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Wet-chemical method for the metallization of a para-aramid filament yarn wound on a cylindrical dyeing package

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Abstract

High-performance yarns such as aramid fibers are nowadays used to reinforce composite materials due to their advantageous physico-chemical properties and their low weight. They are also resistant to heat and fire. Para-aramid filament yarns (p-AFs) wound on a cylindrical dyeing package have been silvered successfully by means of a newly developed wet-chemical filament yarn metallization process on a laboratory scale. The surface morphology of untreated and silvered p-AF was determined by means of scanning electron microscopy. The chemical structure of the surfaces (contents of carbon, oxygen, nitrogen and silver) was determined by means of energy-dispersive X-ray spectroscopy (EDX). The eliminated and newly formed groups of p-AF before and after silvering were detected by infrared spectroscopy (Fourier transform—attenuated total reflectance). After metallization, the silver layer thickness, the mass-related silver content and washing and rubbing fastness were assessed. Furthermore, textile-physical examinations concerning Young's modulus, elongation at break and electrical conductivity were performed. Subsequently, the electrically conductive p-AFs were integrated in thermoset composite materials reinforced by glass fibers and para-aramid.

Keywords

wet-chemical silvering, para-aramid, dyeing apparatus, electrical conductivity, composite material

High-performance yarns such as aramid fibers are nowadays used to reinforce composite materials due to their advantageous physico-chemical properties and their low weight. The distinctive anisotropic structure of para-aramid fibers gives them characteristic mechanical properties such as high strength and rigidity at low density. Aramid fiber materials, in comparison to brittle reinforcement fibers made from glass fibers (GFs) and carbon fibers (CFs), are tenacious, that is, energy absorption causes plastic deformation until breakage. The application of the electrically conductive carbon filament yarn as a strain gauge in thermoset and thermoplastic composite materials is limited due to its low elongation at break (0.8–1.5%) compared to para-aramid filament yarn (p-AF; 2.2–4.4%). p-AF is also predestined for components that have to be very light and are exposed to dynamic and impact loads. Due to its tenacity and high elongation, it is superior to GF

and CF in such cases. It is resistant to heat and fire.^{1–3} Para-aramid fibers have a higher tensile strength (2760–3000 MPa), Young's modulus (58–80 GPa) and melting point (>500°C) than, for comparison, polyether ether ketone (tensile strength: 90–120 MPa, Young's modulus: 3.8 GPa, melting point: 355°C).³ It is therefore necessary to develop a strain gauge sensor from metallized p-AF, with a high elongation at break of up to 4%, for thermoset or thermoplastic composite

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materials reinforced by glass or aramid fibers. The strain gauge should be able to withstand the high temperatures and pressures during the thermoplastic composite material production process.

Due to the extremely high crystallinity, aramid fibers are difficult to access for finishing chemicals. This makes the application of metal layers almost unfeasible. To improve the surface properties or the adhesion between the metal layer and p-AF fiber surface, the latter was pre-treated before metallization. Various chemical were used to that end, including a strong dimethyl sulfoxide solution,⁴ concentrated sulfuric acid solution,⁵ sodium hydride/dimethyl sulfoxide,^{6,7} sodium hydroxide solution/hydrochloric acid⁸ or liquid ammonia^{9,10} for the wet-chemical pre-treatment. In addition, the pre-treated p-AF fiber surface was sensitized using either a palladium chloride (PdCl_2)^{4,5} and tin chloride (SnCl_2)^{6,7,11} solution or a palladium(II)-hexafluoro-acetylacetonate^{12,13} solution. Belmas et al.¹⁴ impregnated the fiber surface with an aqueous triazinthiol solution before the electroless copper deposition. To increase the thickness of the copper layer on the fiber surface, Martinez et al.¹³ and Belmas et al.¹⁴ performed an above-critical, liquid carbon dioxide (scCO_2) heat treatment (150–200°C, 15–25 MPa) of the p-AF before coppering. The electrical conductivity of the aramid fiber surface was created using a conductive, aqueous indium-tin-oxide¹⁵ or polypyrrole solution.^{11,16–18} The electroless deposit bath used ethylene diamine/ammonia⁶ or silane¹⁹ as complexing agents. To keep the copper grains homogenous and small,¹⁶ additives such as polyethylene glycol (PEG) 1000⁶ or PEG 6000 and potassium ferrocyanide trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \times 3\text{H}_2\text{O}$)⁷ were added to the metallization solution. Zhao et al.¹² coppered the pre-treated para-aramid fabrics (150 × 150 mm²) while stirring at 1.160 r/min or under ultrasound application (42 kHz) by means of galvanic, electroless depositing. Martinez et al.,¹³ Zhang H. et al. and Schwarz et al.¹¹ report the electroless depositing of copper of p-AF surfaces. Schwarz et al.¹⁶ gold-plated the polypyrrole-copper-coated p-AF by means of electroless deposition. The coating solution consisted of gold salts, sulfite and thiosulfate. Numerous studies are concerned with the coppering, instead of the silvering of para-aramid fibers by means of galvanic, electroless deposition. Copper is less expensive than silver. Silver, however, has more distinctive antimicrobial and electrically conductive properties. In the $\text{Fe} < \text{Au} < \text{Cu} < \text{Ag}$ sequence, the antimicrobial effectiveness and electrical conductivity of the metals increases.^{20,21} In general, the abovementioned coppering process requires several steps, much stricter process control parameters (temperature, time, pH value, metal concentration) and the use of additives, as well as a

high consumption of chemicals, which is ecologically critical. The bath containers have to be lined with sizing material in places where they come into contact with the process solution. To remove these residues, the process often has to be extended over several days. The large amounts of bath liquids to be disposed of (galvanic, electroless methods) are much higher than in the galvanic, electrolytic processes. The baths are very susceptible to contaminations.

All of this led to the aim of creating special properties such as electrical conductivity and electromagnetic shielding for para-aramid fibers (which have great tensile strength, a high Young's modulus, melting point and elongation at break) in a single-step silvering process without pretreatment, in a high-temperature yarn dyeing apparatus, while they are wound on a dyeing tube.

Experimental details

Material

A Twaron 1000 p-AF by Teijin Aramid GmbH of Wuppertal in Germany with a fineness of 160 tex was used. The individual filaments had a diameter of roughly $d = 15.24 \mu\text{m}$.

N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine (Merck Millipore, Darmstadt, Germany) and silver nitrate (Grüssing GmbH, Filsum, Germany) were chosen as complexing agents for the corresponding silvering. Hexamethylenetetramine (VWR Chemicals, Dresden, Germany) was used as the reduction agent.

Metallization method

The p-AF was “randomly” wound (RW) crosswise on a cylindrical dyeing tube by means of an Autoconor X5 (Saurer Schlafhorst, Übach-Palenberg, Germany) winding machine with a winding speed of 250 m/min. The specifications of this dye tube are summarized in Table 1 and the positioning of the winding width to the silvering package is schematically shown in Figure 1.

Before the wound yarn was inserted into the High temperature (HT) dyeing apparatus for wet-chemical silvering, the stroke length (interior and exterior), the yarn weight and package diameter were noted. The density on the package was calculated (Table 2).

The wet-chemical metallization of filament yarns in package shape was performed for three dyeing tubs each about $137 \pm 5 \text{ g}$ with a liquor ratio of 1:10 on an HT-yarn dyeing apparatus (Vald. Henriksen BV) on a laboratory scale. The silvering and the reduction were carried out at $90 \pm 5^\circ\text{C}$ for 35 min in one process

Table 1. Specifications of used dye tube for silvering (polypropylene (PP))

Dye tube	Weight of empty dyeing tube (g)	Diameter of empty dyeing tube (mm)	Total length of the dyeing tube (mm)	Winding width on a dyeing tube (mm)
Cylindrical, with circular hole	65	Inner: 55 Outer: 65	170	149 ± 1

Figure 1. Positioning of the winding width of the dye tube.

step. The liquor was pumped through the package from inside (I) to the outside (O) and outside to inside (O→I) with a lower liquor flow (40 l/min (I→O) and 50 l/min (O→I) and a slow liquor exchange (3 min (I→O) and 5 min (O→I)) with a constant differential pressure (2 bar/2 bar). After the silvering, the yarns were washed with warm water (50°C) to remove unfixed silver. The parameters for the wet-chemical silvering process of a package shape in an HT dyeing apparatus on a laboratory scale are stated in Table 3.

In order to remove the moisture from the silvered yarn package, the filament yarn was dried in a single filament dryer (ALTERFIL® Naehfaden GmbH, Oederan/Germany) at an optimized temperature of 350°C with a dryer length of 10 m and a yarn speed of 125 m/min.

Analytical methods

Surface characterization by scanning electron microscopy. The morphological investigation of the fiber surfaces was conducted by a scanning electron microscopy (SEM; (DSM 982 Gemini Carl Zeiss AG (Jena, Germany))). The samples were viewed at 20,000-fold magnifications.

Elemental analysis. Through the combination of SEM with an energy-dispersive X-ray spectrometer (EDX), the content of elements such as carbon (C), oxygen (O), nitrogen (N) and silver (Ag) were determined semi-quantitatively.

Fourier transform infrared spectroscopy. For structural analysis fibers were investigated using a Fourier transform infrared-attenuated total reflectance (FTIR/ATR) Nicolet 6700 (Thermo Scientific) spectrometer. The infrared (IR) spectrum was taken in the frequency range from 4000 to 500 cm^{-1} .

Layer thickness. The diameter of the uncoated and silvered p-AFs was measured by means of an AxioImager M1m light microscope (Carl Zeiss, Jena, Germany) with the cross-sectional view at different points of the fiber surface. The layer thickness was calculated.

Mass-related silver content. The mass-related silver content of the silver-coated p-AF was determined by a ZEEnit 700 atomic absorption spectrometer (AAS) according to DIN 38 406 part 18.²²

Rub fastness. The rub fastness of silvered p-AFs was determined in accordance with DIN EN ISO 105-X12 by a crock tester type FD-11, since no separate standard exists for metalized textiles. Cotton fabric (CO) of about $5 \times 5 \text{ cm}^2$ was used as the rubbing fabric. CO fabric was undyed, bleached and freed from sizing and finishing agent. The change in color of the silvered p-AF and of the CO fabric were assessed with standard gray scales according to DIN 54002.

Washing fastness. Wool and polyamide specimens with a size of $4 \times 10 \text{ cm}^2$ were selected to cover the silvered p-AF during washing. To determine the wash fastness, the DIN EN 20 105-C03 (60°C, 30 min) standard for medium wash fastness was modified to confirm the experimental parameters for the testing of the silvered p-AF. The specimens were washed in a laboratory beaker dyeing apparatus (Mathis, Schweiz). The change in color of the silvered yarn, the weight loss and the silver concentration in the bath were evaluated.

Tensile strength and elongation at break. The samples (textile materials) were conditioned in standard testing atmosphere DIN EN ISO 139²³ for 24 hours before the test. The tensile strength, Young's modulus and elongation at break of the filament yarns were tested in accordance with DIN EN ISO 3314^{2,4} using a tensile

Table 2. Specifications of the yarn package format on a laboratory scale

Wind-ing art	Weight of empty dyeing tube (g)	Weight of the dyeing package (g)	Yarn weight (g)	Stroke length (exterior) (mm)	Stroke length (interior) (mm)	Diameter of the dyeing package (mm)	Density package (g/l)
RW	62.30	201.30	139.00	150	148	87.40	348.12

Table 3. The parameters for the wet-chemical silvering of filament yarn in package shape on an HT dyeing apparatus on a laboratory scale

Liquor flow direction	Liquor change (min)	Liquor flow rate (l/min)	Static pressure (bar)	Dynamic pressure (bar)	Temp. raising rate (°C/min)	Temperature (°C)	Treatment time (min)
inside to outside (I to O)/ outside to inside (O to I)	3 (I to O)/ 5 (O to I)	40 (I to O)/ 50 (O to I)	2.0 (I to O)/ 2.0 (O to I)	2.0 (I to O)/ 2.0 (O to I)	5	90 ± 5	35

testing machine Z2.5 (Zwick GmbH & Co. KG, Ulm, Germany).

Electric conductivity. The electrical resistance of the metalized yarns was determined in accordance with DIN 54 345 T5,²⁵ because there is no individual standard available for the textile sector. The linear electric resistance was measured by a Multimeter Fluke 45 (Fluka Germany GmbH) with two or four wire methods in different lengths with five measurements per sample. The mean values were calculated from these results.

Integration of metalized para-Aramid filament yarn in the thermoset composites. Electrically conductive p-AF was integrated as a functional yarn between the two layers of the textile structure of a glass-fiber-reinforced and a p-AF-reinforced thermoset composite in order to evaluate the finishing quality and the textile character of silvered p-AF as well as their processing ability. The impregnation of the textile structure with a thermoset resin system (EpikoteTM Resin MGS RIM 135/EpikureTM, curing Agent MGS RIMH 137 (Hexion Specialty Chemicals B.V.), mixing ratio 1:3) was carried out at 50°C for 15 hours.

Results and discussion

p-AF wound on a cylindrical dyeing tube was successfully wet-chemically silvered in an HT yarn dyeing apparatus by means of a new yarn silvering process on a laboratory scale. This wet-chemical filament yarn metallization achieves complete silver coverage of the p-AF surfaces and superior distribution across the entire winding length and width of the entire package.

Figure 2. Untreated (a) and silvered (b) para-aramid filament yarn on a dyeing package.

Silver complex formation on the para-aramid filament yarn surface

A successful attempt was made to apply silver to the p-AF surface on a package, using an aqueous solution containing silver complexes and reduction agent. This wet-chemical, single-step silvering process relied on an HT dyeing apparatus. The characteristic, yellow color of untreated p-AF (Figure 2(a)) was transformed into a consistent silver layer with silvery gleam on the p-AF surfaces (Figure 2(b)) across the length and width of the entire package.

In the longitudinal direction of the fibers, the para-aramid fiber materials (Scheme 1) are distinguished by rigid macromolecules, in which strong one-dimensional, covalent bonding forces dominate and which consist of amide bridges (–CO–NH–) and aromatic

rings. These molecule chains are connected laterally by hydrogen bridge bonds, and form layers that are regularly folded in the fibers' longitudinal direction. The axially arranged layers are connected with one another due to the van der Waals bond.^{1,26–28}

The NH_2 groups of neighboring polymer chains of para-aramid can form a double-coordinated silver diamine complex $[\text{Ag}(\text{NH}_3)_2]^+$ with a silver cation (Ag^+), as shown in Scheme 2(a). The tertiary amino groups of

Scheme 1. Structural unit of poly-*p*-phenyleneisophthaldiamide.^{26–28}

one *N,N,N',N'*-tetrakis(2-hydroxypropyle)-ethylenediamine ($\text{C}_{14}\text{H}_{32}\text{N}_2\text{O}_4$) can co-ordinate with a silver cation (Ag^+) into single $[\text{AgC}_{14}\text{H}_{32}\text{N}_2\text{O}_4]^+$ complexes (Scheme 2(b)), and the tertiary amino groups of $2\text{C}_{14}\text{H}_{32}\text{N}_2\text{O}_4$ can form double $[\text{Ag}(\text{C}_{14}\text{H}_{32}\text{N}_2\text{O}_4)_2]^+$ complexes with a silver cation.^{29,30} The hydroxyl groups ($-\text{OH}$) of $\text{C}_{14}\text{H}_{32}\text{N}_2\text{O}_4$ coordinate with para-aramid via hydrogen bonding or van der Waals or polar forces, as shown in Schemes 2(b) and (c).

The silvering and the reduction processes were carried out in a single stage. Hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) was used here as the reducing agent. This hexamethylenetetramine decomposes into formaldehyde (HCHO) and ammonia (NH_3) under the influence of heat.^{27,31} The reaction occurs according to the following equation

Formaldehyde is a strong reducing agent. It reduces the silver ions (Ag^+), which are bonded at the fiber surface, so that the insoluble metallic silver (Ag^0) is formed on the p-AF surface. The reaction was conducted according to the following equation

Surface morphology

The surface topography (ST) of untreated and silvered p-AFs was determined by means of SEM. Untreated p-AF is distinguished by an irregular surface structure with microparticles (Figure 3(a)). On metalized p-AF (Figure 3(b)), interconnected silver particles are visible

Scheme 2. Schematic depiction of a $[\text{Ag}(\text{NH}_3)_2]^+$ (a), $[\text{AgC}_{14}\text{H}_{32}\text{N}_2\text{O}_4]^+$ (b) and $[\text{Ag}(\text{C}_{14}\text{H}_{32}\text{N}_2\text{O}_4)_2]^+$ (c) complex formation on the para-aramid filament yarn surface.

Figure 3. Scanning electron microscope imaging (20,000 $\times$) of untreated (a) and silvered (b) para-aramid filament yarn surface.

in a very regular distribution. On the fiber surfaces, silver particles are formed as small, spherical particles.

EDX analysis

By combining SEM with an X-ray spectrometer (EDX), the percental distribution of chemical components on the untreated and the metalized p-AF could be determined semi-quantitatively. The results are summarized in Table 4. On a silvered p-AF surface, silver makes up an element content fraction of 14.83 (weight percent). The carbon weight fraction remained almost identical after silvering, while the content of nitrogen and oxygen were reduced. This is due to the anchoring of the $[\text{Ag}(\text{C}_{14}\text{H}_{32}\text{N}_2\text{O}_4)_2]^+$ complexes on the p-AF surface.

This EDX spectrum shows (Figure 4) that the silvered p-AF contains sufficient amounts of silver on the fiber surface.

An IR spectrum of untreated (a) and silvered (b) p-AF is shown in Figure 5. The peak 3308 cm^{-1} is attributed to the $\nu(\text{N-H})$ stretching vibration of the untreated p-AF. The aromatic ring $\nu(\text{C-H})$ and $\nu(\text{C-N})$ stretching are monitored at 3047 and 1393 cm^{-1} .^{32–34} The band at 726 cm^{-1} is the $\delta(\text{C-H})$ rocking vibration of aromatic rings. The p-AF in Figure 5(a) produces symmetric and asymmetric $\nu(\text{CH}_2)$ stretching vibrations at 2923 and 2854 cm^{-1} , respectively. The first peak located at 1637 cm^{-1} is related to the C=O vibration (amide I) and the second at 1538 cm^{-1} is related to the combined motion of N-H bending and C-N (amide II) and the last at 1301 cm^{-1} is related to the C-N , N-H and C-C combined vibrations (amide III).^{32–34} A large increase in absorbance at 1506 cm^{-1} corresponds to $\delta(\text{N-H})$ deformation stretching vibrations. The series of bands below 1400 cm^{-1} concern $\nu(\text{C-N})$ (1108 and 1016 cm^{-1}), $-\text{C-C}-$ (978 cm^{-1}) and $-\text{CH}_2$ (785 cm^{-1}) modes. The frequency appearing at 892 cm^{-1} is a characteristic

Table 4. Energy-dispersive X-ray spectroscopy analysis data of untreated and silvered para-aramid filament yarn

Element	Untreated		Silvered	
	Atom (%)	Element (wt. %)	Atom (%)	Element (wt. %)
C-K	72.69	67.97	80.26	66.69
O-K	13.48	16.00	9.63	10.63
N-K	13.83	16.03	8.13	7.86
Ag-L	–	–	1.99	14.83

frequency of the $\delta(-\text{OH}\dots\text{O})$ hydrogen bond.^{32–34} In case of the silvered p-AF, the peaks at 3310 and $2968\text{--}2813\text{ cm}^{-1}$ are attributed to the $\text{CH}_3\text{--CH}(\text{OH})\text{--CH}_3$ groups of the N,N,N',N' -tetrakis (2-hydroxypropyl) ethylenediamine (quadrol).³⁵ A large increase in absorbance at 1635 cm^{-1} corresponds to C=O deformation stretching vibration and the peak at 1234 cm^{-1} is a characteristic frequency of the C-O-H stretching of the quadrol.³⁵

Layer thickness

The analysis of the results shows that the average diameter of the untreated p-AF filaments is $15.24\text{ }\mu\text{m}$, while that of the silvered filaments is $16.94\text{ }\mu\text{m}$. The thickness of the silver layer after silvering of the p-AF is therefore $1\text{ }\mu\text{m}$ (Figure 6).

Mass-related silver content

After the wet-chemical silvering processing, the yarn fineness [tex] was increased because of the increment yarn weight [g]. The mass-related silver content of the silvered para-aramid was determined with an AAS ZEEnit 700 to be $3.9\% \pm 0.5\%$. These values were

Figure 4. Energy-dispersive X-ray spectrum of untreated (a) and silvered (b) para-aramid filament yarn.

Figure 5. Fourier transform infrared spectrum of untreated (a) and silvered (b) para-aramid filament yarn.

Figure 6. Cross-section view of the para-aramid filament yarn surface before (a) and after (b) wet-chemical silvering.

stable at the center, the inside and the outside of the package (Figure 7).

Rub fastness

A good rubbing fastness (3–4) of the silvered p-AF was found with standard gray scales tested with dry cotton fabric. The remaining silver was sufficient for electrical properties.

Washing fastness

The silvered p-AF was washed for 10 cycles according to standard DIN EN 20 105-CO3 and the wash fastness

was rated by the weight loss of the fabric. After the first wash, the silvered yarn changed slightly. After 10 washing cycles, only a minimal weight loss of 1.9% and a clear wash bath were observed (Table 5). The polyamide (PA) and wool (WO) fabrics did not absorb silver and no change in color was observed on the silvered p-AF filament yarns. Values between 4 and 5 on the gray scale for the staining were found in all the yarns. The review of the washing fastness demonstrated that the silver layer was stable. The remaining silver was sufficient for electrical properties.

Figure 7. The yarn count and weight-related silver content in the center, inside and outside of the filament yarn package after the silvering.

Figure 8. Length-related electrical resistances of the silvered para-aramid filament yarn.

Table 5. Weight loss of silvered para-aramid filament yarns after 10 washing cycles

Specimens	m_{before} , g	m_{1W} , g	m_{2W} , g	m_{5W} , g	m_{7W} , g	m_{10W} , g	Weight loss _{10W} %
I: WO	0.4908	0.4907	0.4907	0.4906	0.4906	0.4905	0.06
PA	0.2944	0.2944	0.2943	0.2943	0.2942	0.2942	0.07
p-AF	0.3547	0.3501	0.3498	0.3492	0.3487	0.3481	1.90

WO: wool; PA: polyamide; p-AF: para-aramid filament yarn.

Table 6. Mechanical properties of untreated and silvered para-aramid filament yarns (p-AFs)

Parameter	Untreated p-AF	Silvered p-AF		
		Inside	Center	Outside
Filament diameter (μm)	15.24	16.28	15.84	16.34
Fineness (tex)	159.4	184.1	172.2	185.8
Density (g/cm^3)	1.459	1.473	1.460	1.475
Young's modulus (GPa)	92.10 ± 4.51	86.12 ± 2.18	85.30 ± 3.01	86.24 ± 1.79
Elongation at break (%)	2.40 ± 0.05	2.33 ± 0.15	2.38 ± 0.19	2.32 ± 0.21

Figure 9. Schematic view of the contacting points of the electrically conductive para-aramid filament yarn.

Figure 10. Integration of the electrically conductive para-aramid filament yarn in a thermoset, glass-fiber-reinforced (a) and para-aramid-fiber-reinforced (b) composite material.

Table 7. Length-related electrical resistances of the silvered para-aramid filament yarns (p-AFs) before and after integration in the glass-fiber-reinforced and p-AF-reinforced thermoset composite

Composite	Sample number	Measuring length (mm)	Electrical resistance before integration in composite (Ω)	Electrical resistance after integration in composite (Ω)	Average value of electrical resistance after integration in composite (Ω)
Glass fiber reinforced	1	160	15.6	3.7	4.13
	2	160	16.3	4.8	
	3	160	15.7	3.9	
p-AF reinforced	1	160	16.9	3.4	3.67
	2	160	19.6	3.9	
	3	160	18.8	3.7	

Mechanical properties

The Young's modulus of the p-AFs in the initial state was 92.10 GPa. The elongation at break was 2.40%. The aromatic cores in the polymer chain cause the high fiber stability, as their large size keeps the polymer chain "stretched". The chains can therefore align highly

oriented in the fiber axis, resulting in outstanding mechanical properties. The filament diameter (μm), the fineness (tex) and the density (g/cm^3) were only slightly increased after the $[\text{Ag}(\text{C}_{14}\text{H}_{32}\text{N}_2\text{O}_4)_2]^+$ complex formation or silver layer creation on the para-aramid fiber surface. For wet-chemical silvered filament yarn compared to untreated filament yarn, the elongation

at break was reduced by 2.4% and the Young's modulus by 6.7% (Table 6). This is due to the heat treatment, which causes a polymer chain break or a chain fission at the N–C bond on the outer layers of the p-AF, or a partial breakdown of the hydrogen bridge bond of the aramid macromolecules.

Electrical conductivity

The results of the electrical resistance measurement show a linear correlation of electrical resistance and measuring length (Figure 8).

Integration of the silvered para-aramid yarns in fiber-reinforced plastic composite materials

The conductive p-AF was contacted by soldering with copper tin wire, as shown in Figure 9.

Metalized, electrically conductive and contacted p-AF as functional yarn was successfully integrated in thermoset composite materials reinforced with GF (Figure 10(a)) and para-aramid fibers (Figure 10(b)).

The electrical conductivity of the p-AFs was determined before and after integration in a GF-reinforced and a p-AF-reinforced composite. The results are summarized in Table 7. The length-related electrical resistance is determined after integration in a GF-reinforced and a p-AF-reinforced composite. No damage to the contacting points of the silvered p-AF was detected. The silvering quality is excellent and suitable for processing in a composite.

Conclusion

The newly developed yarn silvering technology has to be considered absolutely innovative, as there is no other wet-chemical silvering method for filament yarns available yet in which the yarns are wound on a dye package. In contrast to galvanic, electroless deposition, this process is uncomplicated, single-step, cost-effective and transferable to almost any kind of fiber, including polyester, polyamide, glass, and polyether ether ketone.

The results of the SEM showed that a regularly distributed, completely covering silver layer was achieved, which consists of spherical silver particles of similar sizes on the p-AF surface. The energy-dispersive X-ray spectrometer analysis confirmed the sufficient silvering of the p-AF surface. The eliminated and newly formed groups of p-AF before and after silvering were detected by infrared spectroscopy (FTIR/ATR). The mass-related silver content of the silvered p-AF was $3.9\% \pm 0.5\%$ and is identical in the center, outside and inside of the package. Identical mass-related silver content on the inside, center and outside of the package after silvering signify a homogeneous

application of the silver layer on the entire package body. A successful silvering of p-AF with the newly developed yarn silvering method shows no significant limitation of the stress–strain behavior after wet-chemical silvering. The silvered yarn is soft to the touch, ductile and electrically conductive. After 10 washing cycles, the silvered p-AF only showed a minimal weight loss, which proves that a stable silver layer was obtained. A good rubbing fastness (3–4) of the silvered p-AF was found with standard gray scales tested with dry cotton fabric. The electrically conductive p-AF was successfully integrated into thermoset composites reinforced with GFs and p-AF. After the integration, no damages to the contacting points were detected. A measuring of the electrical resistance over the measuring period revealed constant values. Further examinations of silvered p-AF as functional yarn for the integration in thermoplastic composite materials reinforced with GF and AF, as well as the examinations of fiber-matrix adhesion, will be the subject of future research. Due to the excellent thermal, chemical, mechanical and electrical properties of the silvered p-AFs, their application range is wide and suggests use in various fields, including security and construction, water technology, aeronautics, lightweight construction and automotive engineering.

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