Photobactericidal and photochromic textile materials realized by embedding of advantageous dye using sol-gel technology

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Abstract

The presented study reports on the application of the dye Rose Bengal on textiles to achive photobactericidal properties and spirooxazine type photochromic dye for achieving photochromic properties by using different sol-gel based coating agents. Photochromic dyes changes rapidly and reversibly from colorless form to colored state when activated by ultraviolet irradiation. Color changing technology offers unique design opportunities to the designer and also has an opportunity to obtain camouflage and UV-protective textiles. The obtained phtochromic textiles were tested by means of UPF (Ultraviolet Protection Factor) and ΔE color difference after UV irradiation. After UV irradiation photochromic samples showed UPF values higher than 30 and this effect was developed with concentration of the dye. The prepared photobactericidal textiles were investigated by means of UV/Vis-spectroscopy, scanning electron microscopy and by testing the antimicrobial activity against the bacteria *Bacillus subtilis*. The purpose of this treatment was to realize photobactericidal materials which enabled antimicrobial activity while illuminated with visible light. An antimicrobial effect of the fabrics treated with Rose Bengal was observed with and without light exposition. However in case of illumination this effect was significantly stronger indicating a certain photobactericidal effect. This photobactericidal effect strongly depended on the kind of sol-gel coating agent used for embedding of the dyestuff onto the textile.

Keywords — antimicrobial coating, dye, photoactive coating, sol-gel method, textile

1 Introduction

The sol-gel method is a vertisale method to deposite inorganic coatings onto different types of substrates. Most often sol-gel coatings are reported for materials as SiO_2, TiO_2 or ZnO [1]. However, even very exotic inorganic compounds as e.g. HfO_2 or $BaTiO_3$ can be realized as coating by sol-gel method [2]. The sol-gel method uses colloidal solutions of nano-sized particles as liquid coating agents. Because of the nanoscale of the particles, these colloidal solutions are often named as "nanosols". After the coating agent is applied on a substrate by dipping or spraying, the solvent evaporates and the small particles agglomerate with each other to a threedimensional network forming a coating on the substrate. After that a thermal treatment is often performed to promote further drying and condensation of the coating [3].

Typical nanosols based on silica or titania (SiO_2 and TiO_2) are usually prepared by hydrolysis of metalorganic compounds e.g. tetraethoxysilane TEOS. The hydrolysis can be carried out either under acidic or alkaline conditions. An important point is, that the inorganic sol-gel coating can be modified by organic components. Depending on the specific properties of these compounds the coating intself or the coated product respectively can be equipped with certain properties. In other words, by sol-gel coating functional coatings with several properties can be realized. Very prominent examples are water repellent, oil repellent, flame retardant or UV-protective coatings applied on several kind of substrates [4, 5]. Analogously to these examples the modification of sol-gel coatings by embedding of dyes or pigments is possible. Such modification can be simply done either by adding soluble dyes to a readily prepared nanosol or by addition of dyes to the recipe before hydrolysis is carried out (Figure 1) [3]. After application and drying, the dye molecules will be embedded in the inorganic matrix of the resulting coating. By this, the main property of a dye - its color – is transferred to the coated substrate.

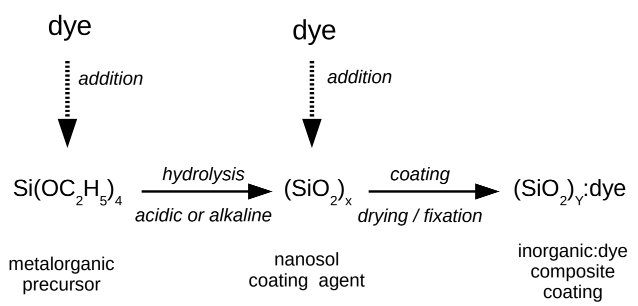

Figure 1: Schematical drawing of sol-gel process with embedding of dyes.

However beside the color, dye can also exhibit several other advantageous properties.

The aim of this paper is now to show two examples for embedding of specific dyes in sol-gel coatings for the functionalisation of textiles. The specific dyes will not only change the textiles color but additionally yield a second functionality. The first example is an antimicrobial function caused by the embedding of a photobactericidal dye. The second example aims on a photochromic functionalisation.

The realization of antimicrobially functionalized textiles is of high economic interest, due to the broad range of possible applications. Antimicrobial textiles are used for wellness clothing, sports- and home textiles further applications can be found in the medical sector. In the medical sector, applications are reported for wound dressings, the treatment of atopic dermatitis or to support the therapy of diabetes. Especially due to the increasing occurrance of penicillin resistant germs a growing demand for antimicrobially acting hygienic textiles is expected for future [6-9]. General two classical approaches should be distinguished for realization of an antimicrobial textile. Both approaches base on the concept that an antimicrobial compound itself is present on the textile. The first approach is a controlled release system. In this case, antimicrobial substances are fixed on the fabric and are released over a longer period of time. This could, e.g. be reached by fixation of silver nanoparticles or by copper releasing materials [10-13]. The second approach is related to quaternary ammonium compounds exhibiting one long alkyl chain, which are permanently fixed onto the fabric. Such systems are often also named and commercialized as so-called "nano-dagger", which can penetrate the membrane of bacteria, killing them this way [14]. In the last years another concept came in the focus of researchers, using semiconducting particles as photocatalysts (e.g. titania, zinc oxide or zinc sulfide). These photocatalysts are not biocides by themselves but they accelerate the production of so-called ROS (reactive oxygen species) from ambient air under light exposition. Such ROS will be able to affect, e.g. harmfull germs and therefore act antimicrobially. However the most common photocatalyst titania is only activated by energy-rich UV-light which is normally in-doors only present with low intensity [15, 16].

Another method to realize photobactericidal materials is the use of dyes which are able to transfer triplet oxygen into the state of singlet oxygen in case of illumination with light [17]. These dyes are known as photosensitizers. The activated singlet oxygen is known to oxidize organic compounds like, e.g. chlorophenol and to react stronger with biomolecules than the unexcited triplet oxygen. By this, an antimicrobial activity is supposed [18-22].

Different groups of researchers have investigated several dyes for purposes as photosensitizers as for example Rose Bengal, porphyrins, phthalocyanines or even dyes attached to polymers [17, 23-25]. For use of these dyes to realize antimicrobial textiles, it is the task to deposite these dyes with a certain light fastness onto the fabric. A high light fastness is especially necessary, due to the fact that the antimicrobial effect will only be observed while the sample is illuminated, so especially for photobactericidal textiles a significant illumination has to be taken into account for their whole life time. One method to fix dyes to a textile is the embedding of dye molecules into a sol-gel coating deposited onto the fiber surface [26-30]. This method is well known and simultaneously the incorporation of dyes into sol-gel-coatings is reported to improve the light fastness [31, 32].

Based on this, the focus of the first part of this study is to realize photobactericidal textiles by embedding the dye Rose Bengal into different sol-gel coatings deposited on textiles. For embedding sol-gel coatings of different composition (e.g. silica, titania, alumina) are used to evaluate optimal conditions to achieve a high photobactericidal effect and a sufficiently high light fastness.

The second part of this study reports on photochromic dyes embedded into sol-gel coatings on textiles, which can be additionally used for UV-protective applications. Ultaviolet (UV) light is a part of solar radiation spectrum which is classified in shortwave UVC (200–280 nm), middle-wave UVB (280–320 nm) and long-wave UVA (320–400 nm). The penetration of UV radiation in human skin causes sun burns, photoaging, immunosuppressive effects [33]. UVA radiation is the major portion (about 95%) of the UV radiation in sunlight that reaches the Earth's surface. Some of the UVB (about 5%) reaches the earth's surface while UVC is absorbed completely by the stratospheric ozone layer and thus does not reach the Earth's surface [34, 35]. However the ongoing reduction of the ozone layer increases the intensity of UV radiation. Thus, the extent of skin diseases increases with ozone depletion in the atmosphere [34]. Clothes can absorb, scatter and transmit UV radiation and therefore provide protection against UV radiation. UV protection provided by fabric depends on a number of properties, such as the type of fiber material, porosity, moisture content, color of fabric, etc. Dyes which undergo reversible photo-induced color changes are called photochromic dyes. By ultraviolet light or visible irradiation, photochromic dyes change their color and they revert to their original color state after removing of light source. Photochromic dyes have an ability for UV protection function since they absorb the UV light [36]. This study reports on application of a photochromic dye onto textiles by using sol-gel coating. The corresponding textiles are investigated by means of UV/Vis-spectroscopy and scanning electron microscopy. The UV protection factor (UPF) is also determined.

2 Experimental Part

2.1 Preparation of photobactericidal materials

For embedding of Rose Bengal into sol-gel coating and its fixation onto textile fabrics four different types of sols are used (Table 1). Sol A1 is a water based, alkaline and SiO_2 containing sol prepared according to references in literature [37, 38]. Sol A1 is prepared from a mixture of 19 mL tetraethoxysilane, 77 mL water to which 3.8 mL triethanolamine are added, before is stirred for at least two days until the solution becomes clear. Sol B1 is a water based, acidic SiO_2 sol which is organically modified and exhibits epoxy functionalized groups. The preparation is done according to reference in literature [39, 40]. Sol B1 is prepared from a mixture of 7 mL tetraethoxysilane, 3 mL (3-glycidoxypropyl)triethoxysilane, 60 mL water and 30 mL 0.01-N-HCl, which is stirred for at least 12 hours to be ready to use. Sol C1 is an acidic alumina modified SiO_2 sol containing alkyl and epoxyfunctionalized alkyl groups. Its preparation is carried out according to reference in literature [26, 41]. A solution of 35 g $Al_2(OH)_5Cl$ (Clariant) in 65 mL water is added to 250 mL ethanol, 65 mL tetraethoxysilane and 150 mL (3-glycidoxypropyl)triethoxysilane and stirred for two days. Afterwards this mixture is diluted with ethanol in a ratio 1:1. Sol D1 is ethanol based, acidic and contains TiO_2/SiO_2 particles (preparation according to reference [42]. Sol D1 was prepared starting from a mixture of $Ti(OC_3H_7)_4$ and tetraethoxysilane in a ratio of 3:1. 40 mL of this mixture are stirred in 280 mL ethanol and are hydrolyzed by addition of 7 mL 1N HCl. After 24 hours stirring of the resulting solution at room temperature, sol D1 was ready for further use.

Table 1: Summary of the sol recipes used for embedding of Rose Bengal.

Sol recipe	Solvent	Composition	References
A1	Water	SiO_2	[37, 38]
B1	Water	SiO_2; epoxymodified silane	[39, 40]
C1	Water and ethanol	SiO_2; alumina; epoxymodified silane	[26, 41]
D1	Ethanol	SiO_2; TiO_2	[42]

For embedding of Rose Bengal, an amount of 2 g/L Rose Bengal is added to the sols described above and the mixtures are stirred until the dye was dissolved completely. Only in case of sol D1, the dye was not dissolved completely therefore a saturated solution was used. For all preparations Rose Bengal ($C_{20}H_2Cl_4J_4Na_2O_5$) AcidRed94 supplied by Sigma-Aldrich was used (Figure 2). All dye containing sols are applied to viscose fabrics by dip-coating. After application the fabrics are allowed to dry at room temperature, followed by a thermal treatment at 120°C for 30 minutes.

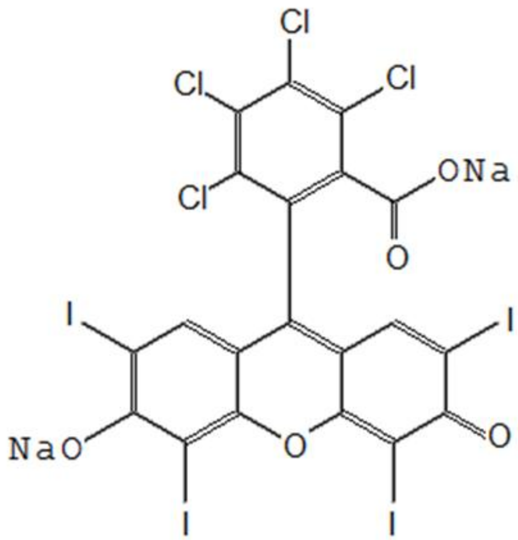

Figure 2: Chemical structure of the dye Rose Bengal.

2.2 Preparation of photochromic materials

Three different types of sols are used for embedding of photochromic dye into sol-gel coating (Table 2). Sol A2 is prepared from a mixture of 7 ml tetraethoxysilane (TEOS), 3 mL (3-Glycidyloxypropyl)trimethoxysilane (GPTMS), 60 mL aceton and 30 mL 0.01 N of hydrochloric acid (HCl), which is stirred for 24 h. Sol B2 is prepared from a mixture of 10 mL TEOS, 60 ml aceton and 30 mL 0.01 N HCl, which is stirred for 24 h. Sol C2 is prepared from a mixture of 9 ml TEOS, 1 mL GPTMS, 60 mL aceton and 30 mL 0.01 N of HCl, which is stirred for 24 h.

Table 2: Sol recipes used for embedding of photochromic dye, amount given in mL.

Sol recipe	SOL A2	SOL B2	SOL C2
TEOS	7	10	9
GPTMS	3	0	1
Aceton	60	60	60
HCl, 0.01 N	30	30	30

Three different concentrations of photochromic dye are used as 1 g/L, 3 g/L and 4 g/L. Photochromic dye was added to these sols and the mixtures are stirred for two hours until the dye was dissolved completely. For all preparations spirooxazine based photochromic dye (1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine]) supplied by Sigma-Aldrich was used (Figure 3). All dye containing sols are applied to 100% polyester fabrics by pad-cure process. After application the fabrics are allowed to dry at 80 °C, followed by a thermal treatment at 150°C for 5 minutes.

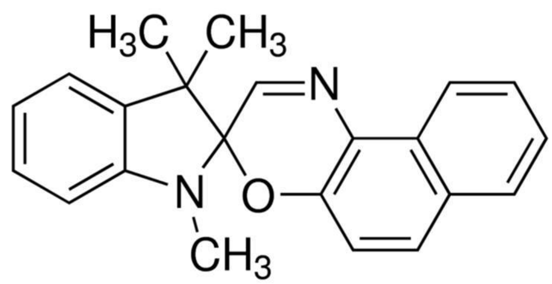

Figure 3: Chemical structure of the photochromic dye 1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine].

2.3 Analytics on photobactericidal materials

Optical spectroscopy in arrangement of diffuse reflection was used to investigate the colored sol-gel coated samples. As reference for these optical measurements an uncoated viscose fabric was used. These measurements were performed with an UV/VIS-spectrometer MCS 501 (Carl Zeiss Jena GmbH, Germany). The scanning electron microscopy (SEM) was used to investigate the topography of the sol-gel treated fabrics. All SEM measurements are performed using a Hitachi S-3400N. The antimicrobial properties of the coated textiles are tested against Bacillus subtilis as well under dark conditions as illuminated with light. For testing, the coated viscose fabrics are shaken with bacteria suspension and inoculated for 6 hours or 24 hours at a temperature of 30 °C under dark condition or while illuminated with white light. The white light is gained from an array of six white lamps (OMNILUX 18Watt, 60 cm – supplier

Eurolite). The optical transmission spectrum of the white lamps has been reported earlier [43]. The lamps are mounted in a distance of 45 cm from the textile sample. After illumination the fabrics are leached in phosphate buffer solution (pH = 7) and the buffer solution is inoculated on agar plates. Finally, after 24 hours the colony forming units CFU are counted. The photostability of the colored viscose fabrics was evaluated with a Xenotest 150S (Hereaus) [44]. For this test, textile samples were exposed to light for 20 hours.

2.4 Analytics on photochromic materials

Scanning electron microscopy (SEM) was used to investigate the topography of the sol-gel treated fabrics. All SEM measurements are performed using a FEI Quanta250 FEG. Color measurements were carried out according to CIELab standard by a portable spectrophotometer (Colorlite sph 860) in a UV cabinet (UVP- UV2/PCR) with a UV light bulb (USHIO G25T8 UVA type bulb, 25W, maximum wavelength 365 nm). The fabrics were placed into the UV cabinet and irradiated with UV light for 2 minutes. After irradiation the UV light was switched off and color measurement were carried out immediately with a delay of 3 seconds. The color value of the samples not irradiated with UV light was regarded as the standard. Color change on irradiation of the treated fabrics was discussed by the difference between the standard and UV irradiated and therefore colored fabrics by using ΔE (color difference) values. Reflectance% values of the samples were also used to evaluate the color change. UV Protection Factor (UPF) values of the fabrics were measured with Labsphere UV2000F device according to standard test method AS/NZ 4399:1996.

3 Results and discussion

3.1 Optical and material properties

UV/Vis-spectra of the colored sol-gel-coatings containing Rose Bengal applied to viscose fabrics are shown in figure 4. The related sol-gel materials containing no dye are uncolored. The optical properties of the sol-gel embedded Rose Bengal is different from Rose Bengal dissolved in water. Compared to the absorption maximum of 526nm in aqueous solution the maximum of absorption is shifted to longer wavelength around 555nm. A similar effect has been reported in literature for dissolving Rose Bengal in solvents with different polarity [45].

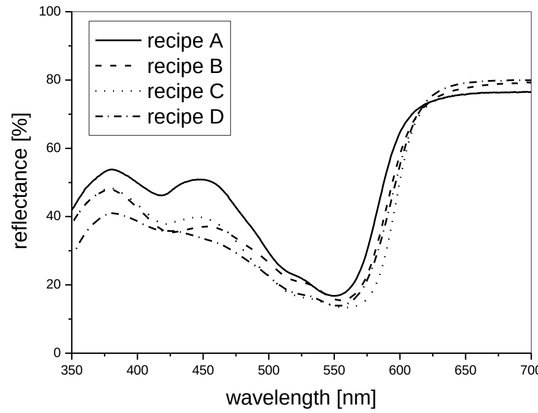

Figure 4: Reflectance spectra of viscose fabrics treated with the four sols containing the dye stuff Rose Bengal.

With decreased polarity of a solvent a red-shift of the absorption maximum of the dye has been observed. Based on this, it can be concluded that the sol-gel embedded Rose Bengal is in a more hydrophobic surrounding than in case of solvation in water. However, also the spectra of the different sol-gel coatings with Rose Bengal here exhibit significant differences (Figure 4). These differences can not be explained by the optical properties of the pure sol-gel material, because these materials are mainly optical transparent. It has been reported earlier that by use of epoxy modified SiO_2 sols the absorption characteristics of embedded dye can be significantly changed by interaction between dye and the epoxy group [31]. Changes in optical properties after embedding Rose Bengal into sol C1 or sol D1 may be also explained by interactions with the aluminium or titanium component, which are present in the sol-gel matrix [31, 42]. Another important point is that by embedding into sol-gel coatings the light fastness of a dye can be enhanced [32, 46].

This issue is especially interesting for application with Rose Bengal, because this dye is known for its extremely low light fastness. The light fastness is especially of interest in case of usage of photobactericidal applications, because for these applications the illumination with light is necessary to gain the biocidal effect. As seen in figure 5 (compared to figure 4), the sol-gel embedded Rose Bengal is strongly degradated after illumination in Xenotest arrangement.

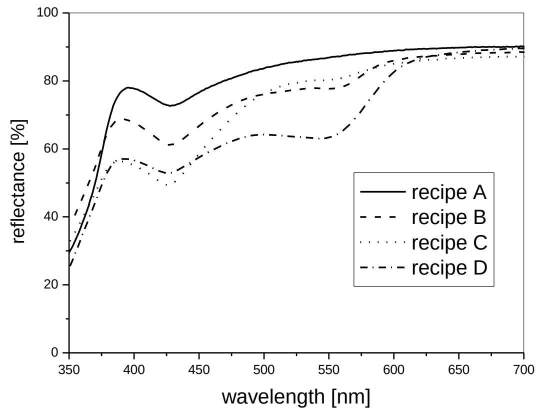

Figure 5: Reflectance spectra of viscose fabrics treated with the four sols containing the dye stuff Rose Bengal. These reflectance spectra are recorded after illuminating the samples in the Xenotest.

However it should be mentioned that by embedding in different sol-gel materials the light fastness of Rose Bengal is influenced (Figure 5). The lowest bleaching rate is gained for embedding in the titania containing sol D1. This improvement in light stability may be explained by a UV-protective property of the titania matrix, which due to the well-known absorption of UV-light by TiO_2. However even after embedding into the sol A1, B1 and C1 differences in light fastness can be seen (Figure 5), even though these sols do not exhibit absorption of near UV-light. After embedding in sol B1 and C1, a higher light fastness compared to the pure silica sol A1 is observed, which is comparable to investigations reported earlier regarding an enhanced light fastness of triphenylmethane dyes embedded in epoxysilane modified SiO_2-sols [31, 32].

The topography of the sol-gel coated fabrics is different for each sol-gel recipe while the incorporation of the dye stuff seems not to influence the appearance of the surface (Figures 6). From evaluation of the coating topography the recipes B1 and C1 seems to be most appropriate for textile treatment due to the fact that the resulting coatings are mainly smooth and no crack formation is observed. In comparison the deposition of larger particles by application of sol A1 or the crack formation with sol D1 indicate that the applied coating could be more easily abraded from the fiber surface than coatings of sol B1 and sol C1.

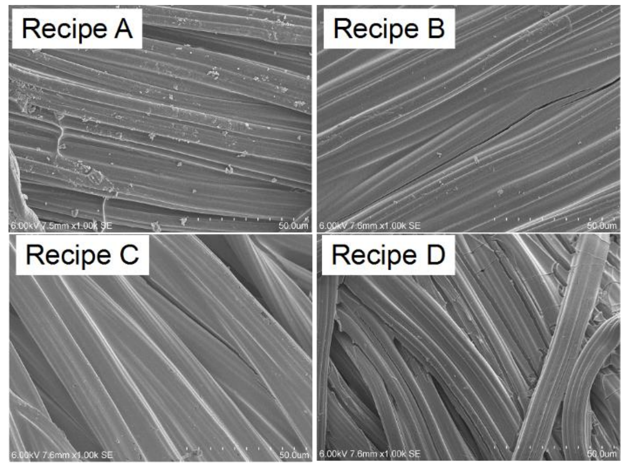

Figure 6: SEM-micrographs of viscose fabrics treated with the four different sol-gel recipes containing the dye Rose Bengal.

3.2 Photobactericidal properties

The antibacterial properties of the prepared sol-gel coated viscose fabrics are summarized in table 3. The results are given for dark conditions and for samples illuminated. It can be clearly seen that the antimicrobial properties are strongly depended on the illumination of the Rose Bengal modified fabrics. For this, the occurrence of a photobactericidal effect can be stated. However the antibacterial effect is also strongly influenced by the type of the sol-gel material used for the fixation of Rose Bengal onto the viscose fabric.

For both silica containing sols A1 and B1, the strongest photobactericidal effect is observed, because in case of illumination no or only a small bacteria growth is observed compared to a moderate growth under dark condition (Table 3). However even under dark conditions a reduction in bacteria growth is observed compared to the strong growth in presence of the uncoated viscose reference. For this, it can be stated, that the dye stuff Rose Bengal exhibits a certain bactericidal effect without light exposition, which is of course significantly increased by illumination due to the photobactericidal effect.

Table 3: Summary of the antibacterial effect of sol-gel coated viscose fabrics against Bacillus subtilis. Results are shown for samples kept under dark conditions and those illuminated with white light. The number of colony forming units (CFU) after incubation is given.

Sol recipe	CFU determined under dark conditions		CFU determined under illumination with white light	
	6 hours incubation	24 hours incubation	6 hours incubation	24 hours incubation
A1	30	>500	0	0
B1	87	>500	2	21
C1	98	>500	>200	>500
D1	35	54	136	214
Reference without coating	>500	>500	>500	>500

In contrast to this, the other sol recipes C1 and D1 show no significant photobactericidal effect. Compared to the uncoated viscose reference, the growth of bacteria is decreased for these samples but no significant decrease is observed in case of illumination compared to dark conditions (Table 3). Sol recipe C1 contains an alumina component and sol recipe D1 a titania component, so a possible interaction of the embedded Rose Bengal by complex bonding to the aluminium or titanium component, which are present in the sol-gel matrix, might yield the reduced activity [26, 42]. This complex interaction might be the reason for the absence of the photobactericidal effect, because by interaction between the dye stuff and the metal components a change in the electronic structure of the dye could be expected.

As a result, it could be stated that for realization of a photobactericidal textile by embedding a photosensitive dye into a sol-gel coating, the final photobactericidal activity is strongly determined by the type of sol-gel material used. Especially the titania containing sol D1, which seems to be at first more suitable for use due to improved light fastness, will lead in the end to a nearly useless material, because the photobactericidal effect is obviously diminished by the presence of titania in the sol-gel matrix.

3.3 Photochromic samples and their properties

SEM images of polyester fabrics coated with sol-gel coatings containing 4 g/L photochromic dye are shown in Figure 7. No crack formation is observed for all coatings. The surface topography is quite similar to the topography of the coating of sol A1 with Rose Bengal on viscose fabric. The absence of crack formation after embedding of the dye, gives the hint that this type of sol-recipe is quite useful for dye embedding.

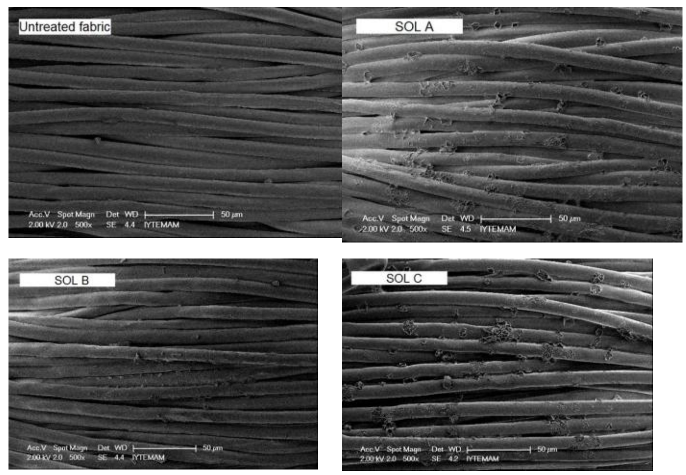

Figure 7: SEM-micrographs of polyester fabrics treated with the three different sol-gel recipes (sol A2, B2 and C2) containing 4 g/L of the photochromic dye.

Color values of the samples are related to determined L* values. It was observed that after irradiation the L* values of fabrics modified with the photochromic dye were lower than those of untreated polyester fabric, which confirms the occurance of a color change under UV irradiation. This statement is supported by the reflectance and K/S-spectra of the samples (Figures 8 and 9). It can be clearly seen that the color intensity of the fabrics equipped with coatings containing the photochromic dye is significantly enhanced during UV irradiation. Strongest changes are obviously gained with sol A2 and sol C2. Less color change intensity is observed for coatings prepared from sol recipe B2. Sol B2 contains only SiO_2 while the sols A2 and C2 are SiO_2 sols modified with an epoxysilane. Obviously the addition of the epoxysilane component supports the photochromic effect of the embedded photochromic dye.

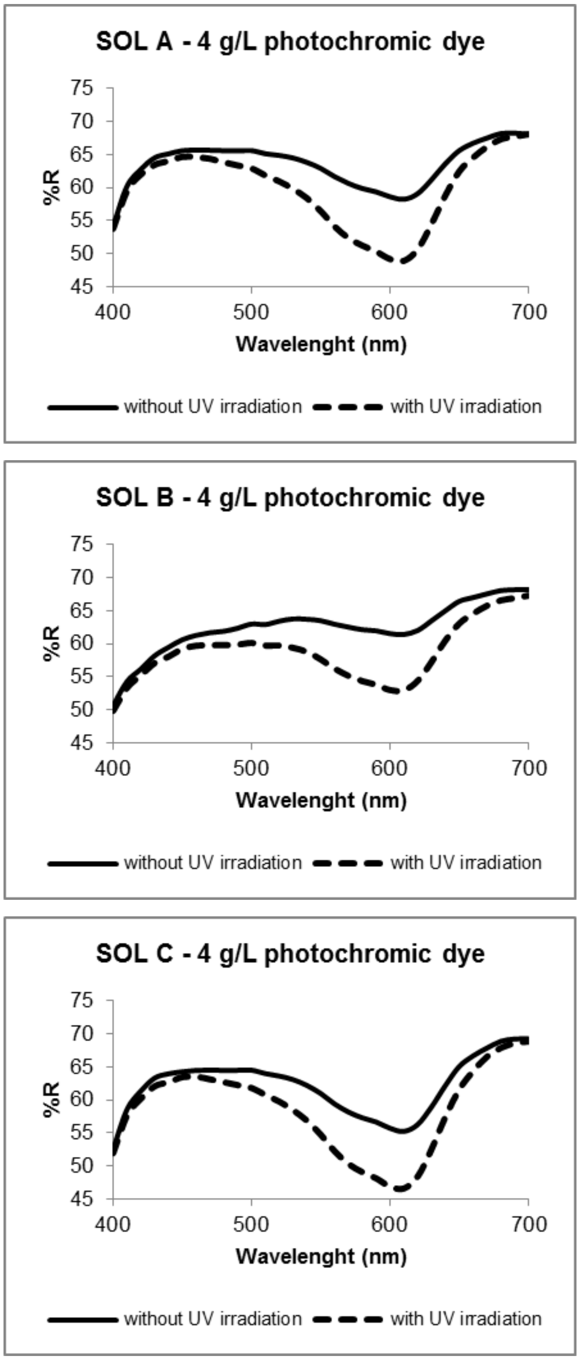

Figure 8: Reflectance spectra of polyester fabrics treated with the three sol-recipes (A2, B2 and C2) containing the photochromic dye with a concentration of 4g/L.

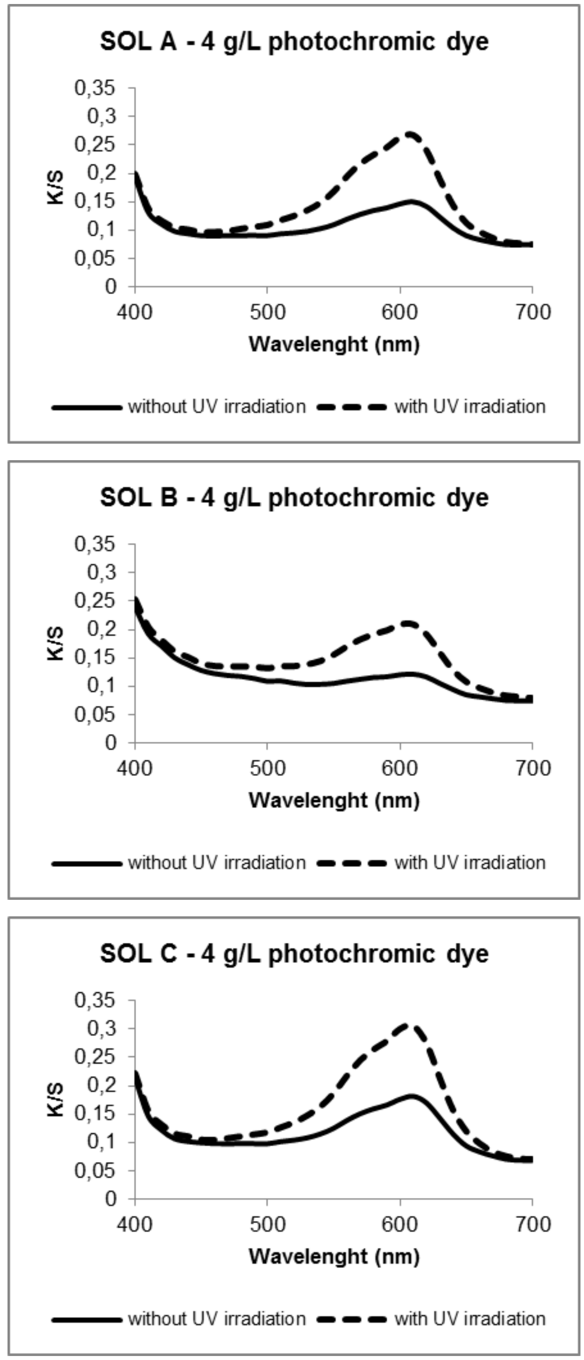

Figure 9: K/S spectra of polyester fabrics treated with the three sol-recipes (A2, B2 and C2) containing the photochromic dye with a concentration of 4g/L.

UPF values of the same fabrics are shown in Figure 10. UPF values increased with the application of photochromic dye and the specific type of sol composition influences UV protection obtained by the photochromic dyes. The results show that application of 4 g/L of the photochromic dye provides excellent UV protection according to AS/NZ 4399:1996 standard. Again the epoxysilane modified SiO_2 sols A2 and C2 lead to best results which means highest UPF values.

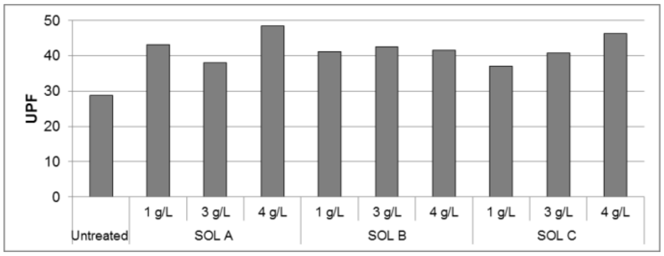

Figure 10: UPF values of polyester fabrics coated with different sol-recipes containing photochromic dye with increasing concentrations from 1g/L to 4g/L.

4 Conclusions

It has been demonstrated that the deposition of a photosensitive dye onto textiles by using sol-gel coatings can be used to realize photobactericidal textile materials or photochromic textiles with UV protective properties, respectively. However, the intensity of the photobactericidal effect is strongly determined by the type of sol-gel material used for embedding the dye. The promising results open up an interesting approach for developing a new kind of antimicrobial textiles. The strong influence of the surrounding matrix material as well as the low light fastness are aspects that will be in the focus of future investigations. For practical applications the use of dyes with high light fastness is more appropriate and these dyes have to be again investigated according to possible interaction with the surrounding sol-gel matrix, because of a possible decrease in photosensitivity.

The intensity of the photochromic effect is as well dependent on the sol-gel matrix used. Especially epoxysilane modified SiO_2-sols lead to promising results and should be the starting point for further developments in future.

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