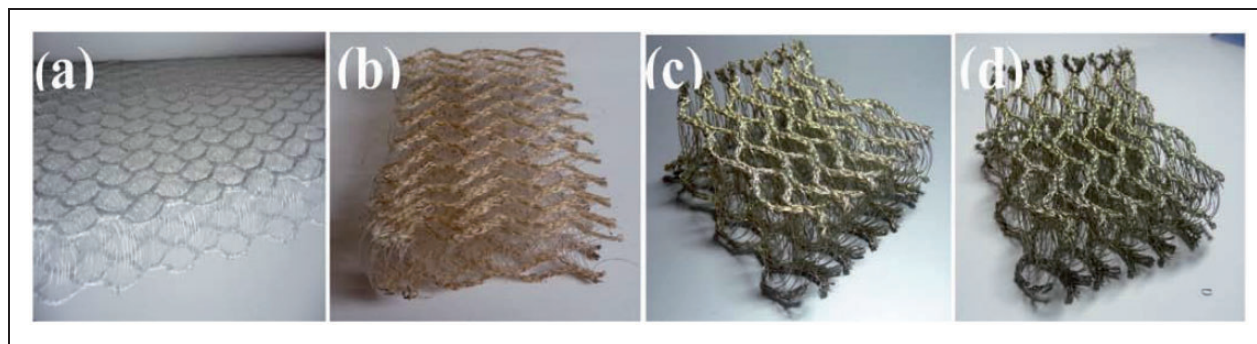


Figure 2. Color phenomena of polyethylene terephthalate spacer fabrics: (a) untreated; (b) silvered; (c) reduced; (d) observation after one month.

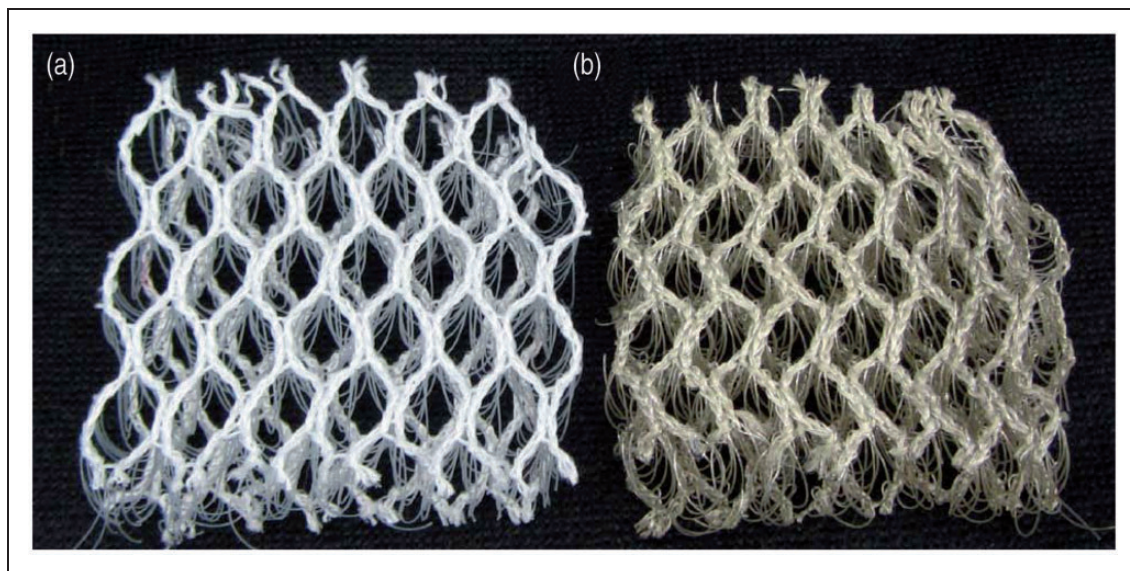


Figure 3. (a) Untreated and (b) silvered polyethylene terephthalate spacer fabrics.

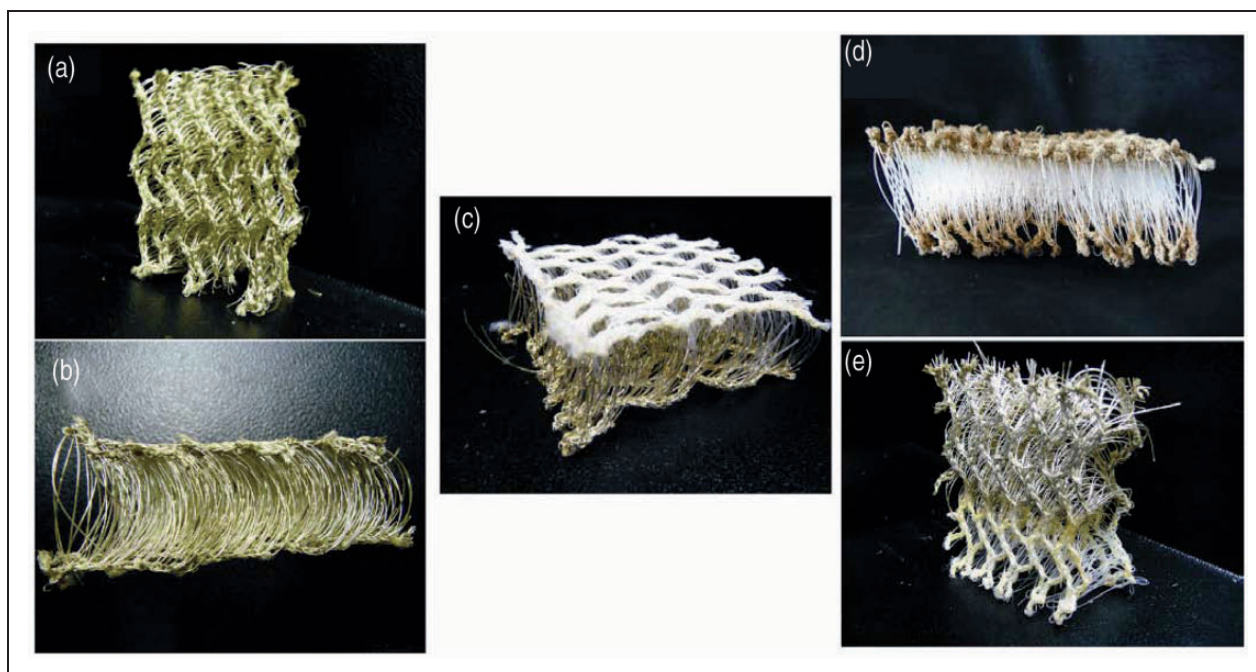


Figure 4. Wet-chemical silvering possibilities for polyethylene terephthalate spacer fabrics: (a) and (b) complete silvering; (c) one covering layer with the pile yarns; (d) only covering layers; (e) the spacer fabric section.

Two amino groups from the amino silane and one silver ion form a silver diamine complex. A silver diamine complex was formed with a primary amino group of two silane chains (Scheme 1(b1)) or with primary and secondary amino groups of a silane chain (Scheme 1(b2)).¹⁸ Ionic silver (Ag^+) on the fiber surface has been reduced to metallic silver (Ag° in Scheme 1(c))

by using L(+)-ascorbic acid. The reaction occurs according to the following equation:



Uniform silver layer distribution on the PET fiber surface was determined using a SEM. The SEM images of the PET multi- and monofilament yarns of the

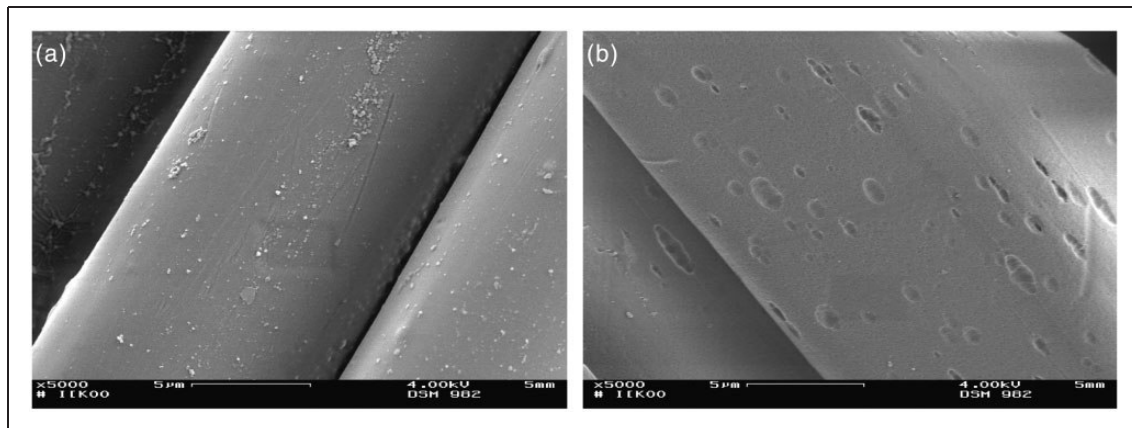


Figure 5. Scanning electron microscope images ($\times 5000$) of (a) untreated and (b) polyethylene terephthalate multifilament yarn (cover yarn) of a spacer fabric pretreated with 0.5 N NaOH.

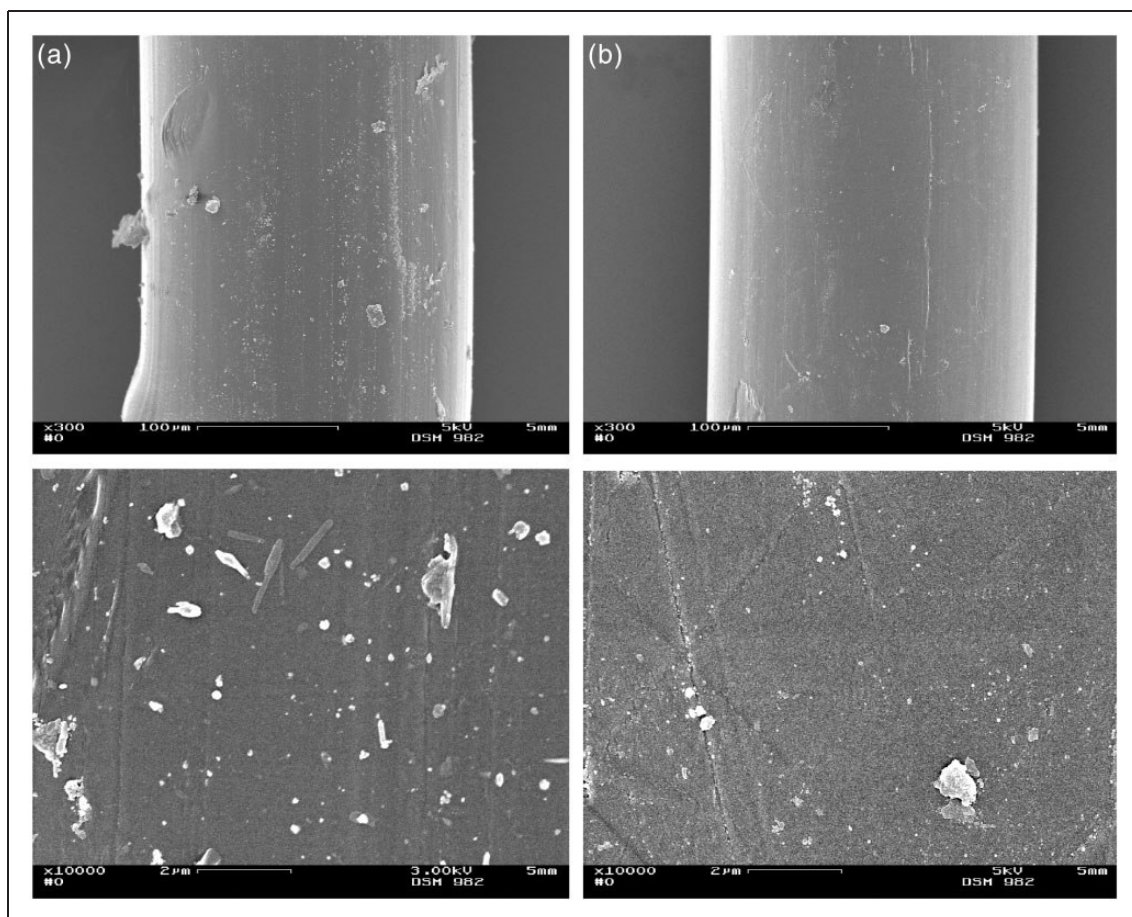


Figure 6. Scanning electron microscope images ($\times 300$ and $\times 10,000$) of (a) untreated and (b) polyethylene terephthalate monofilament yarn (pile yarn) of a spacer fabric pretreated with 0.5 N NaOH.

silvered spacer fabrics are presented in Figures 7 and 8. The fiber surface was fully covered with a silver layer after the silvering process. The silver particle size is $60 \text{ nm} \pm 10 \text{ nm}$.

Another adhesion possibility of the silver layer on the substrate was presented by mechanical anchoring. The sodium hydroxide (NaOH) solution slowly entered in to the outer PET fiber surface. By doing so, the NaOH

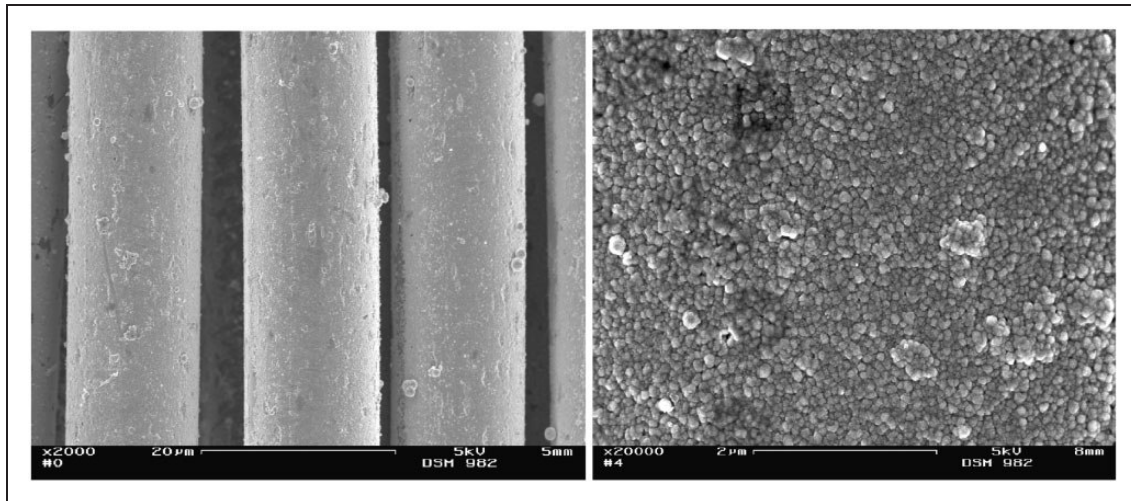


Figure 7. Scanning electron microscope images ($\times 2000$ and $\times 20,000$) of a silvered polyethylene terephthalate multifilament yarn of the spacer fabric.

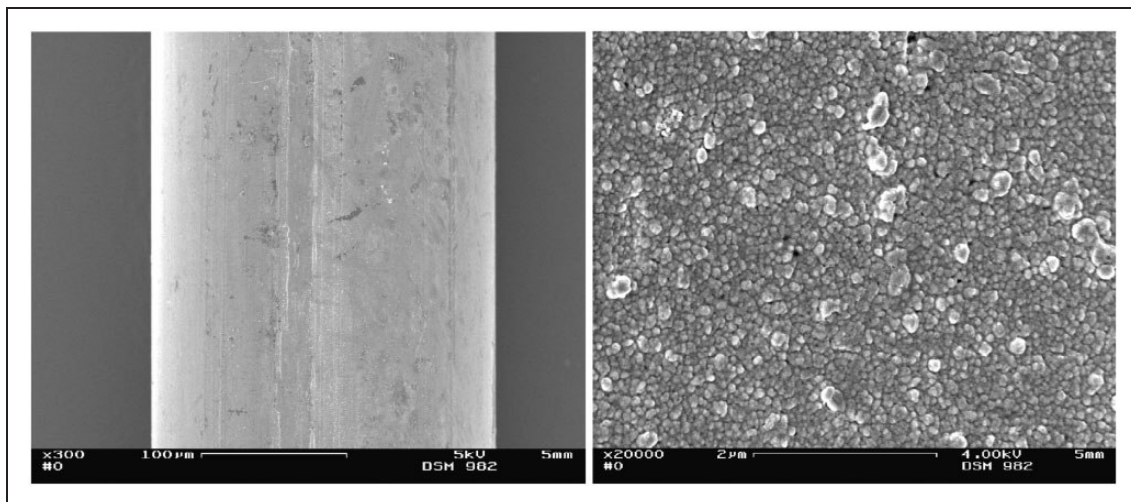


Figure 8. Scanning electron microscope images ($\times 300$ and $\times 20,000$) of a silvered polyethylene terephthalate monofilament yarn of the spacer fabric.

solution destroyed the amorphous areas of the polyester and created micro-fine holes or cavities (voids) on the fiber surface (see Figure 5). In these places silver was deposited and “ingrained” in the fiber surface. The silver coating on the PET fiber surface was generated based on this process (Figure 9).¹⁸

The number of carboxyl (COOH) groups at the PET fiber surfaces was increased by alkaline hydrolysis (Scheme 2). Due to the alkaline pretreatment, the polar part of the surface energy (SE) was significantly increased from 5.9 to 27.9 mN/m for the multifilament and from 6.6 to 9.7 mN/m for the monofilament. Thereby, the reactive center was created for the silver and the wettability was improved. As a consequence,

the adhesion between the silver layer and the fiber surface was significantly enhanced.

The SE of the multifilament yarn was 30.2 mN/m and the monofilament yarn 44.8 mN/m from the silvered spacer fabrics. They were determined with the Owens–Wendt–Rabel–Kälble method.

The carbon, oxygen, silicon, nitrogen, and silver percentages are semi-quantitatively determined by EDX analysis. EDX analysis results of the original, pretreated, and silvered PET spacer fabrics are reproduced in Figure 10 and Table 1. After the pretreatment of the PET yarn, the percentage of oxygen increased, while the percentage of carbon decreased. Alkaline hydrolysis caused the increased oxygen percentage. The ester

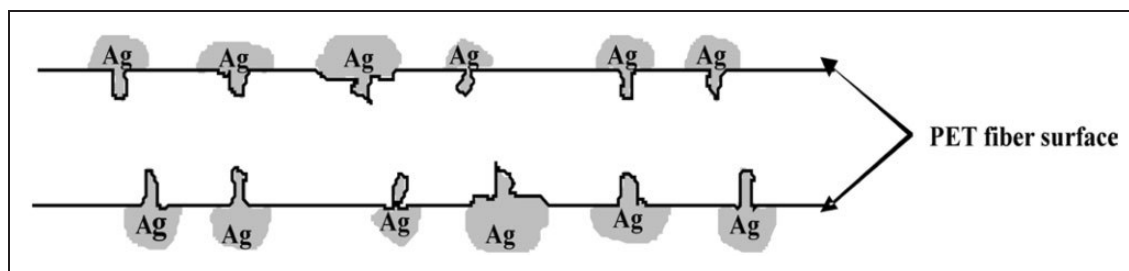
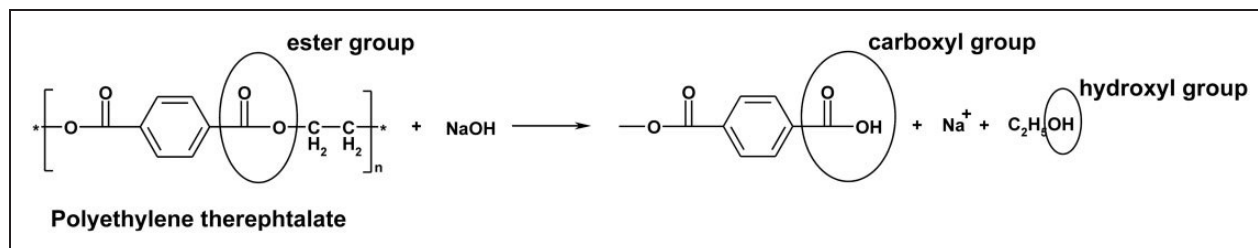


Figure 9. Exemplary layout of the mechanical anchoring of silver on the polyethylene terephthalate (PET) fiber surface.



Scheme 2. Chemical hydrolysis at the polyethylene terephthalate (PET) fiber surfaces after the NaOH pretreatment.

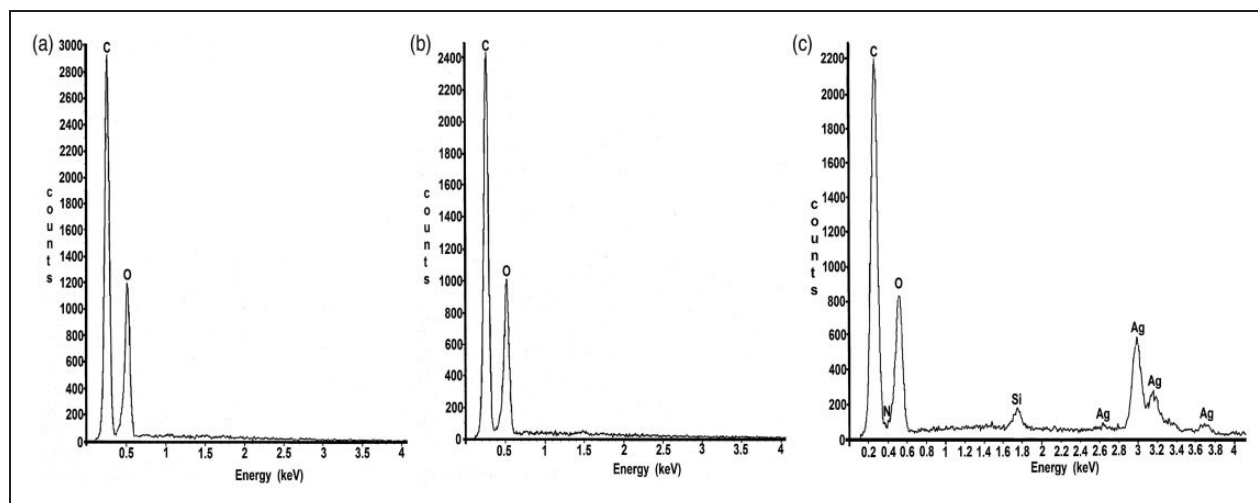


Figure 10. Energy-dispersive X-ray spectroscopy (EDX) analysis spectrums of (a) untreated, (b) NaOH-pretreated, and (c) silvered polyethylene terephthalate spacer fabrics.

groups ($-\text{COO}^-$) from the polyester are hydrolyzed, forming carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{OH}$) groups of the polymer chain end of the polyester. The silver percentages were 54.74% (wt.) and 59.21% (wt.), respectively, for multifilament yarn and monofilament yarn after the silvering process.

Figure 11 shows the 2θ XRD patterns of the silvered PET fiber surface. The peaks at 22° , 27° , and 31° correspond with the polyester substrate. The four strong characteristic peaks of the silvered sample at $2\theta = 44^\circ$, 52° , and 77° correspond with the crystal faces of (200),

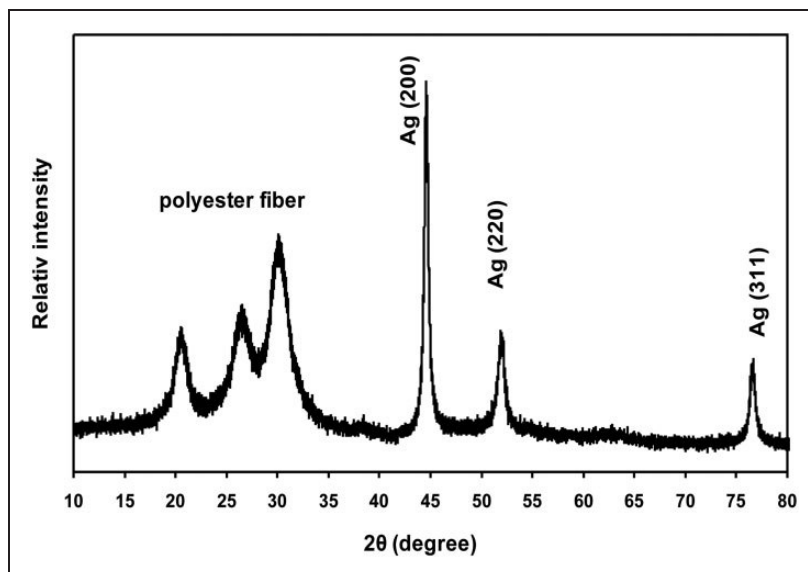
(220), and (311) of the silver (JCPDS card number 04-0783).^{19–23} However, no silver hydroxide (AgOH) or silver oxide (Ag_2O) was found.

Layer thickness

The PET spacer fabric to be silvered requires a thicker silver layer to increase the life-cycle time of the silvered spacer fabrics in the water/aqueous system up to three years. The silver layer thickness increases with higher silver concentration in the silvering solution, and with

Table I. Energy-dispersive X-ray analysis data of the untreated, NaOH-pretreated, and silvered polyethylene terephthalate spacer fabrics

Spacer fabrics	Element	untreated		Pretreated with NaOH		silvered	
		Atom (%)	Element (wt.%)	Atom (%)	Element (wt.%)	Atom (%)	Element (wt.%)
Multi-filament yarn from spacer fabrics	C	90.61	87.87	84.76	81.84	75.29	38.94
	O	9.39	12.13	15.24	18.16	9.64	5.88
	N	-	-	-	-	1.78	0.39
	Si	-	-	-	-	0.08	0.05
	Ag	-	-	-	-	13.21	54.74
Mono-filament yarn from spacer fabrics	C	91.61	87.92	83.89	79.73	74.40	34.09
	O	8.39	12.8	16.11	20.27	9.90	5.40
	N	-	-	-	-	1.15	0.75
	Si	-	-	-	-	0.10	0.55
	Ag	-	-	-	-	14.45	59.21

**Figure 11.** X-ray diffraction spectrum of silvered polyethylene terephthalate fiber surface.

longer silvering time (1 h). This silver layer growth leads to a closed silver film formation on the fiber surface. The layer thickness is 4.201 μm for the multifilament yarn and 4.440 μm for the monofilament yarn of silvered PET spacer fabrics, measured by means of confocal microscopy (Figure 12). The layer thickness difference between mono- and multifilament yarn is 0.239 μm .

Washing fastness

The adhesion stability of the silver layer on the fiber surface is an essential quality parameter, as it is crucial in retaining the functional characteristics of the textiles for their entire working life. Insufficient adhesion and

wash fastness of the metalized textiles often are the main problem for their use in the textile industry. Therefore, in the framework of this study, silvered PET spacer fabrics underwent several washing cycles in order to analyze their usability characteristics.

Wool (WO) is a natural fiber, while PA is a synthetic fiber. The chain molecules of wool contain different amino acids such as arginine, histidine, lysine, leucine, cysteine, tyrosine, etc., and NH_2 -, OH - and COOH -functional groups. PA has NH_2 -functional groups. If silver ions release in the water, then the NH_2 groups of both the fibers can form silver diamine complex with the released silver ions (Ag^+). For this reason, both PA and wool samples were selected for the washing test. The first washing liquor was turbid. The weight loss of

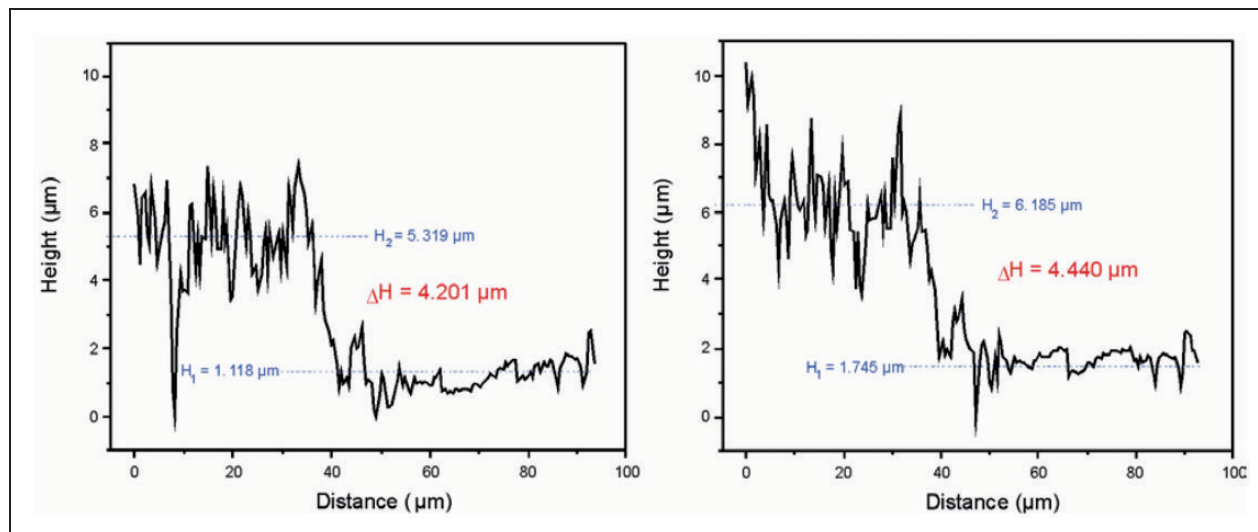


Figure 12. Layer thickness profiles of silvered (a) multi- and (b) monofilament yarn from polyethylene terephthalate spacer fabrics.

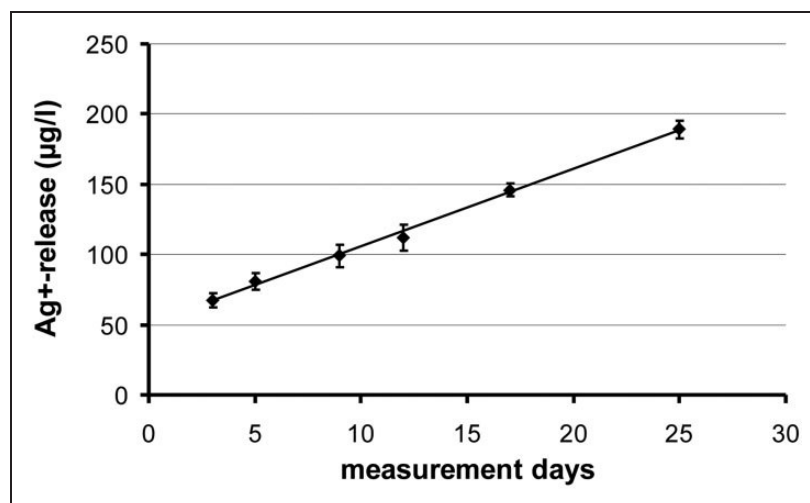


Figure 13. The amount of the Ag⁺-release in water after 3, 5, 9, 12, 17, and 25 days from the silvered polyethylene terephthalate spacer fabric.

the silvered spacer fabrics was found to be 1.09% after the first washing cycle, 0.37% after the fifth washing cycle, and unchanged after the tenth washing cycle. The released silver ion in the washing liquor with the function of the wash cycle was detected by means of AAS. The silver ion release 250 μg/l after first, 85 μg/l after five and 20 μg/l after ten wash cycles was obtained in the washing liquor. It can be assumed that the unfixed silver and the remaining reduction agent on the fiber surface dissolved into the washing liquor. Clear washing liquor was found after the fifth and tenth washing cycles and the color of the silvered PET spacer fabrics remained unchanged. The adjacent materials wool and PA do not absorb silver. The silver particle size (60 nm ± 10 nm) remained constant after

the washing. The coating of the applied silver layer was stable, which is proven by the washing fastness test.

Silver amount

Gravimetric analysis was carried out to examine realistic values of the silver on the textile surfaces after the first wash cycle. After heating the silvered textile materials in the muffle oven at 900°C for 3 h, only silver and the matting agent remained. The amount of matting agent in the untreated PET and inorganic component after the silvering was 0.3% and 1.2%, respectively. The amount of amino silane absorbed by the spacer fabrics was about 5%. The amount of the silver on the silvered PET spacer fabrics was 5.06% in

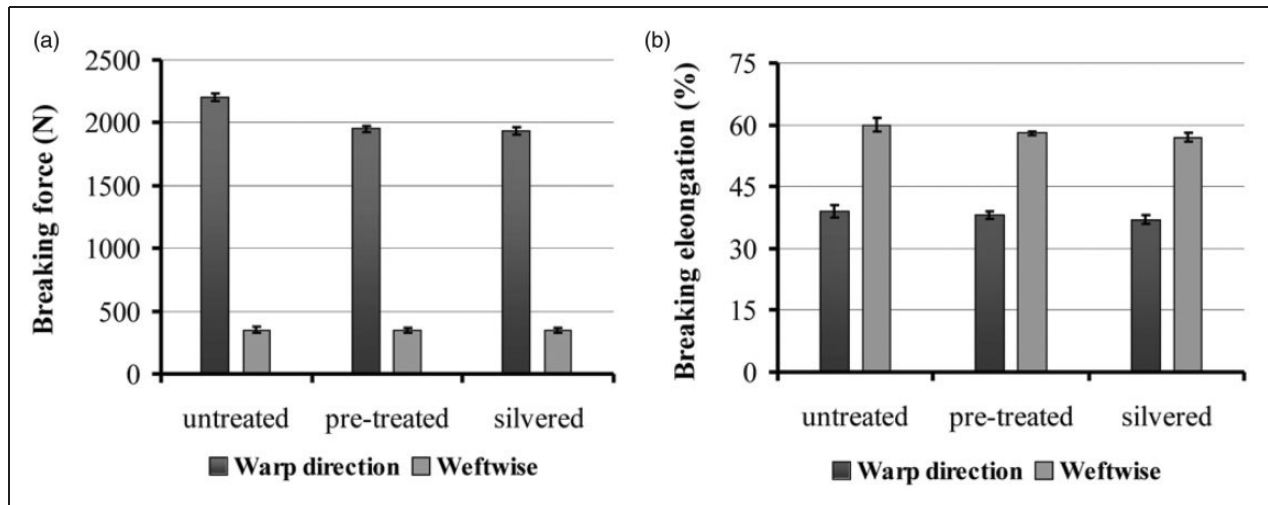


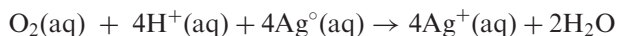
Figure 14. Breaking force (a) and breaking elongation (b) in the warp and weft directions of the original, pretreated, and silvered polyethylene terephthalate spacer fabrics.

multifilament yarn, and 6.03% in silvered monofilament yarn. The average silver content of the silvered PET spacer fabrics is 5.54%.

Silver ion release

The silvered spacer fabrics will be used in cooling or sealing water circuits in industries in the future. Therefore, it is important to detect the silver ion release from the silvered spacer fabrics in water.

Ionic silver (Ag^+), which is required for the microbiological efficacy, originates from the effects of oxygen in the air and humidity on the metallic silver (Ag^0) surface. The following equation applies:



The silver ion release property of silvered textile materials depends on internal (silver layer thickness, silver amount) and external (water temperature, the pH value of the water, and the water hardness) factors.¹⁷ The Ag^+ -release from the silvered spacer fabrics in water after 3, 5, 9, 12, 17, and 25 days is given in Figure 13. The WHO allows a maximum silver concentration of 100 $\mu\text{g}/\text{l}$ of water. The measured silver ion release values are all in the normal range of up to 9 days. After the silvering on the fiber surface, a compacted metal layer structure was formed, which has a layer thickness of about 4 microns, in the further sequence prevents the penetration of water into the interior of fiber. PET absorbs less humidity PET due to the relatively low SE and hydrophobic properties. So this material is suitable to eliminate the biological contamination in sealing or cooling water systems.

Breaking force and breaking elongation

The results of the tensile test show that the minimum loss of breaking force (11.8%) and breaking elongation (9.1%) occurred in the warp direction of the PET spacer fabrics due to pretreatment and silvering (Figure 14). However, the breaking force and elongation remained unchanged in the weft direction. It can be concluded that there is no significant change in breaking force and elongation in pretreated and silvered spacer fabrics.

Conclusions

The PET spacer fabrics were directly silvered by means of dipping. The results show the possibility for directly silvering of the surface of PET spacer fabrics by means of a newly developed wet-chemical dipping process. The key to the silvering of the PET 3D textile materials is the wet-chemical dipping method with silane-silver diamine complex solution. Before the silvering of the PET spacer fabrics, silver cations were complexed with the long-chain *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane. This complex is stable and suitable for the silvering of the PET spacer fabric. The morphological analysis was carried out to observe the surface microstructure of the silvered PET after the successful implementation of the developed concept for the silvering of PET spacer fabric. A completely covered silver layer was achieved on the multi- and monofilament PET yarn surface by means of the developed wet-chemical dipping method. XRD and EDX analysis spectrums showed that the silver was immobilized on the PET fiber surface. The silver layer thickness was 4.201 μm on the multifilament and 4.440 μm on the

monofilament yarn of the silvered PET spacer fabrics. After 10 wash cycles, the silvered PET spacer fabrics showed only a minimum weight loss, proving the stability of the achieved silver layer. The average silver content of the silvered PET spacer fabrics is 5.54%. No significant change of the breaking force and breaking elongation in the warp and weft directions of the PET spacer fabrics was found after the silvering.

The silvering processes were carried out at a low temperature ($35^{\circ}\text{C} \pm 3^{\circ}\text{C}$). Toxic chemicals were not used for the silvering. Therefore, the developed method is a more economical, ecological, environment-friendly, and easier technology than the previously known methods. No considerable effect on the physical properties of the metalized spacer fabric was found after the wet-chemical silvering process. Moreover, the measured values of silver ion release of silvered PET spacer fabrics in water after 9 days were lower than the limit values of the WHO. To test the life-cycle of the silver layer or the silvered 3D PET textile materials, the silver ion release in water will be tested on an industrial scale in future.

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