Ultrathin, Flexible, and Transparent Polymer Multilayer Composites for the Protection of Silver Surfaces

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S *Supporting Information*
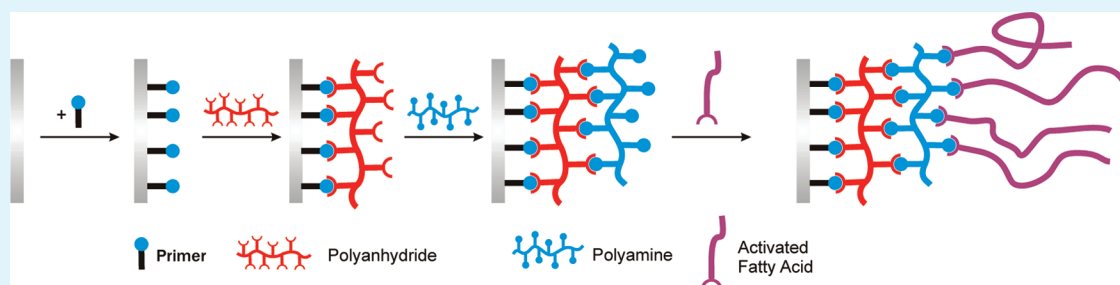
ABSTRACT: Silver coatings at the nanoscale became of high interest for the integration of electronic functionalities on all kinds of objects for daily use. In these thin coatings, corrosion is a big problem as it destroys these thin layers and leads to a loss of conductivity due to missing bulk material. For protection of thin silver coatings against H_2S induced corrosion, we developed nanocoatings based on the covalent layer-by-layer technique. We prepared composites by subsequent deposition of polyamines like polyethylenimine (PEI) or polyallylamine (PAAm) and polyanhydrides like poly(maleic anhydride-*alt*-methyl vinyl ether) (Gantrez) or poly(styrene-*co*-maleic anhydride) (PSMA). For the tuning of the hydrophobicity, the layers were terminated by reaction with palmitoylic acid derivatives. Reflectivity measurements, contact angle measurements, and AFM measurements were made to investigate how the coatings affect the surface properties. All coatings show a lower reflectivity below 450 nm compared to pure silver, depending on the number of layers deposited. The addition of a palmitoylic derivative to the surface increases the hydrophobicity, but only in case of the Gantrez-PVAm-composite, this approach leads to real hydrophobicity, reaching contact angles above 90°. AFM measurements show a decrease of the roughness of the polymer coated surfaces compared to the pure metal surfaces. Corrosion tests in a H_2S atmosphere show a good protective effect of the palmitoyl-terminated composites. Martindale abrasion tests on coated textiles reveal a good stability of the prepared polymer composites.

KEYWORDS: layer-by-layer, covalent layer-by-layer, corrosion, corrosion protection, nanocoating, transparent composites, reflectivity

■ INTRODUCTION

Metallized textiles and clothing are of high interest not only since the past few years as it is mentioned already in old fairy tales. In newer ages, next to simple fashion purposes, several further applications are possible, reaching from medical textiles for the therapy of skin diseases like neurodermitis or tissues with antibacterial coatings to the integration of electronic functionality like diodes, transistors smoothly into textile fibers or yarns.[1−4] The deposition of metal layers onto textiles usually affects its properties like flexibility, strength, haptics, durability, and hence decreases the wearing comfort.

Recent developments in metallization techniques utilizing plasma processes have made possible to deposit very thin layers — from a few to hundreds of nanometers — of metals like copper, silver, titanium, and others onto various substrates, like glass, polyesters, polyethylene, polypropylene, and natural fibrous polymers like cotton or wool.[5] This continuous plasma process of metallization is particularly suited to produce 100−200 nm thin, well-adhering metal coatings, with minimum impact on the mechanical property of the substrate. Relatively high conductivity of 10−100 Ω/cm combined with a neat metallic appearance can be achieved.[6]

Metallized surfaces produced by this technique may play a key role in the development and integration of electronics to build up smart objects or smart textiles. The metal of choice for imparting of electronic functionalities to textile fibers is silver. Its high conductivity, its oxidative stability, relatively affordable cost, and good sputtering efficiency in plasma process makes it
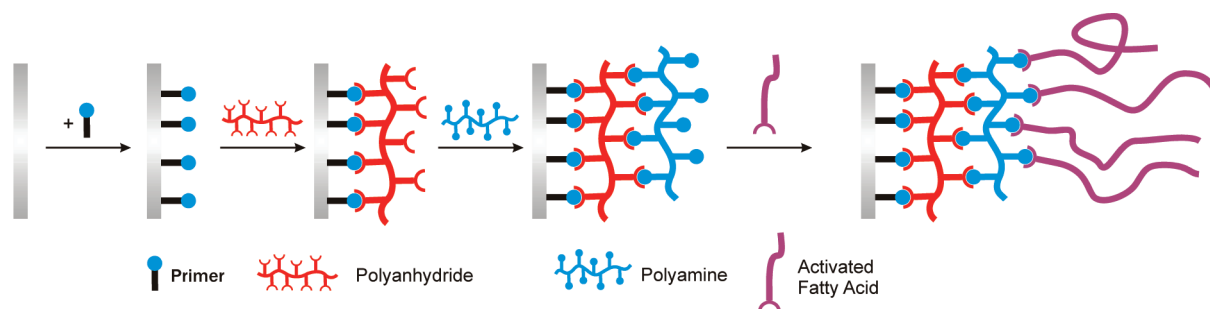
Figure 1. Schematic outline of the layer-by-layer technique. Deposition of a primer followed by stepwise addition of polyanydrides and polyamines leads to a highly cross-linked polymer network. Its properties are tuned by terminating the layers with an activated fatty acid (see text for details).

an ideal candidate for the development of conductive fibers. Despite a high oxidative stability of silver, it suffers from sulfur induced corrosion. The source of sulfur based corrosion for silver could be from human sweat or the environment and will lead to a decrease or loss of optical and/or electronic functionality. This problem becomes very critical where the thickness of silver deposited is only 200 nm or less.

Many effort has been spent on the research of corrosion and hence many methodologies exist to prevent various types of corrosion.[7−13] One approach is the formation of a protective monomolecular self-assembling layer on the metal surface.[11,14−17] Although such monomolecular layers do not alter the mechanical properties of the substrate, they might have faults and maybe be prone to excessive abrasion, which significantly limits its applicability. Moreover, sulfides of transition metals are chemically often the most stable compound[18] and hence a thermodynamically anticorrosive H_2S-stable surface modification is infeasible. Thus, a method to prevent sulfur-induced corrosion is to avoid the direct contact of silver with the environment (e.g., human skin). However, adding just a protective coating (e.g., like a thick polymer coating) on top of a metallized textile fiber may adversely affect the mechanical properties of the material.

The layer-by-layer approach, described by Decher[19−21] for polyelectrolytes and Bergbreiter[22] for covalently bound polymer networks allows the production of stable submicrometer polymer coatings of a defined thickness using self-assembling mechanisms. Both techniques were applied to a wide range of materials and polymers.[23−39] Extensive studies on the anticorrosive effect of polyelectrolyte multilayers were made by Shchukin and Moehwald, using polystyrene sulfonic acid, polyamines, and further additives like for example zircona or benzotriazole.[40−44]

In our approach, we followed the covalent layer-by-layer approach to combine anticorrosive surface active adhesives with the prevention of contact of corrosive media by using polyanhydrides and polyamines. The formation of cross-linked polymer composites provides a suitable stability for the use in mechanically demanding applications. As polyamides are a common material in textile applications[45] we decided to build up the polymer network by use of polyanhydrides like poly(maleic anhydride-*alt*-methyl-vinyl ether) and polyamines or imines like polyallylamine (PAAm) or polyethylenimine (PEI). For functionalization of the silver surfaces with amino groups we used 4-aminothiophenole contrary to the literature where ω-mercapto-alkanoic acids are used and which need further activation of the carboxylic group.[46,47] To modify the surface properties of the multilayer composite, we deposited reactive fatty acid derivatives on the last amino polymer layer.

This procedure opens a great variety of structurally different fatty acids with various functional groups like double bonds, hydroxyl groups and others. They are commercially available and can be used directly after activation. This allows a fine-tuning of surface properties.

In this paper, we describe our studies of adopting the covalent layer-by-layer approach to silver coated glass slides and furthermore on plasma-silvered textiles. We present UV/vis reflection measurements to determine the influence of the deposited polymer layers on the optical properties of the surfaces in the case of polymer coated glass slides and on polymer coated silver textiles. We evaluated the preventive effect of the coatings against H_2S-corrosion. We also assessed the stability of the polymer multilayer on metallized textiles using established Martindale abrasion test. This harsh testing conditions allows a good insight into the practical rigidity of the deposited and surface polymer multilayer.

■ RESULTS AND DISCUSSION

Deposition of Primary Polymer Layers. The synthesis of the covalently branched polymer films by stepwise reaction of polyanhydrides and polyamines/-imines (covalent layer-by-layer, outlined in Figure 1 is a well-known approach and described in the literature.[13,22,47,48] We adopted this method for the preparation of homogeneous thin films (8−10 nm) for the deposition onto silver-coated glass substrates.

As primary layer, 4-aminothiophenol **1** was used. Its structure prevents forming non- or less-reactive surface complexes by acting as multidentate ligand by binding with both functional groups − thiol and amine − onto surface silver atoms. These aminogroups are used as anchor for the reaction of polyanhydrides. Angle-resolved XPS measurements[49−51] at photoemission angles of 15 and 75° show a decrease of the intensity of nitrogen to sulfur (N:S ratio) toward higher angles from 1.73 to 1.26. This confirms the binding of 4-amino-thiophenol **1** to the silver surface via the thiol group and not via the amino group.

Poly(methyl vinyl ether-alt-maleic anhydride) **2** or poly-(styrene-co-maleic anhydride) **3** were used as polyanhydrides (Figure 2). These were deposited by simply immersing the primer coated silver substrates into a 10 wt % solution of the desired polyanhydride and − after a certain reaction time − washing off excess material by thoroughly rinsing with THF. Afterward, the polyanydride coated substrates were dipped into a solution of polyvinylamine **4** or polyethylenimine **5**, and after a while, the excess polymer was removed by rinsing with THF.

Termination with Fatty Acid Layers. To transform the polyamine terminated surface into a hydrophobic composite, we used the well-elaborated method of acylation via N-hydroxy-
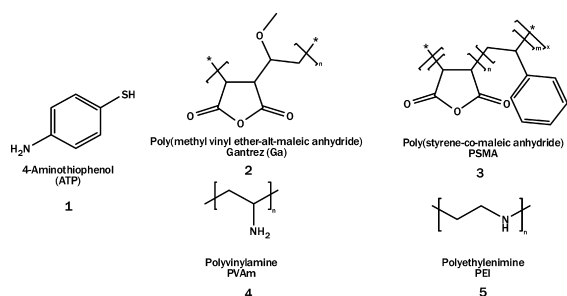
Figure 2. Primer and polymers which are used for the formation of the cross-linked polymer layers according to the layer-by-layer-method..

succinimid esters.[52,53] The unreacted amino groups of the last polyamine layer were acylated by palmitoyl-N-hydroxysuccinimide ester **9** as outlined in the scheme in Figure 3. This ester
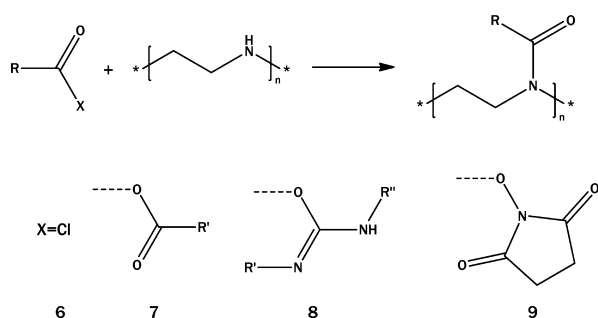

Figure 3. General reaction for performing the hydrophobization of the amino layers using PEI for example. Reactions were carried out with pyridine (acyl chloride) or triethylamine (NHS-ester) as base. The isourea is an intermediate of palmitoylic acid and carbodiimide reagents.

was synthesized according to a literature procedure,[54,55] by simply treating commercially available palmitoyl chloride with 1.1 equiv. of N-hydroxysuccinimide and triethylamine as base in 82% yield.

Trials to use palmitoyl chloride **6** as acylating agent led to delamination of the whole silver surface from the glass slide, independently of whether or not pyridine or triethylamine as base was added. Using 1-ethyl-3(3-dimethylaminopropyl)-carbodiimide (EDC) or dicyclohexylcarbodiimide (DCC) as activator of palmitoylic acid via an intermediate isourea **8** led only to insoluble products and therefore no or incomplete reaction with the surface occurred even if N-hydroxy-succinimide was added.

Properties of the Layers. *Surface Properties.* AFM measurements were made on Gantez-PVAm-palmitoyl coated glass slides to investigate the surface roughness before and after coating (Figure 4) and furthermore the homogeneity of the coatings. The two-dimensional root-mean-square roughness R_q of the uncoated silver surface is about 2050 pm within an area of 500×500 nm^2. The surface of the coated substrates (Figure 4C) shows some grains on a flat surface. The average height of these grains is about 20 nm and the dimensions are about 1 μm in shape. They may originate from polymer aggregation when deposited onto the surface. In flat areas, R_q is between 1600 and 1950 pm measured on two different positions of the sample and as expected less rough than the plain silver surface. This is caused by a filling effect of the deposited polymer composite which flattens the surface. Trials in measuring SEM pictures of the coated surfaces did only show vague profile above the silver

layer and are therefore omitted. Furthermore, EDX element mapping measurements confirmed the homogeneity of the deposited coating additionally to the AFM measurements.

Chemical Properties. One interesting question was, if the same level of hydrophobicity can be reached with our approach, compared to the system described by Bergbreiter and co-workers.[13] They deposited *n*-octadecylamine onto the second generation of polyanhydride for termination and hydrophobization. With this method, a contact angle against water of about 102° starting from 61° on polyanhydride was reached. Using the procedure described above, we prepared four composite systems consisting of polymers shown in Figure 2. The contact angles are depicted in Table 1. As can be seen, the polystyrene-*co*-maleic anhydride-polyamine based layers are more hydrophobic (approximately 50−60°) than the Gantrez based thin layer systems, where the contact angles are approximately half the values (∼30°). After terminating the polyamine layers with fatty acid NHS-ester, this order changes and the Gantrez based films become more hydrophobic with a contact angle above 100 degrees, in contrast to fatty acid terminated polystyrene based films, where hydrophobicity also increased compared to the nonterminated films, but still staying in the hydrophilic region with contact angles below 90°. An explanation of this higher hydrophilicity of the polystyrene-*co*-maleic anhydride based films is the much lower number of anhydride groups in the polyanhydride than in the bound polyamine or polyimine. Thus, more aminogroups will remain unreacted into the formed polymer film consisting of poly(styrene-*co*-maleic anhydride)-polyamine/polyimine than in polymer composites based on Gantrez, where each second monomer unit consists of an anhydride group.

Optical Properties. For the optical properties of the polymer coatings, UV/vis reflectivity measurements of the coated glass slides were made to determine, if and how the growing polymer composites deposited on the surface result in a change of the reflected spectra. For this, we measured spectra after the deposition of each layer. The reflectivity spectra of the multilayer composites Ag-ATP-polyanhydride-polyamine-palmitoylic acid with polyanhydride: Gantrez, PSMA; polyamine: PEI, PVAm are displayed in Figure 5a−d.

Within the range of 250−475 nm, all coated glass slides show a decrease of reflectivity compared to pure silver. Table 2 shows the maximum differences of reflectivity compared to uncoated silver in the range of 340−450 nm. As expected, the intensity of this absorption band increases with the number of layers deposited. Above 475 nm, the reflectivity of all coated samples is almost the same as pure silver. The band at 319 nm belongs to the plasma edge of silver. The primary 4-aminothiophenol layer decreases the reflectivity to 93% at a wavelength of 354 nm compared to silver.

Influence of Polyanhydrides. The deposition of both PSMA and Gantrez polyanhydride layers decreases the reflectivity to 88 (PSMA, Figure 5 c,d) and 86% (Gantrez, Figure 5 a,b) compared to that of uncoated silver. The slightly higher decrease of the Gantrez coating compared to the PSMA layers is caused by the higher amount of carbonyl groups in Gantrez than in PSMA. This behavior continues at ranges below 320 nm, where Gantrez-coated slides also have less reflectivity than PSMA slides. The maximum of the decrease is moving from 354 nm on aminothiophenole coated slides to 363 nm on PSMA coatings and to 365 nm on Gantrez coatings, respectively.
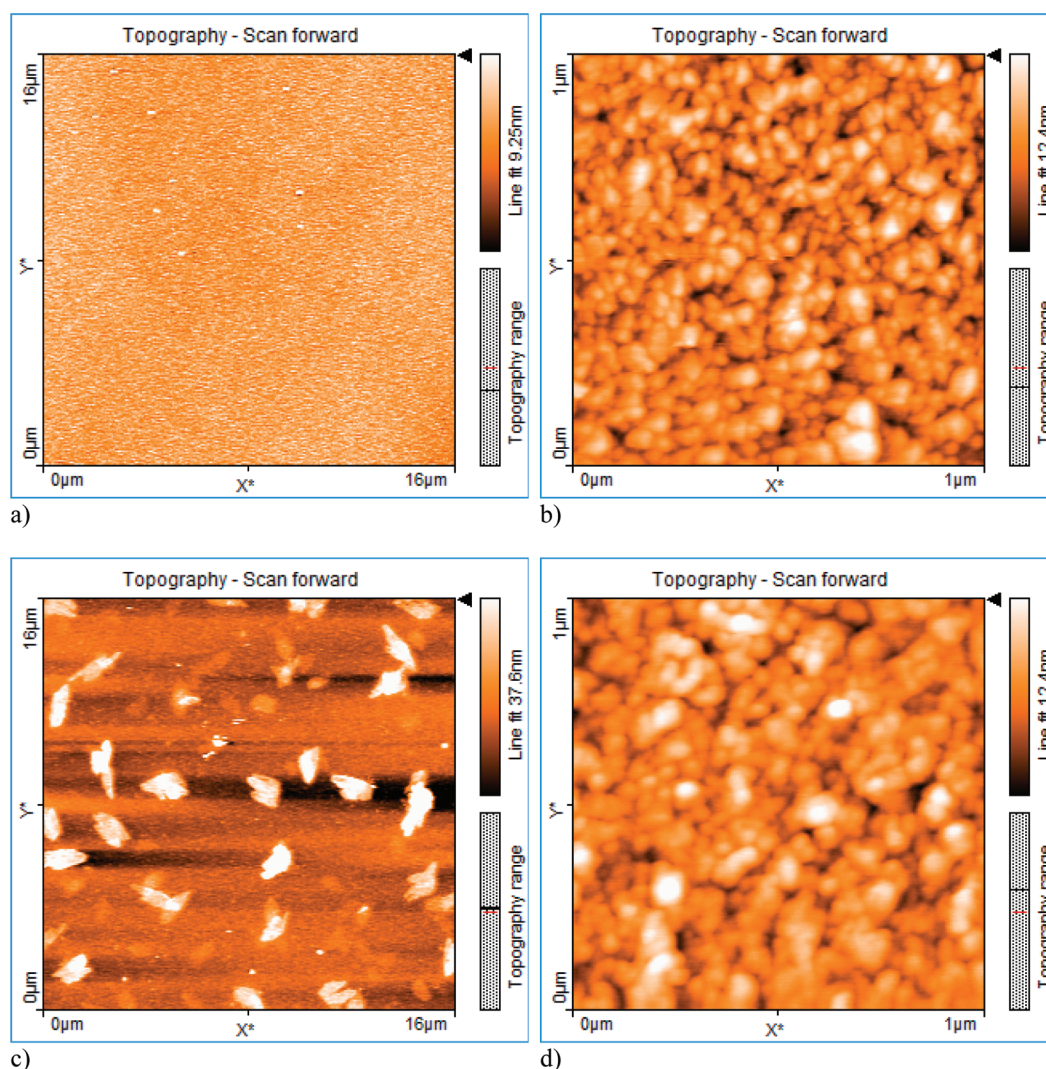
Figure 4. AFM images of the surface topography: (a, b) silver, 16 and 1 μm; (c, d) ATP-Gantrez-PVAm-palmitoyl coated substrates (16 and 1 μm).

Table 1. Water Contact Angles of Polymer-Coated Silver Glass Substrates[a]

	PSMA		Gantrez (Ga)	
	PEI	PVAm	PEI	PVAm
plain	50	62	34	25
fatty acid termination	72	80	100	109

[a]Gantrez-based polymer networks give a higher shift from strong hydrophilic to hydrophobic.

Influence of Polyamines. The further addition of a polyamine layer reduces the reflectivity. Interestingly, additional layers of both polyamines PEI and PVAm affect the reflection spectra slightly more in the case of the PSMA-based composites than on the Gantrez composites. This difference may be due to an interaction with the optically more active aromatic side chains of the polystyrene than the optically less active methyl ether side chains of Gantrez. In the case of PVAm-based coatings compared to PEI based composites, reflectivity increases in the range of 340−355 nm with a maximum at 345 nm, whereas in PEI-based coatings, the reflectivity still decreases (Figure 6).

Influence of Palmitoyl Termination. The addition of the fatty acid termination layer increases the absorption band additionally independent of the polymer. This effect can be drawn back to the increase in the amount of carbonyl groups in the polymer composites. The decrease in reflectivity is higher in PVAm-based composites. This shows the higher acylation rate of the primary amino groups of PVAm compared to the mostly secondary amino groups of PEI.

Corrosion Protection. To test the protective effect of the coatings described above, silver coated glass slides with polymer coatings were exposed to 0.5 ppm H_2S-atmosphere under constant humidity and continuous gas flow in a pollution gas chamber for two days. The reflectivity of the corroded samples were measured in ranges between 250 to 800 nm. The spectra are shown in Figure 7a−d.

In addition to the reflectivity rate itself, the presence and intensity of the plasma gap at 320 nm is also a good indicator for the quality of the protection coating.[9] It shows whether or not the reflection is caused by silver.

As expected, the unprotected silver turns to black, when exposed to H_2S-asmosphere. In contrast to our expectations the impact of H_2S to coated surfaces does neither correlate with the number of layers nor with the fatty acid termination but strongly depends on the deposited polymer types.

The generally best systems for protection of H_2S-induced corrosion are the Gantrez-PEI-based coatings (Figure 7b). A
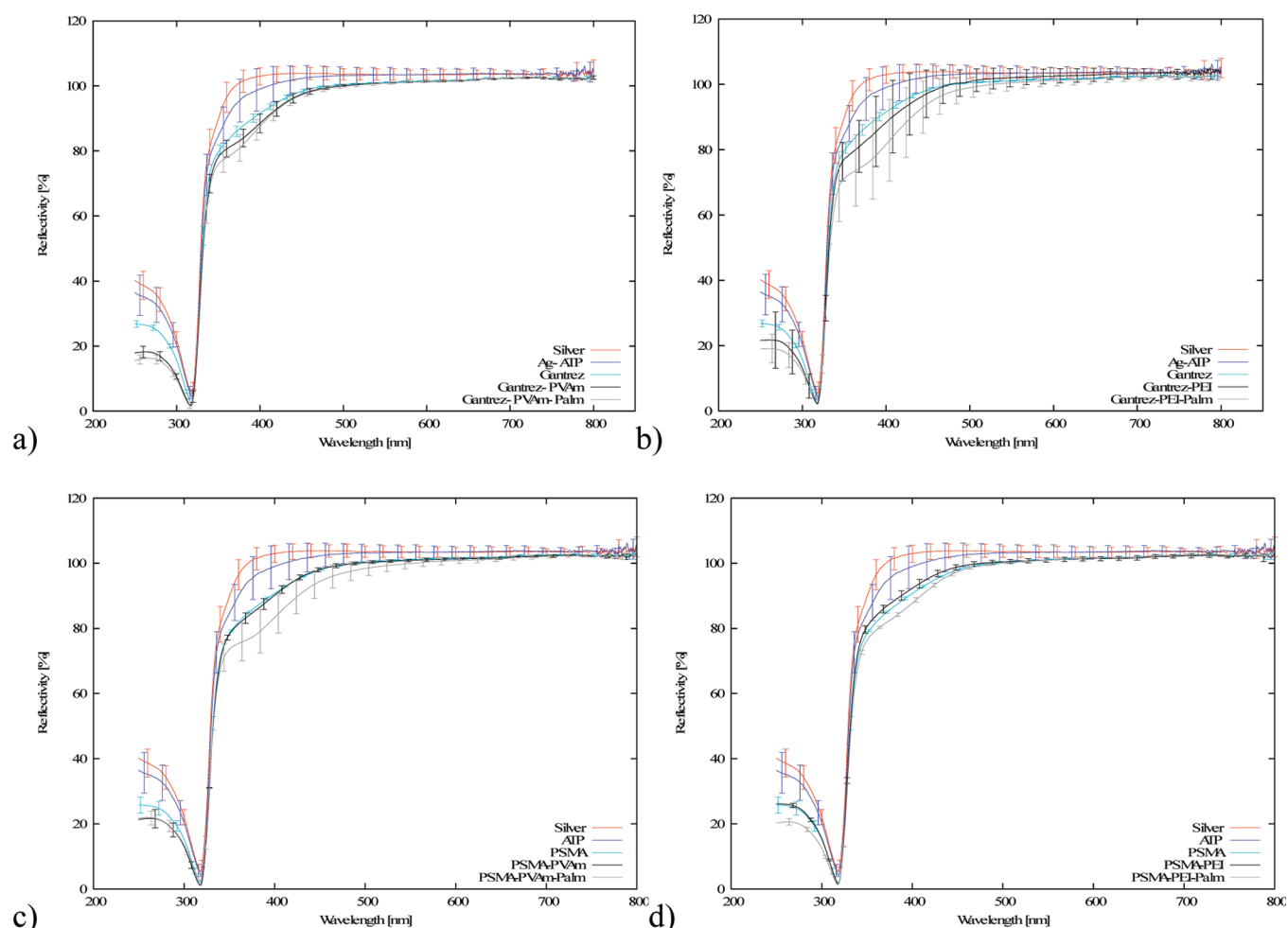
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Figure 5. Lambda-9 reflection spectra of the coating systems Ag-ATP-polyanhydride-polyamine-palmitolyic acid showing the influence of each subsequently deposited layer. The spectra were collected after each deposited layer. (a) Ag-ATP-Gantrez-PVAm-palmitoylic acid, (b) Ag-ATP-Gantrez-PEI-palmitoylic acid, (c) Ag-ATP-(PSMA)-PVAm-palmitoylic acid, (d) Ag-ATP-(PSMA)-PEI-palmitoylic acid.

Table 2. Relative Reflectivities of the Composites, In Comparison to Uncoated Silver after Each Deposited Layer. The Maximum Difference Is Given in Percent Reflectivity (rel. reflectivity/wavelength) of Maximum Difference

	PSMA-PEI	PSMA-PVAm	Gantrez-PEI	Gantrez-PVAm
ATP		93/354		
polyanhydride	88/363		86/365	
polyamine	82/362	81/369	83/363	84/366
fatty acid	80/363	78/369	83/364	82/368

single Gantrez layer already shows a good protective effect, which can be increased by the addition of a further layer of polyethylenimine (PEI). The addition of palmitoylic acid unexpectedly leads to a decrease of protection. But because of a more consistent reflection over the whole visible spectral range, the palmitoyl-terminated coatings appears less colored than the other two samples. All coated samples show a distinct plasma gap and hence a good protection behavior.

In contrast to the Gantez-PEI-coating system, Gantrez-PVAm-based coatings (Figure 7a) are inferior to a single Gantrez-coating. The Gantrez-PVAm-composite offers a marginal protection. The reflectivity is about 40% together with a weak distinctive plasma gap. The palmitoyl-terminated samples show an inconsistent behavior. In case of the

palmitoyl-terminated Gantrez-PVAm-composites there are two groups. One shows a superior protection with a defined plasma gap. The other reveals a complete loss of the protection by a rather low reflectivity ratio and a complete loss of the plasma gap.

In contrast to the Gantrez based composites, all PSMA based composites fail completely during the H_2S-corrosion test in both criteria, reflectivity and plasma gap, except one sample of plain PSMA. Even additional layers of the polyamines PEI and PVAm (Figures 7c,d) and fatty acid termination were not improving the protective effect of the composites. The reflectivity of the samples were 40% at best over the whole visible range (400−700 nm). Additional measurements at the intact PSMA-sample revealed, that its high reflectivity is not only located at a single spot but spread over the whole sample surface and shows surprisingly a high consistency.

In contrast to our expectations no hydrophobic composite, terminated with palmitoylic acid, showed better results than the nonterminated coatings. This reveals that the hydrophobic coatings are a weak barrier for the H_2S molecule. Because of the reduced polarity of the hydrophobic network no interaction with the H_2S molecule occurs and hence does not impede the diffusion through the polymer layer. The interpretation, that the interaction of the polymer coatings with H_2S by polar groups result in a protective effect is supported by the
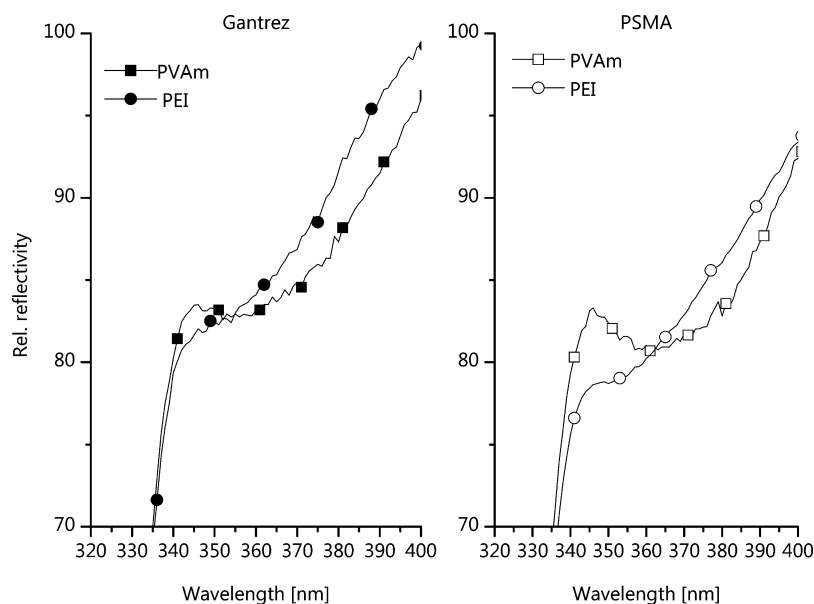
Figure 6. Differences in the reflectivity between PEI- and PVAm-based composites show an increase of reflectivity at 345 nm for PVAm composites and therefore forms a reflection minimum at about 360 nm. The reflectivity of PEI composites decreases continuously. For better comparability, the graphs show only the spectra of the palmitoyl terminated layers. Left, Gantrez-based composites; right, PSMA-based composites.

observation that Gantrez and Gantrez-PEI systems, which both contain a high density of polar groups are the best protecting composites tested. This interpretation is confirmed by the observation that the protective effect of most PSMA based coatings is rather low. PSMA itself contains only a minor amount of anhydride groups whereas non interacting styrene groups are main part of the polymer. The worse protection of Gantrez-PVAm composites compared to plain Gantrez or Gantrez-PEI coatings can be explained by polarity effects too. Under the chosen testing conditions, the anhydride groups of Gantrez coating will be almost completely hydrolyzed to carboxylic acids. By the reaction of the PEI polymer, which mostly consists of secondary amino groups, each reacting anhydride group forms an amide group and a corresponding carboxylic acid group, which neutralizes with a further amino group of PEI. During the reaction of Gantrez and PVAm to form the Gantrez-PVAm composite, an imide group can be formed easily by the reaction of anhydride groups and the primary amine of PVAm. The imide group is less polar than free carboxylic acid or carboxylate group and is quite stable against hydrolysis under the testing conditions used.

The results show that an increasing level of hydrophobicity does not improve protection against H_2S and related corrosion. Contrary, increasing the polarity results in a higher protective effect. A question to be answered in further studies is if the protective effect through polar groups persists or if the protection decreases during periodic treatments with H_2S.

Layers on Textiles. Abrasion Tests and Contact Angles. For our purpose of corrosion protection, the polymer composites on silverized textiles were of high interest. For textile coatings, hydrophobicity is often desired as well. Generally, palmitoyl-terminated composites show a decreased corrosion protection compared to unterminated coatings. However, hydrophobic Gantrez-based palmitoyl-terminated coatings still keep a protective effect and do not fail, even though they are inferior compared to their unterminated hydrophilic counterparts. Hence, we applied Gantrez based composite systems on silverized textiles to investigate the

surface properties on abrasion using the Martindale abrasion method. Table 3 shows the contact angles of water on yarn.

As expected, the contact angle increases when depositing the hydrophobic polymer composites onto metallized cotton yarns. This is a consequence of the microstructure of the cotton yarn, which contains more air inside and provides less surface for interaction with the saddling water drop. Interestingly, the polymer coatings itself without hydrophobic termination are completely permeable for water. Waterdrops put on such a surface were soaked into the fibers within a few seconds. On fatty acid terminated polymer composites, the drops remained stable onto the surface and did not permeate through the polymer layer into the fibers. This shows that a good protection can be achieved only by the properties of the composite surface and not by the polymer layers itself.

To test the stability of the polymer composite surfaces, we performed abrasion tests using the Martindale method. As shown in Table 3, the contact angle increased from the starting angle of about 159 (PEI-based composites) or 151 (PVAm-based composites) to 161° after 200 cycles. By applying more abrasion cycles to the yarn, the contact angle decreases to 150°, independent of the coating polymer composite. After 1000 abrasion cycles, no further change of the contact angle occurs, showing two facts. First: the contact angle remains at 150° far in the hydrophobic region and the water drop is not soaked into the yarn. This shows that the hydrophobic polymer composites are staying stable onto the surface, not being destroyed by the Martindale test, even at high numbers of testing cycles. Second: The increase and decrease in the contact angle is caused by a change of the micro structure of the cotton yarn. The permanence of the contact angles after more than 1000 cycles in all cases means that no further rearrangement/destruction of the structure of the yarn occurs. Principally, the stability of the cross-linked polymer composites can be demonstrated by these results. Corrosion tests of coated textiles will be part of further work.

Optical Properties. To see the effect of the coatings on textiles, reflection spectra of polymer-coated silverized cotton
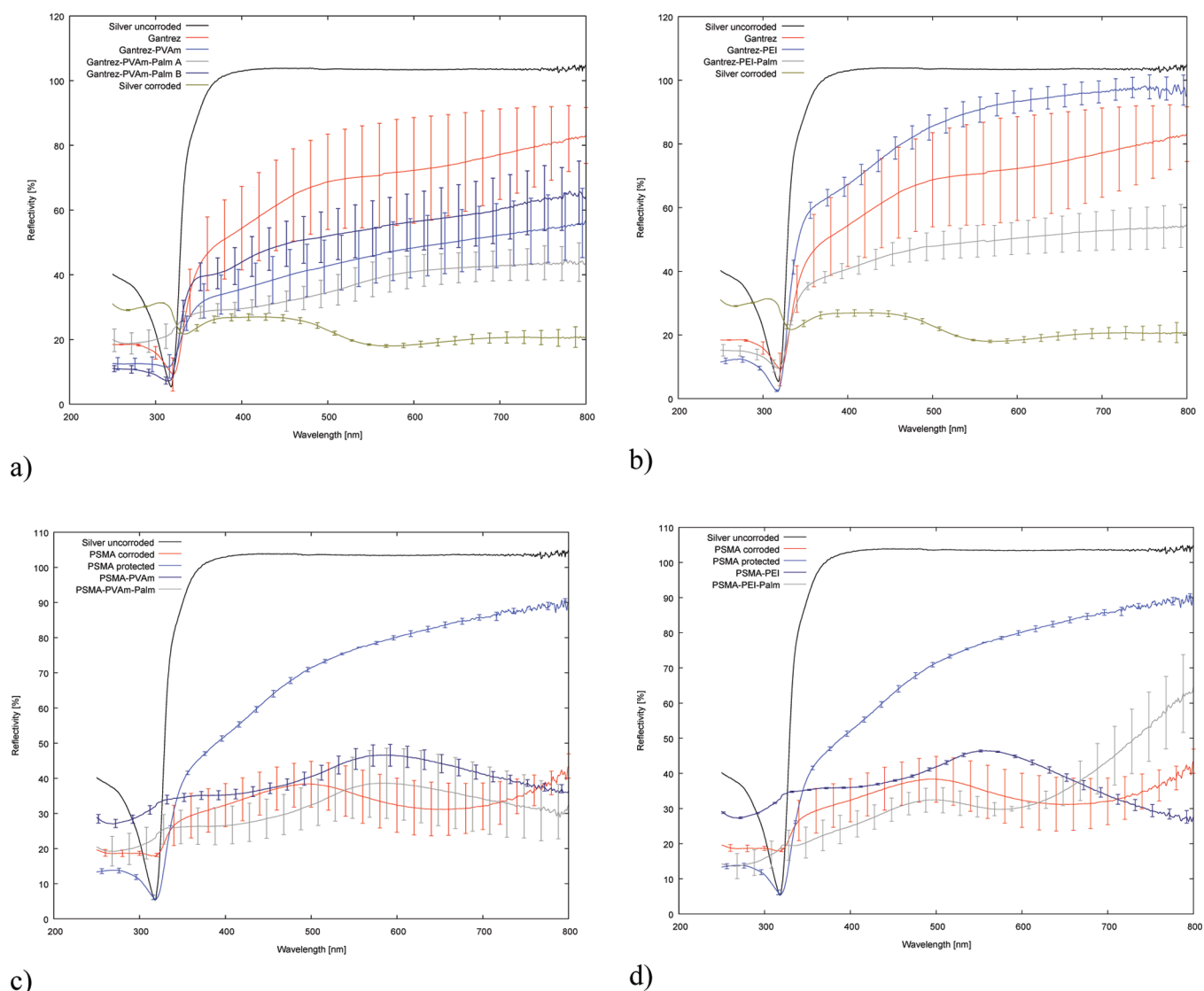
Figure 7. Reflectivity spectra of the composite systems: (a) Gantrez-PVAm-palmitoyl, (b) Gantrez-PEI-palmitoyl (c) PSMA-PVAm-palmitoyl, (d) PSMA-PEI-palmitoyl.

Table 3. Contact Angles on Polymer Coated Silverized Textile Yarns As a Function of Abrasion Cycles

		Gantrez	
without abrasion	primary layer		
	second layer	PEI	PVAm
	plain	[a]	[a]
	fatty acid terminated	159	151
with abrasion	50	161	158
	100	162	160
	200	161	161
	500	153	153
	1000	150	150

[a]Water drop is soaked into the yarn within a few seconds.

yarns were made. As expected from the glass slides, the spectra of the coated yarns are differing mainly only in regions below 560 nm. As can be seen in the spectra in Figure 8, the reflectivity is only about 60−70% of the reflectivity of silver slides. This has its reason in a more diffuse reflection of the textiles and makes an absolute comparison of the spectra difficult. The unexpected extreme reduction of the reflectivity after the formation of the Gantrez−PVAm composite can be

drawn back to sample preparation. This is supported by the fact that after the addition of the palmitoyl layer the spectrum does not show any further reduction.

■ CONCLUSION

We successfully prepared polymer composites based on polyanhydrides poly(maleic anhydride-*alt*-methyl vinyl ether) (Gantrez) or poly(styrene-*co*maleic anhydride) (PSMA) and polyamines polyethylenimine (PEI) or polyvinylamine (PVAm) followed by termination with fatty acid chains onto silver-coated glass slides, using the established covalent-layer-by-layer method. Optical measurements show a reduced reflectivity of such coated silver slides below 480 nm, depending in its intensity on the number of deposited layers. In corrosion tests, we investigated the protective effect of the deposited composites against H_2S-induced corrosion.

Contrary to our expectations, reflectivity measurements of corroded samples revealed that increased hydrophobicity does not lead to an increased protective effect, whereas higher polarity leads to an increased protection. This protective effect correlates with the number of polar groups in the polymers
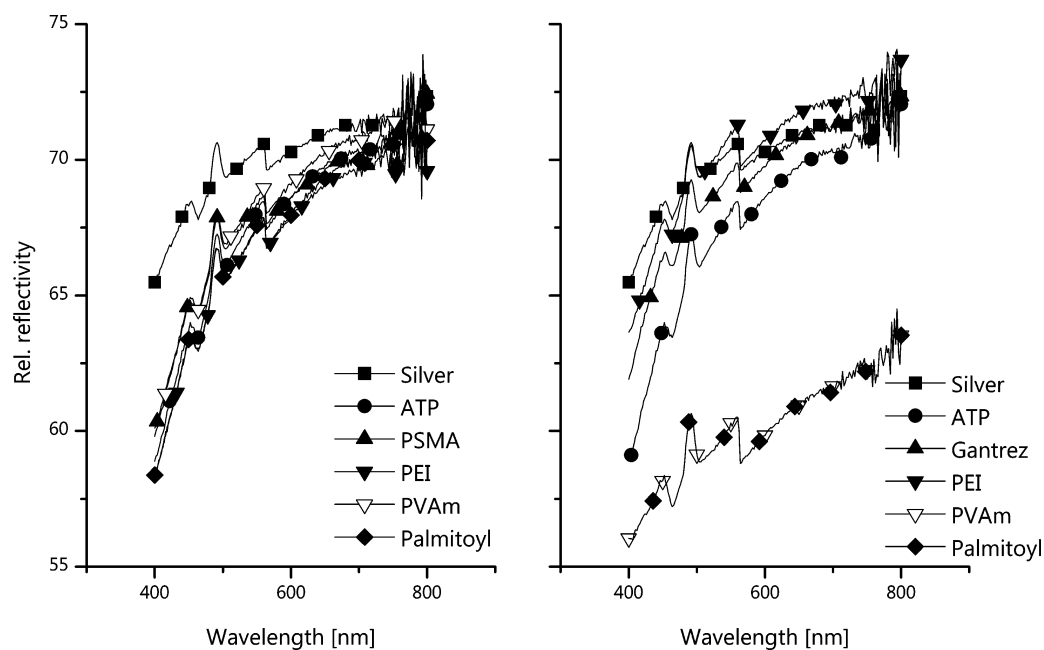
Figure 8. Reflection-spectra of layer-by-layer coatings on silverized cotton yarns. Left, PSMA-based composites; right, Gantrez-based composites. The major influence on the reflectivity on silverized textiles is from the textile itself. The polymer coatings have only minor influence.

deposited. Abrasion tests on polymer coated silverized textiles show the high stability of the deposited polymer coatings. Thus, our presented polymer composites are promising candidates for corrosion protection on silver, especially when flexibility of the substrate is demanded like in silverized fibers or foils.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, full characterization and images of corrosion analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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626

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