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Tailoring of a Dual-active Antibacterial Coating for Polylactic Acid Fibres

Izdelava protibakterijske apreture z dvojno aktivnostjo za vlakna iz polimlečne kisline

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Abstract

The aim of this research was to develop a new, dual-active antibacterial coating for fibres made from polylactic acid and, consequently, to increase the possibility of their use for a variety of technical textiles. The process of finishing was performed on a knitted fabric in three stages by applying silver chloride and 3-(trimethoxysilyl)-propyldimethyltetradecyl ammonium chloride, which provided simultaneous dual antibacterial activity based on the mechanisms of controlled release and bio-barrier formation. The presence of the coating on the fibres was confirmed by scanning electron microscopy with energy–dispersive X–ray spectroscopy, inductively coupled plasma mass spectroscopy and a test with bromophenol blue. The results of microbiological tests confirmed the excellent bactericidal activity of the coating, with a 99.99% reduction in the gram-positive bacteria *Staphylococcus aureus* and the gram-negative bacteria *Escherichia coli.* Application of the coating reduced the lightness and increased the yellowing of the fibres from polylactic acid, which were disadvantages.
Keywords: fibres from polylactic acid, antibacterial coating, dual antimicrobial activity, silver, trialkoxysilane with quaternary ammonium group

Izvleček

Namen raziskave je bil razviti novo protibakterijsko apreturo z dvojno aktivnostjo na vlaknih iz polimlečne kisline in s tem povečati možnost njihove uporabe za različne tehnične tekstilije. Apreturni postopek je bil izveden na pletivu v treh stopnjah z nanosom srebrovega klorida in 3-(trimetoksisilil)-propildimetiltetradecilamonijevega klorida (Si-QAC), ki sta zagotovila dvojno hkratno protibakterijsko aktivnost po mehanizmih nadzorovane sprostitve in tvorbe biobariere. Prisotnost apreture na vlaknih smo potrdili z vrstično elektronsko mikroskopijo z energijsko-disperzijsko spektroskopijo rentgenskih žarkov, masno spektroskopijo z induktivno sklopljeno plazmo ter testom z bromofenol modrim reagentom. Rezultati mikrobioloških testov so potrdili baktericidno delovanje apreture z 99,99-odstotno bakterijsko redukcijo za grampozitivno bakterijsko vrsto Staphylococcus aureus in gramnegativno bakterijsko vrsto Escherichia coli. Nanos apreture je zmanjšal belino in povečal porumenitev vlaken iz PLA, kar je njena pomanjkljivost.
Ključne besede: vlakna iz polimlečne kisline, protibakterijska apretura, dvojna protimikrobna aktivnost, srebro, trialkoksisilan s kvarterno amonijevo skupino

1 Introduction

Fibres from polylactic acid (PLA) constitute an important group of non-toxic, biodegradable and biocompatible polyester textile fibres made from renewable resources. Due to their thermoplasticity, which enables melt spinning, as well as their chemical resistance and good mechanical and barrier

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properties, PLA fibres have become one of the most promising alternatives for polymer fibres derived from petroleum [1–4]. Their use has already been extended to the field of technical textiles. They are particularly suitable for single-use products, such as sanitary materials, specific medical textiles and textile filters [5, 6]. For this type of textile products, a functional antimicrobial protection provides high added value and is therefore of great technological and economical importance.

When preparing the antimicrobial protection for textiles, two groups of antimicrobial agents can generally be used, which vary according to the mechanism of antimicrobial activity [7–9]. The first group comprises antimicrobial agents that act by the mechanism of controlled release. Because most of these agents are bound to the fibres with physical forces, they can be slowly released from the fibres into the surrounding area in the presence of a sufficient amount of moisture where they wholly destroy or inhibit the growth of microorganisms. An important weakness of physically bonded agents is the lowering of their concentration in the fibres due to leaching, eventually falling below the limit of efficiency. The second group includes agents that operate on the principle of bio-barrier formation. In this case, agents are chemically bonded to the textile fibres where they create a biological obstacle for the microorganisms that come in contact with the fibres. Because they do not leach from the fibres, their concentration does not change with time. However, chemical bonding cannot ensure the permanent antimicrobial activity of agents because the settling of dead microorganisms on the bio-barrier can greatly reduce or even eliminate their effectiveness.

To eliminate the problems related to the mode of antimicrobial action and thereby to increase the effectiveness of antimicrobial protection, the research work in recent years has been oriented towards finding new approaches for the preparation of antimicrobial coating preparations. One such approach is the tailoring of antimicrobial coatings to obtain dual activity. To this end, combinations have been used, consisting of antimicrobial agents that operate by the mechanism of controlled release and those that form a biological barrier [10–15]. These results have encouraged us to develop a novel, dual-active antimicrobial coating for the textile fibres from PLA, which would also be appropriate for chemical modification of other hydrophobic and low-adhesive fibres. The previous research on the PLA fibres or PLA films has been mostly directed towards the preparation of monocomponent antimicrobial coatings exhibiting either the controlled release of essential oils, antibiotics, silver nanoparticles, or zinc oxide, [16–20], or the formation of the chitosan bio-barrier [21, 22].

For the preparation of an antimicrobial coating with dual antimicrobial activity, we chose silver as a representative agent for the controlled-release mechanism of action, and an organic-inorganic hybrid sol-gel precursor with a quaternary ammonium functional group as a representative agent with the bio-barrier-forming antimicrobial mechanism. Assuming that because of their morphological and chemical structure, PLA fibres have insufficient adhesive ability for silver, we decided to create a silica matrix on the fibre surface to increase their adsorption capacity. In fact, it was found that the silica matrix significantly increases the concentration of the adsorbed silver, resulting in more uniform distribution as well as the reduced size of silver particles [23, 24]. Thus, we have developed a three-stage finishing procedure that includes the following stages: (i) the creation of a silica matrix, (ii) the *in situ* synthesis of AgCl and (iii) the creation of a bio-barrier. An important objective of our study was to determine the effectiveness of the antibacterial coating as well as to determine the influence of the coating on the colour of PLA fibres, which is an important feature of the product from an aesthetic point of view.

2 Experimental

2.1 Materials

We used a double weft knitted fabric in 1 × 1 rib structure made from 100% PLA multifilament (10 capillaries) with linear density of 11.1 dtex, breaking force of 40.7 N and breaking elongation of 31.8%. The PLA multifilament was kindly supplied by Applied Polymer Innovations BV (Emmen, Netherlands). The thickness and weight of the fabrics were 5.2 mm and 428.3 g/m^2, respectively.

The commercial products 3-(trimethoxysilyl)-propyldimethyltetradecyl ammonium chloride (Si-QAC), namely, Sanitized T 99-19 (Sanitized, Switzerland) and silver chloride (AgCl), prepared from silver nitrate ($AgNO_3$; Sigma-Aldrich) and sodium chloride (NaCl; Carlo Erba) were selected as the antimicrobial agents. To create a silica matrix, we used the commercial

product iSys MTX (CHT, Germany), which is a water–borne Si– and Zr–based sol-gel precursor (RV), in combination with Kollasol CDO (CHT, Germany), which is an anti–foaming and wetting agent. All solutions were prepared in bidistilled water.

2.2 Finishing

Chemical modification of the PLA samples was accomplished in a three-stage finishing procedure. In the first stage (1S), the samples were immersed in 100.0 g/L RV and 10.0 g/L Kollasol CDO for 10 minutes at room temperature, followed by wringing via squeezing on a two-roll padder with a pick-up of 80 ± 5%, and drying in an oven at a temperature of 110 °C for 5 minutes. After drying, the samples were left for 7 days at standard atmospheric conditions to allow complete crosslinking of iSys MTX. In the second stage (2S), the *in situ* synthesis of AgCl on the RV-treated samples was performed in the Gyrowash 815 (James Heal, UK) apparatus at room temperature, with occasional stirring, as follows: the specimens were immersed for 10 minutes in a 0.5 mM solution of $AgNO_3$ with a liquor ratio of 50:1 and then subsequently immersed for 10 minutes in a NaCl solution of the same concentration and liquor ratio. The procedure was repeated twice. Then, the samples were washed in bidistilled water to remove the excess chemicals and dried at room temperature. In the third stage (3S), Si-QAC was applied to the samples by the pad-dry-cure method, with full immersion of the samples in a 100 g/L solution of Si-QAC, followed by squeezing on a two-roll padder with a pick-up of 80 ± 5% and drying in an oven at temperature of 110 °C for 5 minutes. After drying, the samples were left for 7 days at standard atmospheric conditions to allow complete crosslinking of iSys MTX. The three-stage finishing procedure is schematically presented in Figure 1.

For comparison, the two- and one-step application procedures were also performed with the same antimicrobial agents under the same conditions as in the three-stage procedure. Accordingly, in the two-step procedure, RV was applied as in 1S, followed by the application of AgCl as in 2S. In the one-stage procedure, AgCl and Si-QAC were applied to the PLA samples as in 2S and 3S, respectively. The sample codes in relation to the application procedures are summarized in Table 1.

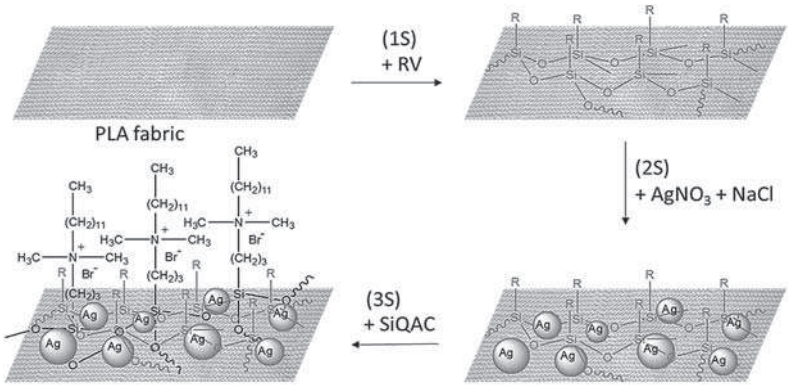

Figure 1: Schematic presentation of the three-stage procedure of antimicrobial finishing

Table 1: Application procedures, sample codes and sol concentrations

Finishing procedure	Sample code	Sol concentration
No treatment	PLA-N	/
Three–stage	PLA-RV-Ag-SiQAC	(1S): 100.0 g/L RV, 10.0 g/L Kollasol CDO (2S): 0.50 mM $AgNO_3$ + 0.50 mM NaCl (3S): 100.0 g/L Si-QAC
Two–stage	PLA-RV-Ag	(1S): 100.0 g/L RV, 10.0 g/L Kollasol CDO (2S): 0.50 mM $AgNO_3$ + 0.50 mM NaCl
One–stage	PLA-Ag	(2S): 0.50 mM $AgNO_3$ + 0.50 mM NaCl
	PLA-SiQAC	(3S): 100.0 g/L Si-QAC

2.3 Analytical methods

Fourier transform infrared spectroscopy (FT-IR)
FT-IR spectra were obtained on the Spectrum GX (Perkin - Elmer, UK) spectrophotometer equipped with a diamond cell. The spectra were recorded over the range of 4,000–600 cm^{-1}, with a resolution of 4 cm^{-1} and an average set of 32 spectra per sample. Before the measurements, the samples were dried to a constant weight.

Scanning electron microscopy (SEM) with energy–dispersive X–ray spectroscopy (EDS)
SEM was conducted on the Jeol JMS 6060LV and Jeol JSM 5610 microscopes, equipped with an Oxford–Link ISIS 300 EDS system with an ultra–thin window Si(Li) detector. Prior to performing the SEM and EDS analyses, we applied a 20–nm–thick carbon layer to each fabric sample to ensure sufficient electrical conductivity and to avoid charging effects. SEM micrographs were recorded using the secondary electron (SE) and backscattered electron (BSE) imaging modes. The BSE compositional contrast (Z-contrast) was applied to accentuate the differences between the added particles and the fibre matrix. Two parallel assessments were performed for each coated fabric sample, and the corresponding atomic concentration was reported as the mean value.

Inductively coupled plasma mass spectroscopy (ICP-MS)
ICP–MS was performed on the Perkin Elmer SCIED Elan DRC spectrophotometer. The fabric samples (0.5 g) were prepared in a Milestone microwave system by acid decomposition, using 65% HNO_3 and 30% H_2O_2. Three measurements were taken for each sample, and the Ag concentrations were reported as the mean values.

Test with bromophenol blue (BPB) reagent
Qualitative determinations of Si-QAC on the coated samples were performed by using the BPB reagent, which is an alkaline dilution of the sodium salt 3'-3"-5'-5"-tetrabromophenolsulfonphtalein. The test was based on the formation of a complex between the BPB reagent anion and the quaternary ammonium group of Si-QAC on the surface of the fabric. Due to the formation of the complex, the samples were coloured blue. For the BPB test, 1 g of sample was immersed in 50 mL of 0.005% BPB reagent diluted in water and stirred vigorously for 20 min. The samples were subsequently removed from the BPB solution, thoroughly rinsed with cold tap water and dried at room temperature. The intensity of the blue coloration on the samples was assessed by the reflectance, R, measurements of the samples on the Datacolor Spectraflash SF 600 spectrophotometer, using D 65/10° light. Before these measurements, the samples were conditioned at relative humidity of 65 ± 2% and temperature of 20 ± 1 °C for 24 hours. For each sample, ten measurements of the R value were obtained, and the corresponding K/S values were calculated according to the Kubelka-Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1),$$

where K/S is the ratio of the coefficient of light absorption (K) to the coefficient of light scattering (S), and R the reflectance at the maximum absorption wavelength, determined at 610 nm. Afterwards, the mean K/S value was determined.

Antibacterial activity
The antibacterial activity was examined by a modified AATCC standard method 100-1999 for the bacteria *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 6538). In aseptic conditions, the sample was placed into a 250-mL container and inoculated with 400 µL of a nutrient broth culture containing $1–2 \times 10^5$ colony-forming units of bacteria. After incubation at 37 °C for 24 hours, the bacteria were eluted from the swatches by shaking in 100 mL of neutralizing solution for 1 minute. After preparing serial dilutions in sterilised water, the suspensions were plated on nutrient agar and incubated at 37 °C for 24 hours. The number of bacteria was counted, and the reduction of bacteria, R, was calculated as follows:

$$R = \frac{(B-A)}{B} \cdot 100\ (\%) \quad (2),$$

where A is the number of bacteria recovered from the inoculated swatch of the cotton sample in the jar incubated for the desired contact period (24 hours), and B is the number of bacteria recovered from the inoculated swatch of the cotton sample in the jar immediately after inoculation (at "0" contact time). For each fabric sample, four parallel assessments were performed and the mean value was determined.

Whiteness and yellowing index

The whiteness of the samples was determined on the basis of the measurements of the CIE colour values using the Spectraflash 600 PLUS-CT spectrophotometer (Datacolor, Switzerland). The measurements were performed at the following conditions: 20 mm size of the measuring aperture, standard light D65 and T = 6500 K, using D65/10° with an excluded specular as an observer. The whiteness, W_{10}, was calculated from the following equation:

$$W_{10} = Y_{10} + 800(0.3138 - x_{10}) + 1700(0.3310 - y_{10}) \quad (3),$$

where Y_{10} is the standardized colour value of the sample, and x_{10} and y_{10} are the standardized colour portions of the sample. The yellowing index, *YI*, was calculated from the following equation:

$$YI = \frac{100(1.3013\,X - 1.1498\,Z)}{Y} \quad (4),$$

where *X*, *Y* and *Z* represent the values in the CIE colour space. Before these measurements, the samples were conditioned at relative humidity of 65 ± 2% and temperature of 20 ± 1 °C for 24 hours. For each sample, ten measurements of Y_{10} and *YI* were obtained and the mean values were calculated.

3 Results and discussion

The ATR spectra of PLA-N and PLA-RV-Ag-SiQAC samples (Figure 2) show that the application of the antimicrobial coating caused chemical changes in the PLA fibres, resulting in the increase of the intensity of the absorption peaks at wavenumbers 2927 and 2856 cm^{-1}, which are characteristic of asymmetric and symmetric stretching of the C–H bond in aliphatic alkyl groups [25]. This can be attributed to the tetradecyl groups in the structure of the Si-QAC film. Furthermore, the application of the coating caused a reduction in the intensity of the absorption peak at the wavenumber of 1759 cm^{-1}, which is characteristic of the C=O stretch of ester groups in the macromolecules of PLA. This result indicates that the antimicrobial polymeric film coated the PLA fibres, which resulted in partial shading of the peaks characteristic of the fibre structure. Furthermore, a broad absorption peak appeared at the wavelength of 1565 cm^{-1} in the spectrum of the finished PLA fibres, which is characteristic of amide II, which shows a strong absorption in the spectral region between 1570 and 1515 cm^{-1} [25]. In this spectral region, high intensity absorption peaks can be detected in the spectrum of RV, which suggests the presence of this group in the structure of RV. However, because RV is a commercial product, its exact structure is not evaluable by the producer. In the spectrum of the PLA-RV-Ag-SiQAC sample, the absorption peaks at the wavelengths 1129, 1083 and 1043 cm^{-1}, which are characteristic of the asymmetric stretching vibration of the Si-O-Si group in the polysiloxane network [25, 26], are overlapped by the peaks characteristic of the fingerprint of PLA. Silver could also not be detected in this spectrum.

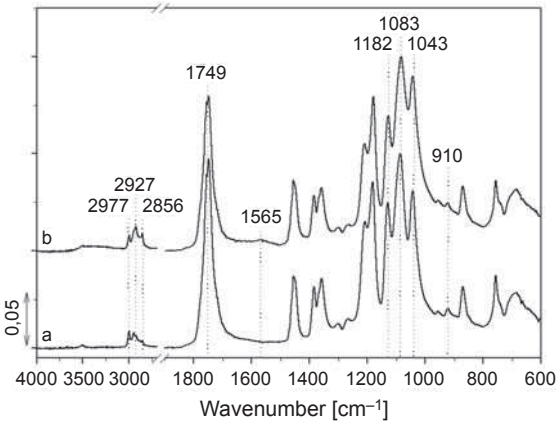

Figure 2: ATR spectra of PLA-N (a) and PLA-RV-Ag-SiQAC (b) samples

Therefore, to prove the presence of Si-QAC in the coating, the BPB test was used, and the results are presented in Figure 3. Blue colour in the samples indicated the binding of the BPB anions to the cationic nitrogen atoms of the quaternary ammonium groups of Si-QAC via electrostatic attractive interactions. Accordingly, the K/S values, determined for the samples after shaking in the solution of BPB, highly increased from 0.2 for the PLA-N sample without Si-QAC to 10.2 and 11.4 for the PLA-SiQAC and PLA-RV-Ag-SiQAC samples, respectively.

The presence of the antimicrobial coating on the PLA fibres was also confirmed by the SEM and EDS analysis. The SEM/BSE images of the PLA-N, PLA-Ag, PLA-RV-Ag and PLA-RV-Ag-SiQAC samples (Figure 4) revealed that spherical silver particles, visible as bright spots, were formed over the entire surface of the fibres in the *in situ*

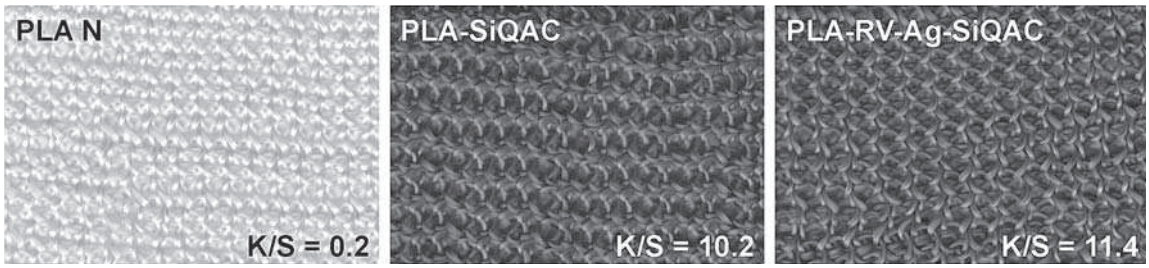

Figure 3: Photos of PLA samples after shaking in the solution of the BPB reagent

synthesis of AgCl (Figure 4b). The presence of AgCl was also confirmed by the EDS analysis, from the peaks of Ag-Lα and Cl-Kα (Table 2). The application of RV and Si-QAC greatly increased the roughness of the fibres, confirming the formation of the polymer coating from the sol-gel precursors (Figures 4 c and d). In these images, the presence of AgCl is not clearly perceptible. In addition, the Si-Kα peaks and Zr-Lα belong to the RV and Si-QAC silica matrix, while the C-Kα and

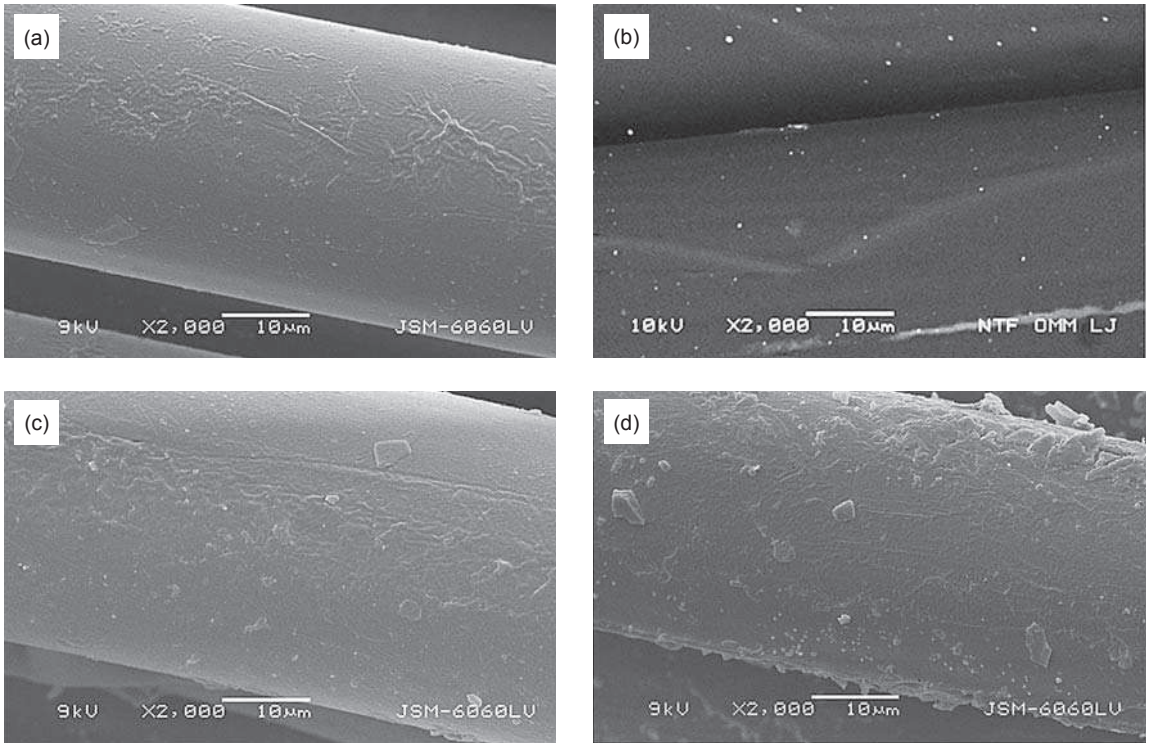

Figure 4: SEM/EDS images of PLA-N (a), PLA-Ag (b), PLA-RV-Ag (c) and PLA-RV-Ag-SiQAC (d) samples

Table 2: Elemental composition of the coated samples obtained by EDS analysis

Sample code	Atomic concentration of element [%]						
	Ag-Lα	Cl-Kα	Si-Kα	Zr-Lα	Na-Kα	C-Kα	O-Kα
PLA-Ag	0.275	7.988	0.000	0.000	2.936	74.000	1.145
PLA-RV-Ag	1.340	0.416	1.556	2.159	0.000	80.430	16.240
PLA-RV-Ag-SiQAC	0.636	3.649	2.595	1.919	0.000	83.004	8.198

Table 3: Concentration of silver, c_{Ag}, on the finished samples and the bacterial reduction, R, against bacteria E. coli in S. aureus

Sample code	c_{Ag} [mg/kg]	R [%]	
		E. coli	*S. aureus*
PLA-N	0.0	–	–
PLA-Ag	9.2 ± 1.8	50.5	59.2
PLA-SiQAC	0.0	67.5	78.1
PLA-RV-Ag	140 ± 28	100	100
PLA-RV-Ag-SiQAC	53 ± 11	100	100

O-Kα peaks belong to the silicon matrix as well as to the PLA fibres. The peak for nitrogen in the structure of Si-QAC could not be determined on a PLA-RV-Ag-SiQAC sample because it was overshadowed by the much more intense peaks of carbon and oxygen.

Table 3 shows that different samples absorbed different amounts of silver, namely: PLA-Ag <PLA-RV-Ag-SiQAC <PLA-RV-Ag, from solutions with the same concentrations of $AgNO_3$ and NaCl. These results confirm that the silica matrix created by RV highly increased the adsorptive capacity of fibres, resulting in the incorporation of a fifteen times higher concentration of silver into the PLA-RV-Ag sample in comparison to the PLA-Ag sample. The decrease of the concentration of silver on the fibres after the application of Si-QAC from 140 mg/kg (PLA-RV-Ag sample) to 53 mg/kg (PLA-RV-Ag-SiQAC sample) was expected because we assumed that silver particles were physically bonded to the silica matrix, enabling them to partially leach out of the sample when it was immersed in the solution of Si-QAC.

The results of the antimicrobial test, presented in Table 3, clearly demonstrate that the PLA fibres do not show any bacterial reduction. The concentration of silver on the PLA-Ag sample was too low to provide a bacterial reduction higher than 60%, which represents a threshold value for the biostatic action of the antimicrobial agent. Even the antibacterial activity of the one-component coating prepared with Si-QAC was only biostatic with the R values of 67.5% and 78.1% for *E. coli* and *S. aureus*, respectively. The biocidal activity with the R values equal to 100% for both studied bacteria was achieved on the PLA-RV-Ag and PLA-RV-Ag-SiQAC samples, which proves that the creation of a silica matrix is absolutely necessary for the PLA fibres with very low adhesion ability to AgCl, to achieve effective antimicrobial activity in the coating. The results also show that the presence of the Si-QAC polymer film on the PLA fibres did not hinder the leaching of silver particles from the coating, resulting in the synergistic action of the bio-barrier and controlled-release antimicrobial mechanisms.

The results of the colorimetric measurements presented in Figures 5 and 6 reveal that the presence of coatings decreased the lightness and increased the yellowing of the PLA fibres, especially in the case of the application containing RV and Si-QAC. At the same solution concentration (100 g/L), the application of Si-QAC decreased the whiteness of the fibres by 25%, but the application of RV decreased the whiteness by more than 50%. Accordingly, the whiteness of PLA-RV and PLA-RV-Ag-SiQAC fell below the value of 40 (Figure 5), which represents the threshold for which the equation (3) is valid. This represents a significant weakness of the studied antimicrobial coating. In line with the decrease of the whiteness, the highest yellowing was caused by the application of RV; the yellowing did not significantly increase with further application of silver and Si-QAC (Figure 6).

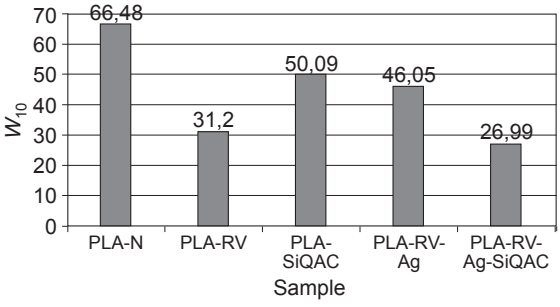

Figure 5: Whiteness, W_{10}, of untreated and finished samples

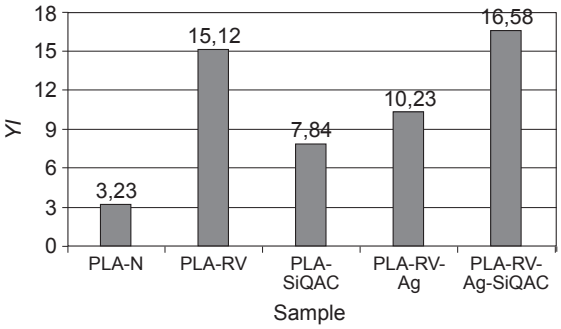

Figure 6: Yellowing index, YI, of untreated and finished samples

4 Conclusion

In this study, we have successfully developed a new three-stage procedure to tailor a dual-active antimicrobial finishing for the PLA fibres, using AgCl and Si-QAC. The procedure included the following steps:

- the application of RV with the aim to create a silica matrix on the surface of the fibres, which was important for increasing the adhesive ability of the fibres;
- the *in situ* synthesis of silver in a silica matrix with two sequential immersions of the PLA samples in the solutions of $AgNO_3$ and NaCl to create an antimicrobial coating with physically incorporated silver particles, which can be released into the environment in a controlled manner, acting as a poison for microorganisms;
- the application of Si-QAC with quaternary ammonium groups with the aim to create a polymer film on the fibre surface, which could act as a biological barrier and destroy microorganisms that come in contact with the fibres. The mode of preparation of the coating allows its application to other hydrophobic fibres, such as polyethylene terephthalate, polypropylene, and polyamide fibres.

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