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Elementarno srebro nano delcev kot antibakterijsko sredstvo na bombažni tkanini

Izvirni znanstveni članek

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Izvleček

Pripravljena je bila protimikrobna apretura z uporabo elementarnega srebra velikosti delcev nano dimenzij brez in v kombinaciji anorganske oksidne matrice. Apretura je bila nanesena na bombažno tkanino v šestih koncentracijah srebra od 0,01 do 0,5 % na maso blaga po izčrpalnem postopku, izvedenem v Launder-ometru. Zamreženje matrice je bilo doseženo toplozračno. Morfološke lastnosti apreturnega filma so bile določene s SEM, njegova sestava pa s FT-IR in EDXS analizo. Koncentracija Ag na tkanini je bila določena z ICP-MS. Baktericidne lastnosti apreture so bile določene na podlagi meritev bakterijske redukcije za bakterijsko vrsto *Escherichia coli*. Določen je bil vpliv apreture na spremembo beline tkanine, njene svetlobne obstojnosti, omočljivost, togost in zračno prepustnost. Iz rezultatov raziskave je bilo razvidno, da se je z naraščajočo koncentracijo Ag v apreturni kopeli povečevala tudi koncentracija Ag na tkanini, ki se je v prisotnosti oksidne matrice še povečala. Bakterijska redukcija se z naraščajočo koncentracijo Ag na tkanini ni bistveno spremenila. V vseh primerih, tudi pri najvišji koncentraciji Ag je ostala nižja od 60 %, kar je pomenilo nezadovoljivo baktericidno delovanje. Prisotnost oksidne matrice v apreturi je še poslabšala njene baktericidne lastnosti. Medtem ko nanos srebra ni bistveno spremenil omočljivosti tkanine, se je le-ta povečala pri vzorcih apretiranih s kombinacijo srebra in oksidne matrice. Prisotnost apreture je na splošno vplivala na znižanje beline tkanine, ki se je z osvetljevanjem vzorcev z umetno svetlobo še poslabšala. Oksidna matrica v apreturi je povzročila rahlo zmanjšanje zračne prepustnosti tkanine, zmanjšala pa je tudi togosti tkanine v primerjavi s tkanino, apretirano le s srebrom.

Elementary nano sized silver as antibacterial agent on cotton fabric

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Abstract

Antimicrobial finish was prepared by the use of elementary silver of nano dimensions, without and with a combination of anorganic oxide matrix. Finish was applied on cotton fabric in six different concentration of silver, ranging from 0.01 to 0.5 % on fabric mass. Application was performed by the exhaustion method using Launder-ometer. Network formation of the matrix was obtained by worm air. Morphological properties of the coating film were studied by SEM, while its composition by FT-IR and EDXS analysis. Concentration of silver was determined by ICP-MS. Bactericidal properties were quantitatively studied in terms of bacterial reduction for bacterium Escherichia coli. Influence of finish on whiteness of the fabric, light fastness, wettability, stiffness and air permeability was studied as well. The results showed that by increasing Ag concentration in the finishing bath, the concentration of Ag on textile increased as well, while it further increased in the presence of oxide matrix. However, the bacterial reduction did not significantly change by the increase of Ag concentration and stayed bellow 60 % in the case of all studied concentrations, even at the highest one, showing in-

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sufficient bactericidal activity. The presence of the oxide matrix, further decreased its antibacterial properties. While application of silver did not significantly influenced the wettability of the fabric, latter increased on the samples treated by a combination of silver and oxide matrix. In general, application of finish influenced on a decrease of whiteness of the fabric, which further decreased by illuminating the samples with an artificial light. The presence of oxide matrix in the finish caused slight decrease of air permeability of the fabric, compared to the air permeability of the fabric where only silver was applied.

Key words: antibacterial finish, elementary silver, oxide matrix, cotton fabric, bacterial reduction, whiteness, wettability, physical properties.

1 Introduction

For centuries, silver is known as a very effective natural antibiotic. Due to its medicinal, antiseptic and antimicrobial characteristics, people have applied it to wounds in order to prevent infections and accelerate healing, put silver powder in socks in order to prevent fungal infections and used silver containers to disinfect water. With the development of penicillin, silver was used less and less frequently due to various undesirable effects. Recently, it gained attention again when researchers succeeded to prepare silver particles of nano dimensions [1–6]. Nano silver has a large specific surface area and is effective even at very low concentrations. Therefore, its unique and specific characteristics, such as chemical stability, excellent electric conductivity, catalytic activity, non-linear optic characteristics and biocidal activity are well exploited. When used in low concentrations, nano silver is not known to be harmful to humans.

The preparation of nano silver particles enabled the development of a new generation of biocides. Their use has increased in various fields of biology, biochemistry, biomedicine and pharmacy. As an antimicrobial agent, silver has also a place in textile chemistry, where it is used as a nano additive to the polymeric melt when spinning antimicrobial synthetic fibres [7] or as a

Ključne besede: antibakterijska apretura, elementarno srebro, oksidna matrica, bombažna tkanina, bakterijska redukcija, belina, omočljivost, fizikalne lastnosti.

1 Uvod

Že stoletja je srebro poznano kot zelo učinkovit naravni antibiotik. Zaradi svojih zdravilnih, antiseptičnih in protimikrobnih lastnosti so ga ljudje nanašali na rane, da bi preprečili infekcije in pospešili zdravljenje, posipavali v nogavice ter s tem preprečili glivična obolenja, posode iz srebra so uporabljali za dezinfekcijo vode. Z razvojem penicilina se je srebro kot antibiotik zaradi različnih stranskih učinkov vse manj uporabljalo. Ponovno je vzbudilo pozornost v zadnjih letih, ko je uspelo raziskovalcem pripraviti srebro z velikostjo delcev nano dimenzij [1–6]. Nano srebro ima veliko specifično površino in je učinkovito že pri zelo nizkih koncentracijah. Pri tem se izkoriščajo njegove edinstvene in specifične lastnosti, kot so kemijska stabilnost, odlična električna prevodnost, katalitična aktivnost, nelinearne optične lastnosti in biocidno delovanje. Nano srebro nizkih koncentracij naj ne bi bilo škodljivo za ljudi.

Priprava nano delcev srebra je omogočila razvoj nove generacije biocidov. Njihova uporaba je močno narasla na različnih področjih biologije, biokemije, biomedicine in farmacije. Kot protimikrobno sredstvo se je uveljavilo tudi v tekstilni kemiji, kjer se uporablja kot nanoaditiv v polimerni talini pri predenju protimikrobnih sintetičnih vlaken [7] ali kot apreturno sredstvo za zaščito naravnih in sintetičnih vlaken pred mikroorganizmi [8–12]. Srebro se na tržišču nahaja v različnih oblikah, največkrat kot trdna prahasta snov, koloidno srebro, ali kot disperzija težkotopne srebrove soli.

Lastnosti srebra v prahasti obliki so neposredno odvisne od postopka njegove proizvodnje [13]. Prahasti delci imajo specifično morfologijo, ki direktno vpliva na njihove funkcionalne lastnosti. Pri tem je pomembno, da so kristalni delci čim manjši, neaglomerirani, njihova velikost pa čim bolj enotna. Srebro v prahu, ki ga uporabimo kot apreturno sredstvo, je potrebno predhodno dispergirati. Disperzije se največkrat pripravijo v vodi z uporabo ustreznega dispergirnega sredstva. Pri tem je zagotovitev stabilne vodne disperzije ter preprečitev agregacije delcev še vedno pereč problem, posebej v primeru večjih delcev in višjih koncentracij srebra. Če visoka stabilnost disperzije ni dosežena, se srebro kot apreturno sredstvo ne more nanašati po impregnirnem postopku. Le-ta zaradi samega načina izvedbe ne omogoča konstantnega mešanja apreturne kopeli ter s tem povečanja enakomernosti porazdelitve delcev v suspenziji, ki je nujna za enakomeren nanos srebra na tekstilna vlakna. V tem primeru je bolj uporaben izčrpalni postopek.

Biocidno delovanje srebra na tekstilnih vlaknih temelji na postopnem sproščanju srebrovih ionov v okolico [14], kjer deluje kot strup za širok spekter mikroorganizmov. Ker je na vlakna vezano

finishing agent for the protection of natural and synthetic fibres against micro-organisms [8–12]. On the market, silver can be found in various forms, most often as a solid powdered substance, colloid silver or a dispersion of hardly-soluble silver salts.

The characteristics of silver in a powder form directly depend on the production procedure [13]. Powdery particles have a specific morphology, which directly affects their functional characteristics. It is important that the crystal particles are as small as possible, non-agglomerated and the more uniform in size as possible. When used as a finishing agent powdered silver must be dispersed. Dispersions are mostly prepared in water by using an appropriate dispersing agent. Namely, the preparation of stable water dispersion and prevention of particle aggregation remains still the main problem, especially in the case when larger particles and higher silver concentrations are used. If high stability of the dispersion is not attained, silver cannot be applied according to the impregnating procedure, since uneven distribution of silver occurs on textile. Namely, a constant mixing of silver dispersion must be provided through the whole process of application in order to achieve uniform distribution of the particles in the suspension. Therefore, in application process exhaustion method is more useful [14].

The biocidal activity of silver on textile fibres bases on a gradual release of silver ions into the environment [15], where it acts as a poison on a wide spectrum of micro-organisms. Since it does not chemically bind to the fibres, a silver finish is not wash-resistant, meaning that it removes from the fibres during repetitive washings. The increase of its washing fastness can be obtained by implementing modern procedures of application, such as sol-gel technology. Namely, sol-gel technology enables the physical binding of silver particles onto an inorganic oxide matrix [16] which is chemically bound to fibres, ensuring mechanical, chemical and photochemical stability. Moreover, it is also biological inert, since it does not represent a food source for micro-organisms. Previous studies have shown that the presence of the matrix increases the concentration of bound silver as well as its uniform dis-

fizikalno, apretura s srebrom ni pralno obstojna, temveč se z večkratnim pranjem s tekstilije odstrani. Povečanje pralne obstojnosti apreture s srebrom lahko dosežemo s sodobnimi postopki aplikacije, med katere uvrščamo tudi sol-gel tehnologijo. Sol-gel postopek omogoča fizikalno vezanje srebrovih delcev v anorgansko oksidno matrico [15]. Matrica je kemijsko vezana na vlakna in zagotavlja mehansko, kemijsko in fotokemijsko stabilnost kot tudi biološko inertnost, saj ne predstavlja vira hrane mikroorganizmov. Dosedanje raziskave so pokazale, da prisotnost matrice poveča koncentracijo vezanega srebra, enakomernost porazdelitve delcev ter podaljša čas njegovega sproščanja v okolico [11, 16–19].

V raziskavi smo pripravili protimikrobno apreturo z elementarnim srebrom nano velikosti na celuloznih vlaknih brez in v kombinaciji z oksidno matrico. Namen raziskave je bil preučiti, kako prisotnost matrice vpliva na velikost in porazdelitev delcev srebra v apreturnem filmu na vlaknih, na njegovo antibakterijsko učinkovitost ter pralno obstojnost apreture. Funkcionalne lastnosti apreture smo primerjali s tistimi dobljenimi s srebrovim kloridom vezanim v oksidno matrico pri enakih pogojih. Pomemben cilj raziskave je bil tudi preučiti, kako apretura s srebrom vpliva na barvo, svetlobne obstojnosti, omočljivosti ter fizikalne lastnosti apretirane tkanine.

2 Eksperimentalni del

2.1 Tkanina in apreturna sredstva

V raziskavi smo uporabili 100 % bombažno tkanino v vezavi platno s ploščinsko maso 164 g/m^2, gostoto osnove 28 niti/cm in gostoto votka 24 niti/cm. Tkanina je bila predhodno beljena s H_2O_2, mercerizirana v raztopini NaOH in nevtralizirana z razredčeno CH_3COOH.

Kot protimikrobno sredstvo smo izbrali tržni produkt Silver Nano Powder NP-30 (v nadaljevanju Ag) (Ames Goldsmith Corporation), ki je elementarno srebro s povprečno velikostjo delcev 30 nm. Je prahasta snov sive barve. Kot dispergirno sredstvo smo uporabili Setamol WS (BASF, Nemčija), ki je kondenzacijski produkt naftalen sulfonata s formaldehidom, kot organsko-anorgansko vezivo pa iSys MTX (BEZEMA, Švica) v kombinaciji s Kollasol CDO (BEZEMA, Švica).

2.2 Apretiranje

Nanos apreture na silicijevo ploščico

Pripravili smo apreturno kopel, ki je vključevala 0,025 g/l Ag in 2,0 g/l Setamola WS. Kopel smo pripravili brez in v prisotnosti 15,0 g/l iSys MTX in 1,0 g/l Kollasol DCO. Kopel smo obdelovali v ultrazvočni kadički 10 minut pri frekvenci 50 Hz in temperaturi 25 °C. V tako pripravljeno kopel smo potopili silicijeve (Si) ploščice, jih počasi izvlekli, posušili in zapekli pri 150 °C 5 min v sušilniku. Na Si ploščico smo ločeno nanesli tudi 15,0 g/l iSys MTX in 1,0 g/l Kollasol DCO na enak način kot apreturno kopel.

tribution and prolongs the time of silver release into the environment [11, 17–20].

In the present research, an antimicrobial finish with elementary nano silver was prepared on cellulose fibres with and without an oxide matrix. We aimed to study how the presence of the matrix affects the size and distribution of silver particles on the coating film on fibres, its antibacterial activity and the wash fastness of the coating. The functional characteristics of the coating were compared to those obtained by using silver chloride incorporated into an oxide matrix applied under the same conditions. An important objective of the research was also to study how the silver finish affects the colour, resistance to light, wettability and physical characteristics of the finished textile.

2 Experimental

2.1 Materials

Plain-weave 100 % cotton fabric with a mass of 164 g/m², warp density of 28 threads/cm and weft density of 24 threads/cm was used in the experiments. In a pre-treatment process fabric was bleached with H_2O_2, mercerised in a NaOH dilution end neutralized by a dilution of CH_3COOH.

Table 1: Concentrations, c, of products used in the finishing bath for different finishes.

Finish	*c* Ag		*c* Setamol WS (g/l)	*c* iSys MTX (g/l)	*c* Kollasol DCO (g/l)
	(% o.w.f)	(mg/l)			
AP1	0.01	2.0	2.0	0	0
				15.0	1.0
AP2	0.025	5.0	2.0	0	0
				15.0	1.0
AP3	0.05	10.0	2.0	0	0
				15.0	1.0
AP4	0.10	20.0	2.0	0	0
				15.0	1.0
AP5	0.25	50.0	2.0	0	0
				15.0	1.0
AP6	0.50	100.0	2.0	0	0
				15.0	1.0

Apretiranje bombažne tkanine

Apretiranje smo izvedli po izčrpalnem postopku v Launder-ometru 30 minut v kopelnem razmerju 1 : 50 pri temperaturi 25 °C. Koncentracije uporabljenih sredstev v kopeli so prikazane v preglednici 1. Po končanem postopku apretiranja smo vzorce oželi na dvovaljčnem fularju s 100 % ožemalnim učinkom, posušili pri temperaturi 120 °C ter kondenzirali 1 minuto pri temperaturi 150 °C v razpenjalnem sušilniku. Sledilo je 10 dnevno odležanje apretiranih vzorcev tkanine, da se je zamrežil iSys MTX.

2.3 Pranje

Apretirane vzorce tkanine smo enkrat in petkrat prali v Launder-ometru po standardni metodi ISO 105-C01:1989E. Masa vzorcev je znašala 7 g. Pranje smo izvedli v kopelnem razmerju 1 : 50 z uporabo 5 g/l SDC standardnega praška pri temperaturi 40 °C, 30 minut. Po pranju smo vzorce sprali pod tekočo vodo in posušili na zraku.

2.4 Osvetljevanje v Xenotestu

Apretirane vzorce smo določili z umetno svetlobo v Xenotest 150 aparatu (Original Hanau, Nemčija) v skladu s standardom ISO 105-B02. Svetlobni vir je predstavljala zračno hlajena ksenonska žarnica z območjem UV sevanja od 300 do 400 nm. Vzorce smo osvetljevali pri temperaturi 45 °C in 50 % relativni zračni vlažnosti. Čas osvetljevanja je znašal 51 ur.

2.5 Metode preiskav

Infrardeča spektroskopija s Fourierjevo transformacijo (FT-IR)

Lastnosti prevleke, ki jo je na površini Si ploščice tvoril iSys MTX v kombinaciji s Kollasol DCO, smo preučili s FT-IR spektroskopijo

As an antimicrobial agent, a commercial product Silver Nano Powder NP-30 (Ames Goldsmith Corporation) (Ag in the following text), which is an elementary silver in a form of grey coloured powder, with an average particles size of 30 nm, was used. As dispersing agent Setamol WS (BASF, Germany), which is condensation product of naphathalen sulphonate and formaldehyde, was used. As organic-inorganic binder iSys MTX (BEZEMA, Switzerland) in combination with Kollasol CDO (BEZEMA, Switzerland) were used.

2.2 Finishing

Application of finish on the Si – wafer

For the preparation of the finishing bath 0.025 g/l Ag and 2.0 g/l Setamol WS were used. Additionally, the bath was prepared with and without 15.0 g/ iSys MTX and 1.0 g/l Kollasol DCO. Finishing bath was treated for 10 minutes by an ultrasound at frequency of 50 Hz and 25 °C. In this manner prepared finishing bath was applied on Si wafers by the deep coating technique. Afterwards, Si wafers were heat treated for 5 minutes at 150 °C. In addition, 15.0 g/l of iSys MTX and 1.0 g/l Kollasol DCO were also separately applied on Si wafer in the same way as for the finishing bath.

Finishing of cotton fabric

Finishing of cotton fabric was obtained by the exhaustion method in a Launder-ometer, whereas samples of cotton were treated in the corresponding finishing baths with a ratio of 1 : 50 for 30 minutes at temperature of 25 °C. Concentrations of agents used in finishing bath are shown in table 1. Afterwards, the samples were wrung by a wet-pick-up of 100 %, dried at 120 °C and cured at 150 °C for 1 minute. The samples were further left for 10 days in order to complete iSys MTX network formation.

2.3 Washing procedure

Finished cotton samples were once and five times washed in a Launder-ometer according to the ISO 105-C01:1989E standard method. The duration of one washing cycle was 30 min and was carried out in a solution of SDC standard detergent of concentration 5 g/l, previous-

na Bruker IFS 66/S spectrofotometeru, opremljenem z ATR celico (SpectraTech). Spektre smo posneli na ATR celici z Ge kristalom (n = 4,0) in na ATR celici z diamantom (n = 2) pri valovnih dolžinah od 4000 do 600 nm.

Vrstična elektronska mikroskopija (SEM) z energijsko-disperzijsko spektroskopijo rentgenskih žarkov (EDXS)

Morfologijo in sestavo apreturnega filma na Si ploščici in bombažni tkanin smo določili z uporabo JEOL JSM 5800 vrstičnega elektronskega mikroskopa, opremljenega z analitskim EDXS sistemom (Oxford-Link ISIS 300). Da bi preprečili nabijanje električno neprevodnih delov vzorca, smo na površino vzorca nanesli tanko plast ogljika (približno 20 nm). Analizo smo izvedli z uporabo energije elektronov 10-keV, gostoto toka elektronov 200 do 500 pA in nagibom vzorca 35°. Topografijo površine vzorca in plast na prelomu vzorca smo opazovali tako s sekundarnimi (SE) kot tudi povratno sipanimi primarnimi elektroni (BSE). Sliko, ki je nastala z BSE elektroni smo uporabili za razlikovanje nanešenih apreturnih delcev od bombažnih vlaken in drugih nečistoč.

Masna spektroskopija z induktivno sklopljeno plazmo (ICP-MS)

Koncentracijo Ag na apretiranih vzorcih tkanine pred in po petkratnem pranju smo določili z ICP-MS na spektrofotometru Perkin Elmer SCIED Elan DRC. Vzorec velikosti 0,5 g smo pripravili v Milestone mikrovalovnem sistemu s kislinsko dekompozicijo z 60 % HNO_3 in 30 % H_2O_2.

Bakterijska redukcija

Bakterijsko redukcijo vzorcev tkanine apretirane z različnimi apreturami smo izvedli po AATCC standardni metodi 100-1999 za bakterijsko vrsto *Escherichia coli* (ATCC 25922). Vzorec apretirane tkanine smo prenesli v erlenmajerico, ga prelili s suspenzijo bakterij določene koncentracije in inkubirali pri temperaturi 37 °C, 24 ur. Po inkubaciji smo vzorec prelili s 100 ml sterilne destilirane vode, 1 minuto intenzivno stresali, ter suspenzijo ustrezno razredčili. Razredčino smo razmazali na agar plošče in inkubirali 24 ur pri 37 °C. Po inkubaciji smo prešteli bakterijske kolonije ter izračunali bakterijsko redukcijo, R, po naslednji enačbi:

$$R = \frac{B - A}{B} \times 100\ [\%] \qquad (1)$$

kjer je A število bakterijskih kolonij v suspenziji po 24 urah stika suspenzije z vzorcem apretirane tkanine, B pa število bakterij v suspenziji po 24 urah stika suspenzije z neapretirano tkanino. Za zadovoljivo protimikrobno delovanje sredstva mora vrednost R preseči 60 %. Za vsak vzorec tkanine smo opravili dve ponovitvi.

Omočljivost

Omočljivost apretiranih vzorcev tkanine z vodo smo določili z metodo tankoplastnega pronicanja. Meritve tankoplastnega pronicanja

ly heated to 40 °C, to give a liquor ratio of 50 : 1. In this case a 7 g samples were used. After washing the samples were rinsed in a cold tap water and air dried.

2.4 Illumination in Xenotest

Finished samples were illuminated by an artificial light in Xenotest 150 aparatus (Original Hanau, Germany) according to the ISO 105-B02 standard. For illumination air colled xenon bulb was used with an UV radiation region from 300 to 400 nm. The samples were illuminated at temperature of 45 °C and 50 % of relative humidity. Duration of illumination was up to 51 hours.

2.5 Analysis and measurements

Fourier transform infrared (FT-IR) spectroscopy.

Properties of the coating, formed by iSys MTX in combination with Kollasol DCO, on a Si wafer was studied by FT-IR spectroscopy, using a Bruker IFS 66/S spectrophotometer, equipped with an attenuated total reflection (ATR) cell (SpectraTech) with a Ge crystal (n = 4.0). The spectra were recorded over the range 4000–600 cm^{-1}, with a resolution of 4 cm^{-1} and averaged over 128 spectra.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS).

Morphology and composition of the coating on Si wafer and cotton fabric were studied by a JEOL JSM 5800 scanning electron microscope (SEM) equipped by an analytic EDXS system (Oxford-Link ISIS 300). The samples for SEM and EDXS analyses were coated with ≈ 30-nm-thick carbon layer to ensure sufficient electrical conductivity and to avoid charging effects. Analyses were performed using a 10-keV electron beam, 200 to 500 pA beam current and X-ray spectra acquisition under a 35° take-off angle. SEM micrographs were recorded using both secondary electron (SE) and backscattered electron (BSE) imaging modes. BSE compositional (Z-contrast) imaging was applied to emphasize and expose the difference between the added particles and the cotton fibre-matrix.

smo izvedli v horinzontalni smeri, ki ga je za tkanine priredil Chibowski [20]. Vzorce tkanine smo sušili 30 minut pri temperaturi 105 °C. Po vzpostavitvi stika med vodo in vzorcem smo merili čas, *t*, v katerem je voda pronicala v vzorec do določene razdalje, *x*. Za vsak vzorec smo opravili najmanj 7 ponovitev.

Belina in barvni odtenek beline

Belino in barvni odtenek beline vzorcev tkanine smo določili na podlagi meritev CIE barvnih vrednosti z uporabo dvožarkovnega spektrofotometra Spectraflash 600 PLUS- CT (Datacolor, Švica). Meritve smo opravili pri naslednjih pogojih: velikost merilne odprtine 9 mm, standardna svetloba D_{65} in T = 6500 K, kot opazovalca je bil $D_{65}/10$ z vklopljenim UV filtrom. Belino, W_{10}, smo izračunali iz naslednje enačbe [21]:

$$W_{10} = Y_{10} + 800\ (0.3138 - x_{10}) + 1700\ (0.3310 - y_{10}) \qquad (2)$$

kjer je Y_{10} standardizirana barvna vrednost vzorca ter x_{10} in y_{10} standardizirana barvna deleža vzorca.

Barvni odtenek beline, TW,10, smo določili na naslednji način:

$$T_{W,10} = 900\ (0.3138 - x_{10}) + 650\ (0.3310 - y_{10}) \qquad (3)$$

Vrednosti W_{10} in $T_{w,10}$ smo določili za neapretirano tkanino ter vzorce tkanine, apretirane z različnimi apreturami, pred in po osvetljevanju z umetno svetlobo.

Zračna prepustnost

Zračno prepustnost vzorcev tkanine smo določili po standardu SIST EN ISO 9237 : 1999. Meritve smo izvedli tako, da smo pri tlaku 20 mm vodnega stolpca določili količino presesanega zraka, *q*, skozi vzorec. Na vsakem vzorcu smo izvedli po 10 meritev. Kot rezultat smo podali količino presesanega zraka, *Q*, skozi ploščinsko enoto tkanine v času ene minute, ki smo jo izračunali iz enačbe:

$$Q = q/6a \qquad (4)$$

v kateri je *Q* količina presesanega zraka v $m^3/min\ m^2$, *q* je količina zraka, ki prehaja skozi površino preizkušanega vzorca v l/h, in *a* pa je preizkusna površina v cm^2, ki je znašala 10 cm^2.

Zračno prepustnost smo merili tudi na rotametru. Pri tem smo pri različnih tlakih določili volumski pretok zraka skozi določeno površino suhega vzorca. Za vsak vzorec apretirane tkanine smo opravili po tri ponovitve, primerjalno pa tudi meritve na neapretiranem vzorcu tkanine.

Togost

Togost tkanine smo določili po standardu ASTM D1388-64. Na podlagi meritev previsne dolžine, l_o, v smeri osnove in vrednosti

Inductively coupled plasma mass spectroscopy (ICP-MS)

The concentration of the silver on finished cotton samples before and after five times washing was determined by ICP-MS on a Perkin Elmer SCIED Elan DRC spectrophotometer. A sample of 0.5 g was prepared in a Milestone microwave system with acid decomposition using 60% HNO_3 and 30% H_2O_2.

Reduction of bacteria

Antibacterial activity of studied samples was determined according to the AATCC 100-1999 standard method, for bacterium Escherichia coli (ATCC 25922). Sample of the finished cotton was put into an Erlenmeyer flask and inoculated with a nutrient broth culture containing certain amount of bacteria and incubated at 37 °C for 24 hours. After incubation, the bacteria were eluted from the swatches by shaking them in 100 ml of neutralizing solution for 1 minute. After making serial dilutions, the suspensions were plated on nutrient agar and incubated at 37 °C for 24 hours. Afterwards, the number of bacteria forming units (CFU) was counted, and the reduction of bacteria, R, was calculated from (Equation 1).

Where A is the CFU recovered from the inoculated cotton sample swatch in the jar incubated over the desired contact period (24 hours), and B is the CFU recovered from the inoculated cotton sample swatch in the jar immediately after inoculation (at "0" contact time). For each finished cotton fabric, two treatments were performed.

Wettability

Water wettability of finished cotton samples was determined by thin-layer wicking method. Measurements were performed in horizontal direction which was special elaborated for textile by Chibowski [20]. Fabric sample was dried at temperature 105 °C for 30 minutes. After providing a contact between the water and the sample, the time, t, needed for water penetration through the sample to a certain distance, x, was measured. For each sample at least 7 measurements were made.

Whiteness Index and tint of whiteness

Whiteness index and tint of whiteness were determined based on CIE measurements of re-

ploščinske mase, T, tkanine smo izračunali togost, U_o, tkanine iz naslednje enačbe:

$$U_0 = T\,(l_0/2)^3 \qquad (5)$$

3 Rezultati in razprava

S FT-IR analizo smo določili funkcionalne skupine, prisotne v apreturnem filmu, ki ga je tvoril iSys MTX. Zaradi zelo močnih trakov, ki pripadajo bombažu v spektralnem območju od 1150–900 cm^{-1} in lahko zasenčijo absorpcijo apreturnega filma v tem območju [22], smo iSys MTX nanesli na Si ploščico. Pri pregledu spektra apreture (slika 1) smo opazili trakove Si–O–Si povezav pri 1130, 1075 in 1025 cm^{-1} (rama), ki dokazujejo, da se je pri procesu kondenzacije tvoril polisiloksanski zamrežen film, ki je sposoben vezati Ag delce [11, 16–19]. Ker z FT-IR analizo nismo mogli določiti trakov, ki pripadajo Ag delcem v apreturi, smo za potrditev njihove prisotnosti ter določitev velikost delcev in koncentracije Ag na apretirani bombažni tkanini pred in po večkratnem pranju uporabili SEM, EDXS in ICP-MS.

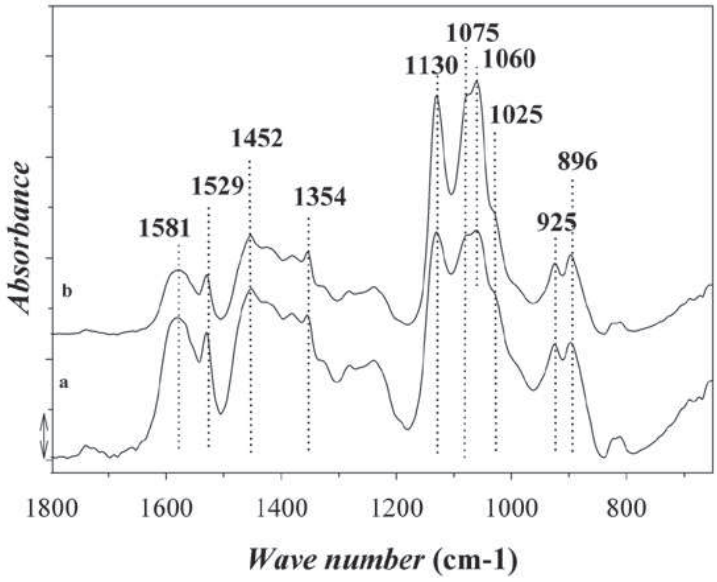


Figure 1: ATR IR spectra of iSys MTX without (a) and in the presence of Ag (b) deposited on Si wafer in the 1800–650 cm^{-1} spectral region.

Iz SEM/BSE mikrografov Si ploščice prevlečene z apreturnim filmom (slika 2a in 2b) je jasno razvidna prisotnost Ag delcev krogelne oblike. Kljub dodatku dispergirnega sredstva in obdelovanju apreturne kopeli v ultrazvočni kopeli so dobro razvidni aglomerati Ag delcev v velikosti do 3 µm (povečava delca na sliki 2a). V nasprotju z apreturnim filmom AP1 brez dodatka iSys MTX

flectance values by the use of double-beam Spectraflash 600 PLUS-CT (Datacolor, Swiss) spectrophotometer. The measurements were made under following conditions: size of measurement port 9 mm, standard light D_{65} and T = 6500 K, observation angle D_{65}/10 with UV filter included. Whiteness index, W_{10}, was calculated from following equation (Equation 2) [21],
where Y_{10} denotes the tristimulus value of the sample and x_{10} and y_{10} denote the chromaticity coordinates of the sample.
Tint of whiteness, $T_{W,10}$, was determined by following equation (Equation 3):
Values for W_{10} and $T_{W,10}$ were determined for unfinished sample and samples coated by the studied finishes before and after illumination with artificial light.

(slika 2a), kjer so lepo razvidni tudi manjši Ag delci, pa smo na silicijevi ploščici obdelani z apreturo AP1 z dodatkom iSys MTX (slika 2b) zasledili le večje aglomerate Ag delcev, vendar šele ko smo energijo elektronov povečali iz 10 kV na 20 kV. To pomeni, da so bili Ag delci popolnoma prevlečeni z polisiloksansko matrico, ki je oteževala njihovo detekcijo s SEM, zaradi česar manjših Ag delcev ni bilo mogoče opaziti. V primeru apreture AP1 z iSys MTX so iz SEM mikrografov (slika 2d) dobro razvidni delci polisiloksanske matrice (bele lise), kar smo potrdili tudi z EDXS mikroanalizo. Tipična EDXS mikrografa srebrovih delcev in delcev polisiloksanske matrice sta prikazana na sliki 3. Iz EDXS spektra Ag delca označenega z „1“ na sliki 2a so jasno razvidni tipični vrhovi Ag-Lα skupine, medtem ko so na EDXS mikrografu, nastalem ob usmeritvi žarka elektronov na značilne bele lise na vlaknih označene z „2“ na sliki 2d, razvidni Si-Kα, Zr-Lα and O-Kα vrhovi, ki nedvomno potrjujejo, da je iSys MTX v prisotnosti katalizatorja tvoril polisiloksansko matrico.

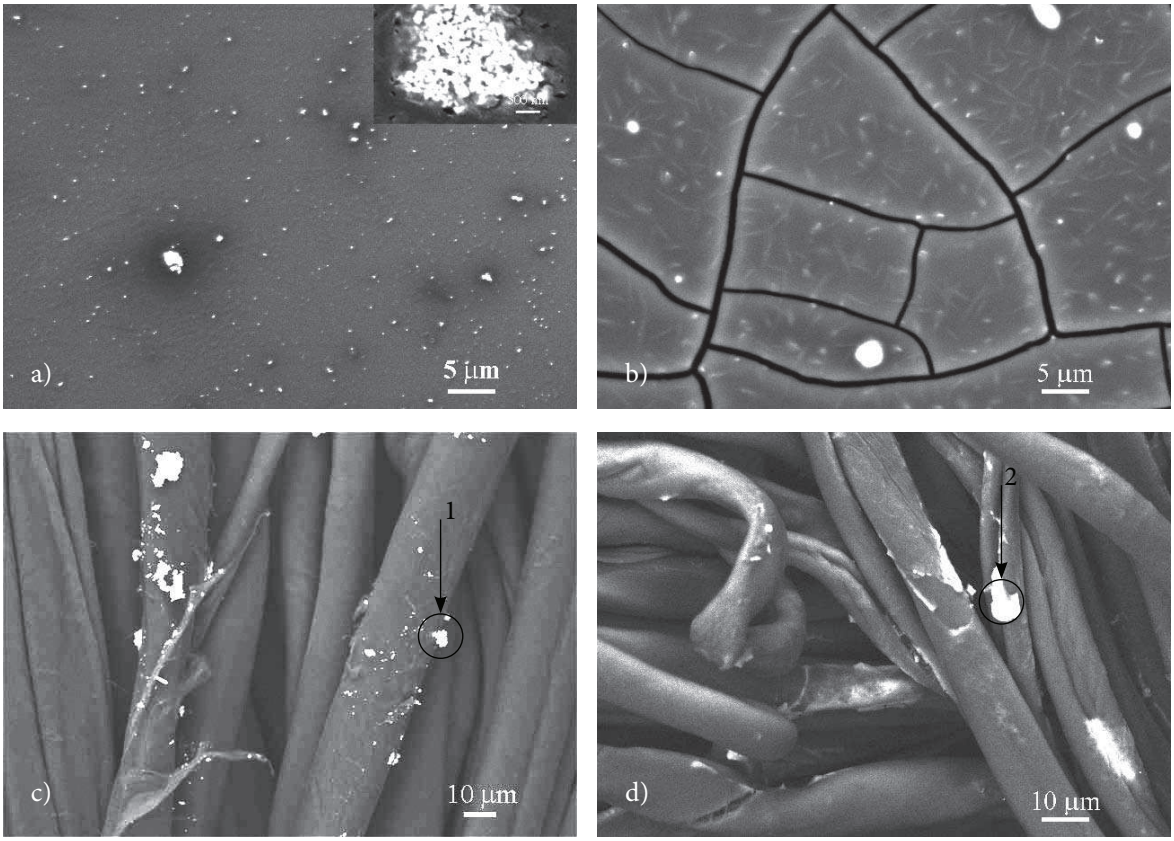


Figure 2: SEM/BSE micrographs of Si wafer (a and b) and cotton fabric (c and d) treated with AP 1 finish without (a and c) and with (b and d) iSys MTX (for sign explanation of "1" and "2" see Figure 3).

Air permeability

Air permeability measurements of the studied samples were carried out according to the SIST EN ISO 9237:1999 standard. From the amount

Koncentracija Ag na bombažni tkanini pred in po petkratnem pranju, določena z ICP-MS, je prikazana v preglednici 2. Iz nje je razvidno, da je z naraščajočo koncentracijo Ag v apreturni kopeli naraščala tudi koncentracija Ag na tkanini. Pri najnižji koncen-

of air passed through the sample under a pressure of 20 mm H_2O, the air permeability was determined as Q given by (Equation 4),
where q is the volume of air flowing through the sample of area, a, (which amounted 10 cm^2) expressed in l/h and Q is the volume of air in m^3 passing through 1 m^2 of the fabric per minute at the required pressure. The results represent the mean values of ten measurements.
Air permeability was also measured on a rotameter, whereas volume of air flowing through the sample of certain area was determined at different preasure. For each finished sample as well as for unfinished one three measurements were made.

Stifness

Stifness of the fabric was determined according to the ASTM Standard D-1388-64. Based on the bending length, l_o, measurements and the mass area, T, stifness of the sample, U_o, was calculated following the equation (Equation 5).

3 Results and discussion

The ATR technique was used to study the molecular groups and species present in the coating film formed by iSys MTX. Due to very strong bands belonging to cotton in the 1150–900 cm^{-1} spectral region, which could blur the detailed absorption of the finish in this region [22], iSys MTX was deposited on a Si wafer. Inspection of the coating spectra (Figure 1) revealed bands of Si–O–Si linkages at 1130, 1075 and 1025 cm^{-1} (shoulder), showing, that during condensation process, the silica network was formed, capable of incorporation of Ag particles [11, 16–19]. Since by FT-IR spectroscopy the bands ascribed to Ag particles in the finish could not be determined, SEM, EDXS and ICP-MS techniques were used, in order to confirm the presence of Ag particles as well as to determined their size and concentration on finished cotton fabric before and after repetitive washing.
The SEM/BSE micrographs of Si wafer covered by the coating film (Figures 2a and 2b) clearly show the presence of spherically shaped Ag particles. Despite the addition of dispersing agent and treatment of the finishing bath by the ultra-

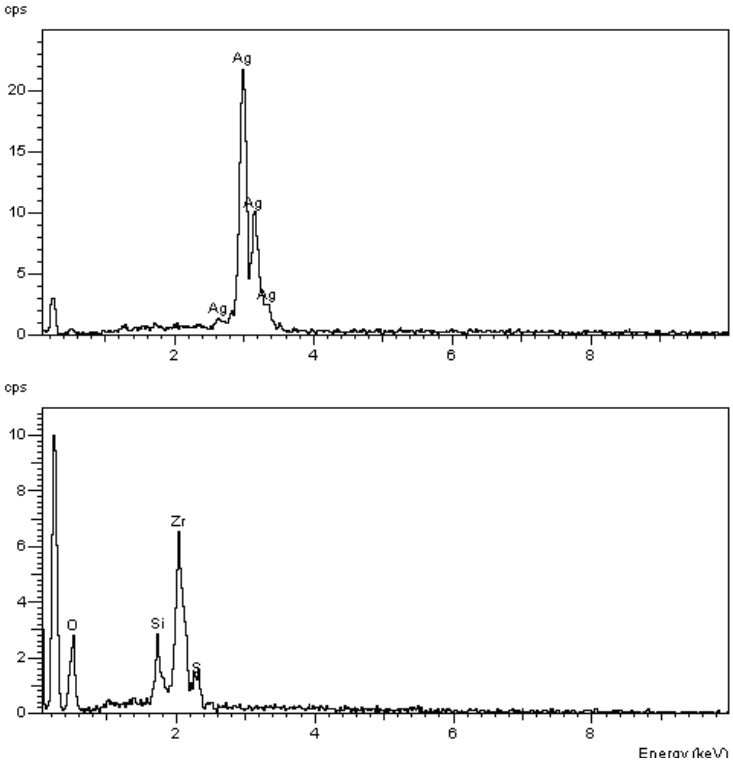


Figure 3: EDXS spectrum acquired from typical inclusions "1" (see Fig. 2c) (a) and "2" (see Fig. 2d) (b) on cotton fabric finished with AP1.

traciji Ag enaki 0,01 % o.w.f. je znašala od 20 do 30 mg/kg tkanine, pri najvišji koncentraciji Ag enaki 0,50 % o.w.f. pa od 295 do 350 mg/kg vlaken. Prisotnost iSys MTX v apreturni kopeli je vplivala na povečanje koncentracije Ag na vlaknih. Prisotnost iSys MTX ni vplival na povečanje pralne obstojnosti Ag delcev na bombažni tkanini. Njihova koncentracija se je po petkratnem pranju apretirane tkanine močno znižala in padla pod 35 mg/kg vlaken ne glede na apreturo. Pralna obstojnost preučevane apreture je bila slabša od tiste dobljene z AgCl v kombinaciji z iSys MTX [19], kjer je bila po desetkratnem pranju določena dvakrat večja koncentracija Ag na vlaknih kot v primeru apreture AP6, in to kljub temu, da je bila koncentracija Ag pred pranjem nižja kot pri apreturi AP6 v prisotnosti iSys MTX.
Bakterijska redukcija, *R*, za bakterijsko vrsto *Escherichia coli* se z naraščajočo koncentracijo Ag na tkanini ni bistveno spremenila (slika 4). V vseh primerih, tudi pri najvišji koncentraciji 350 mg/kg vlaken, je ostala R nižja od 60,2 %, kar pomeni neučinkovito oziroma nezadovoljivo zaščito pred bakterijami. Ti rezultati so veliko slabši od tistih dobljenih z AgCl, kjer je bila 60 % redukcija dobljena že pri koncentraciji 25 mg/kg AgCl, redukcija večja od 88 % pa pri koncentracijah višjih od 50 mg/kg [19]. To pomeni, da je baktericidno delovanje srebrovih kationov na bombažni tkanini bolj učinkovito v primerjavi z elementarnim srebrom enake

Table 2: Concentrations, c, of Ag in finishing baths and on the cotton samples treated by the finishes from AP1 to AP6 before (0 W) and after five (5 W) repetitive washing.

Finish	*c* Ag in bath (% o.w.f.)	*c* Ag on fibres (mg/kg)			
		0 W		5 W	
		A [a)]	B [a)]	A	B
AP1	0.01	27	20	2	2
AP2	0.025	25	48	6	4
AP3	0.05	34	60	8	5
AP4	0.10	97	116	14	10
AP5	0.25	176	180	30	12
AP6	0.50	295	350	32	33

[a)] *A: without iSys MTX, B: with iSys MTX.*

sound, the agglomerates of Ag particles in the size range up to 3 µm are seen (magnification of particle on figure 2a). Contrary to coating film AP1 without the addition of iSys MTX (Figure 2a), where also smaller Ag particles are nicely seen, only bigger agglomerates of Ag particles were observed on Si wafer treated by AP1 finish with the addition of iSys MTX (Figure 2b), but only in the case when the energy of electron beam increased from 10 kV to 20 kV. This indicated that Ag particles were totally covered by polysiloxane matrix, which made the detection of Ag particles by SEM difficult and was the main reason that smaller particles could not be observed. In addition, also some bright inclusions were seen on Si wafer coated by AP1 and iSys MTX which belong to the polysioloxane matrix and were further confirmed by EDXS analysis. Typical EDXS micrographs of silver particles and particles of polysiloxane matrix are presented in figure 3. EDXS spectrum of Ag particle, indicated by "1" in figure 2a, revealed characteristic peaks belonging to the family of Ag-Lα spectral lines, whereby EDXS micrograph, made by directing the electron beam on typical white inclusions on fibres, indicated by "2" in figure 2d, revealed Si-Kα, Zr-Lα and O-Kα peaks, which indubitaly confirmed that iSys MTX formed a polysiloxane matrix in the presence of catalyst.

ICP-MS measurements of Ag concentration determined on cotton fabric before and after five repetitive washings (Table 2) showed that by

koncentracije. To bi tudi pričakovali, saj mora elementarno srebro na vlaknih v prisotnosti oksidanta in vlage preiti v srebrove katione, za katere je dokazano učinkovito biocidno delovanje. V primeru AgCl so srebrovi kationi na vlaknih že prisotni, zato reakcija oksidacije ni potrebna. Njihovo sproščanje je odvisno le od prisotnosti vlage. Ne glede na to pa je bila bakterijska redukcija dobljena z elementarnim srebrom višja od tiste dobljene pri uporabi elementarnega srebra velikosti delcev 80 nm [23], ki je pri enaki koncentraciji 20 mg/l tržnega produkta za bakterijsko vrsto *Escherichia coli* znašala le od 1 do 11 %. To potrjuje, da se z manjšanjem velikosti nano delcev Ag njegova protimikrobna učinkovitost povečuje. Rezultate protimikrobne aktivnosti, dobljene v naši raziskavi, smo primerjali tudi z rezultati, dobljenimi na PA 6 mikrovlaknih [24], pri čemer smo ugotovili, da je bila bakterijska

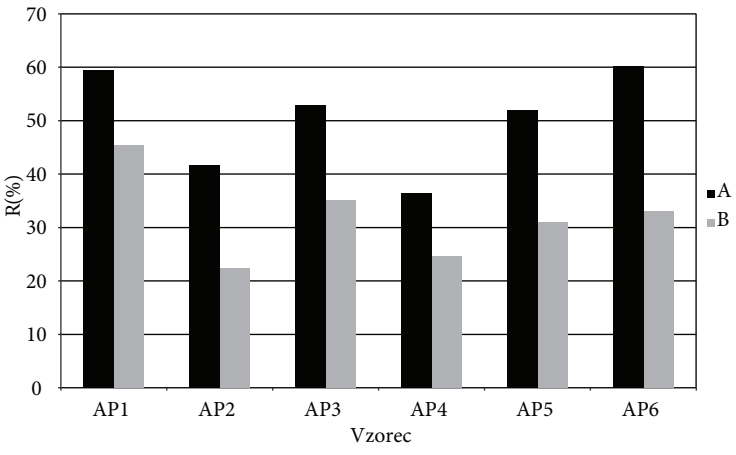


Figure 4: Reduction, R, of bacteria Escherichia coli (ATCC 25922) according to the AATCC 100-1999 Standard Method determined on unwashed cotton samples treated by the finishes from AP1 to AP6. A: without iSys MTX, B: with iSys MTX.

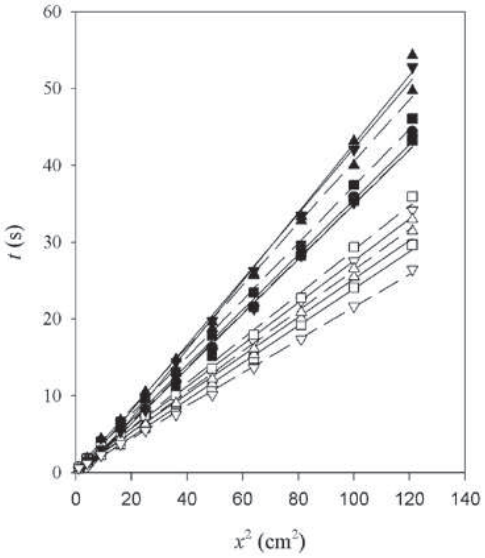
the increasing the Ag concentration in the finishing bath, the Ag concentration on textile increased as well. Namely, at the lowest Ag concentration in the finishing bath (0.01% owf), the Ag concentration on fibres ranged from 20 to 30 mg/kg of textiles, while it reached the values from 295 to 350 mg/kg of fibres when the highest Ag concentration was used the finishing bath (0.50% owf). The presence of iSys MTX in the finishing bath strongly increased the Ag concentration on fibres, but it had no affect on the increase of washing stability of Ag particles on cotton fabric. Therefore, after five consecutive washing the Ag concentration sharply decreased and fell below 35 mg/kg of fibres, regardless of the finish. The washing fastness of the studied finishes was worse than in the case of AgCl finish in combination with iSys MTX [20], whereas after ten washing cycles, two times higher Ag concentration was obtained on the fibres than in the case of AP6 finish, despite the fact that the initial Ag concentration was lower compared to the one obtained on the fibres treated by the AP6 finish in combination with iSys MTX.

The bacterial reduction, R, for bacterium Escherichia coli did not significantly changed by increasing the Ag concentration (Figure 4). Namely, in all studied cases, even when the Ag concentration was the highest (350 mg/kg of fibres), R remained lower than 60.2 %, indicating on inefficient and insufficient protection against bacteria. These results are much worse than those obtained with AgCl, where a 60 % reduction of bacteria growth was attained already at Ag concentration of 25 mg/kg of fibres, while 88 % bacterial reduction at Ag concentrations above 50 mg/kg [20]. These results clearly showed that on cotton fabric bactericidal action of silver cations was more effective than that of elementary silver at the same concentration. This was expected, since for an effective biocidal action elementary silver must oxidise into silver cations. Namely, in the case of AgCl, oxidation was not necessary, since silver cations were already present on the fibres and their release depended only on the presence of moisture. Nevertheless, the reduction of bacterium Escherichia coli obtained by elementary silver was still higher than that ob-

redukcija v primeru PA 6 večja od tiste na bombažni tkanini. Pri slednji namreč nismo presegli vrednost R = 60,2 % niti pri najvišji koncentraciji 295 mg/kg Ag. V primeru PA 6 je bila bakterijska redukcija 64 % dobljena pri 48 mg/kg Ag, in to kljub temu, da je bil uporabljeno srebro z velikostjo delcev 80 nm. Ti rezultati so pokazatelj, da poleg velikosti delcev Ag na njegovo baktericidno aktivnost pomembno vpliva tudi surovinska sestava vlaken.

V primeru prisotnosti iSys MTX so bile vrednosti *R* celo nižje kot v primeru apreture brez iSys MTX (slika 4), in to kljub temu, da je bila koncentracija Ag na vlaknih v prvem primeru celo večja kot v drugem primeru. To lahko razložimo s tem, da je anorganska oksidna matrica zamrežila srebro, zaradi česar je bila njegova oksidacija in posledično sproščanje srebrovih kationov oteženo.

Nanos srebra pri apretiranju ni bistveno vplival na omočljivost tkanine (slika 5). Kljub temu, da se je hitrost pronicanja vode v pore tkanine nekoliko znižala pri višjih koncentracijah Ag, so ostala vlakna hidrofilna in zelo dobro omočljiva z vodo. Prisotnost iSys MTX v apreturi je povečala hitrost pronicanja vode v vse preučevane vzorce tkanine. Vzrok za to smo pripisali tvorbi polisiloksanskega filma na površini vlaken, ki je zaprl najmanjše pore, s tem pa povzročil, da je voda pronicala le v pore med nitmi osnove in ne v pore med vlakni v preji. Zato je vlakno v prisotnosti vode manj nabrekalo, pore med nitmi so ostale odprte, hitrost pronicanja vode pa večja.



Slika 5: Water penetration rates into the untreated sample, N, and the samples treated by the finishes from AP1 to AP6 at 20 °C.
–●–– N, –■–– AP1 without iSys MTX, –□–– AP1 with iSys MTX,–▲–– AP2 without iSys MTX, –△–– AP2 with iSys MTX, –▼–– AP3 without iSys MTX, –▽–– AP3 with iSys MTX, -■- - AP4 without iSys MTX, -□- - AP4 with iSys MTX, -▲- - AP5 without iSys MTX, -△- - AP5 with iSys MTX, -▼- - AP6 without iSys MTX, -▽- - AP6 with iSys MTX.

tained by elementary silver with a particle size of 80 nm [14], which ranged from 1 to 11 % at an Ag concentration of 35 mg/kg of fibres. This confirmed that by decreasing the size of nano Ag particles, its antimicrobial activity increases. The results of antimicrobial activity obtained in our study were also compared to the results obtained on PA6 microfibres [24], whereby the bacterial reduction on PA6 was higher than that on cotton fabric. In the case of the latter, the value of R = 60.2 % was not exceed even when the highest concentration Ag was used. In PA6, a 64 % bacterial reduction was obtained already at Ag concentration of 48 mg/kg of fibres, despite the fact that silver with a particle size of 80 nm was used. These results showed that beside to the particle size of Ag, composition of the fibres also significantly affected the bactericidal action.

In the presence of iSys MTX, the R values were lower compared to the finish without iSys MTX (Figure 4), even though the Ag concentration on the fibres was higher in the case when iSys MTX was added into finishing bath. This could be explained by the finding, that polysiloxane matrix covered Ag particles, which consequently made their oxidation and release of silver cations difficult.

In finishing process the application of silver did not significantly affect the wettability of the fabric (Figure 5). Even though the rate of the water penetration into the fabric pores slightly decreased whit the increasing of Ag concentrations, the fibres remained hydrophilic and well-wetted by water. The presence of iSys MTX in the finish increased the rate of water penetration into fibres in the case of all studied samples. The reason for this was ascribed to the formation of a polysiloxane film on the surface of the fibres which closed the smallest pores, consequently causing the water to penetrate only into the pores between the threads of the warp and not between the fibres in the yarn. Therefore, in the presence of water the fibres were less swollen, the pores between the threads remained opened and the rate of water penetration increased.

Application of the studied finishes decreased the whiteness of the fabric. Namely, when the lowest Ag concentration was used, the white-

Prisotnost apreture je znižala belino tkanine. Njena vrednost je iz 80,4 že pri najnižji koncentraciji Ag padla na 75,4 in se z naraščajočo koncentracijo Ag bistveno ni spremenila (slika 6). Iz rezultatov je razvidno, da več kot desetkratno povečanje koncentracije Ag na vlaknih (od 20 mg/kg pri AP1 na 295 mg/kg pri AP6) ni povzročilo padca beline za več kot 1,5. Iz tega smo sklepali, da sprememba koncentracije Ag v apreturi le malo vpliva na belino apretirane tkanine. Ker se je vrednosti W_{10} v veliki meri zmanjšala že pri nanosu apreture z najnižjo koncentracijo srebra, ki je vključevala tudi Setamol WS, smo predpostavili, da je slednji tisti, ki pomembno vpliva na zniževanje beline. To predpostavko smo potrdili, ko smo za vzorce, na katere smo pri enakih pogojih nanesli le Setamol WS brez tržnega produkta Ag izmerili belino enako 76,5. Na belino tkanine je vplivala tudi prisotnost veziva iSys MTX v apreturi, zaradi katerega se je vrednost W_{10} še zmanjšala. Barvni odtenek beline, $T_{W,10}$, tako neapretiranega kot apretiranih vzorcev tkanine je bil negativen v vrednostih od –0,57 do –0,75 (slika 7), kar pomeni, da so bili vzorci rdečkasti.

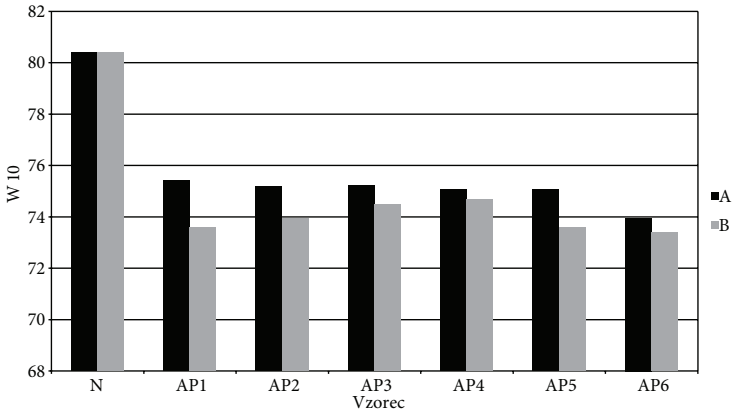
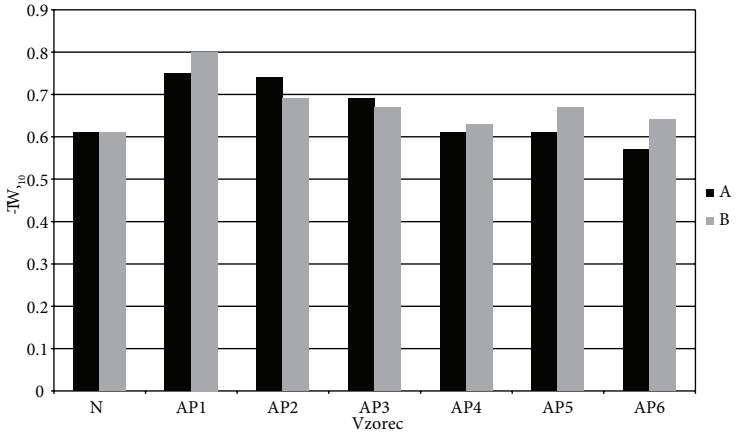


Figure 6: Whiteness, W_{10}, of the untreated sample, N, and the samples treated by the finishes from AP1 to AP6. A: without iSys MTX, B: with iSys MTX.



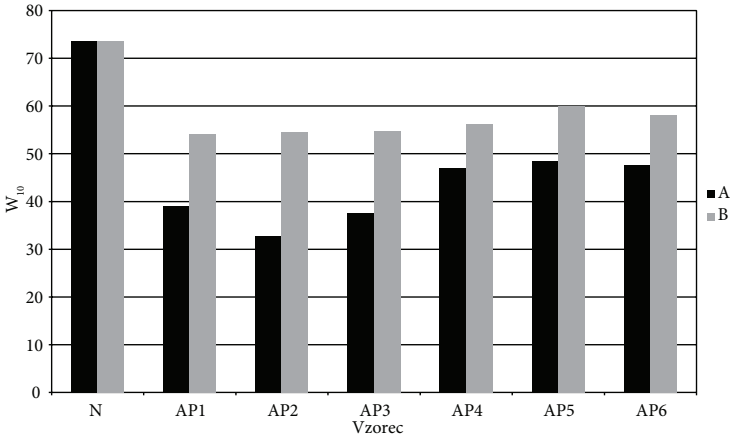
Slika 7: Tint of whiteness, $T_{W,10}$, of the untreated sample, N, and the samples treated by the finishes from AP1 to AP6. A: without iSys MTX, B: with iSys MTX.

ness index, W_{10}, decreased from the value of 80.4 to 75.4 and did not significantly changed by further increase of the Ag concentration (Figure 6). The results showed that more than ten time increase of the Ag concentration on the fibres (from 20 mg/kg with AP1 to 295 mg/kg with AP6) did not cause a decrease of W_{10} value of more than 1.5. Therefore, it was concluded that the change of Ag concentration in the finish had little effect on the whiteness of the finished fabric. Since the W_{10} value already significantly decreased when the finish with the lowest Ag concentration was applied, it was assumed that decrease of whiteness occurred on the account of dispersing agent, Setamol WS. This was confirmed when only Setamol WS (without the commercial Ag product) was applied to the fabric sample under the same conditions and the whiteness index of 76.5 was obtained. The whiteness of the fabric was also affected by the presence of the binding agent iSys MTX in the finish, which resulted in an even lower W_{10} value. Tint of whiteness, $T_{w,10}$, value of the unfinished and finished fabric samples was negative ranging within –0.57 to –0.75 (Figure 7), meaning that the samples were reddish.

Illumination of the finished cotton fabric samples with an artificial light caused a decrease of whiteness when compared to the unfinished sample (Figure 8). Following a 51-hour illumination, a higher decrease was obtained when lower Ag concentrations were present on the fibres. The addition of binding agent iSys MTX in the finish decreased the yellowing of the samples and therefore, acted in a protective way. With illumination, the tint of whiteness also changed, exceeding value of –3.5. The oxide matrix also caused a smaller change of the $T_{w,10}$ value, consistent with the change of whiteness.

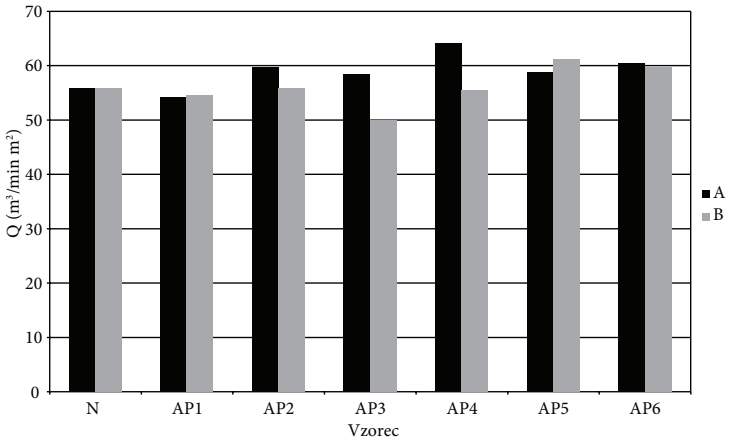
Surprisingly, application of Ag of all studied concentrations increased the air permeability, Q, compared to the unfinished fabric (Figure 9). The reason for this is difficult to explain only on the basis of these measurements. The air permeability of samples finished with the iSys MTX binding agent was lower than that of the samples without it. The decrease in air permeability was attributed to the formation of the polysiloxane film on the cot-

Osvetljevanje apretiranih vzorcev bombažne tkanine z umetno svetlobo je vplivalo na znižanje beline v primerjavi z neapretiranim vzorcem (slika 8). Po 51 urnem osvetljevanju smo večje znižanje dobili pri nižjih kot pri višjih koncentracijah Ag na vlaknih. Prisotnost veziva iSys MTX v apreturi je zmanjšala porumenitev vzorcev ter na tak način delovala zaščitno. Z osvetljevanjem se je močno spremenil tudi barvni odtenek beline, ki je presegel vrednost –3,5. Na manjšo spremembo vrednosti $T_{W,10}$, je v skladu s spremembo beline vplivala tudi prisotnost veziva iSys MTX.



Slika 8: Whiteness, W_{10}, of the untreated sample, N, and the samples treated by the finishes from AP1 to AP6 after illumination with artificial light for 51 hours. A: without iSys MTX, B: with iSys MTX.

V nasprotju z našimi pričakovanji, je prisotnost Ag ne glede na njegovo koncentracijo povečala zračno prepustnost, *Q*, v primerjavi z neapretirano tkanino (slika 9). Vzrok za ta pojav težko razložimo le na podlagi teh meritev. Zračna prepustnost vzorcev apretiranih z vezivom iSys MTX je bila manjša kot pri vzorcih brez iSys



Slika 9: Air permeability, Q, of the untreated sample, N, and the samples treated by the finishes from AP1 to AP6. A: without iSys MTX, B: with iSys MTX.

ton fabric surface, which partially closed the pores among the threads of the warp and weft of the fabric and, consequently, made the air flow into the fabric difficult. Slightly different results were obtained on the basis of measurements of air volume flow, V, through dry unfinished and finished samples of cotton fabric (Figure 10). Namely, it was obtained that the volume flow only slightly depended from the Ag concentration and the presence of iSys MTX in the finish. Therefore, based on these results, it can not be concluded that the addition of the iSys MTX binding agent reduces air volume flow through dry finished samples.

The application of Ag increased the bending rigidity of the fabric, U_o, at all studied concentrations (Figure 11). By the addition of the iSys MTX binding agent, U_o decreased again, due to the softening action of the polysiloxane film on the surface of the cotton fabric.

4 Conclusions

From the results obtained it can be concluded, that elementary silver of nano dimensions, reduced the growth of bacterium Escherichia coli. However, the bacterial reduction was to low in order to assure affective antimicrobial activity and did not increase by increasing concentration of silver on fibres. Namely, even when the highest concentrations of silver were used, the bacterial reduction did not exceed the value of 60%. The presence of oxide matrix increased the concentration of silver on fibres, but did not affect on the increase of its bactericidal activity nor its washing fastness. Therefore, it can be concluded that for the preparation of antimicrobial finishing, combination of elementary silver and oxide matrix is not reasonable, despite of its positive properties in the finish. Namely, it increases the wetabillity as well as decreases the fall of whiteness and stiffness of the fabric in comparison to the finish where the matrix was not present.

Acknowledgments

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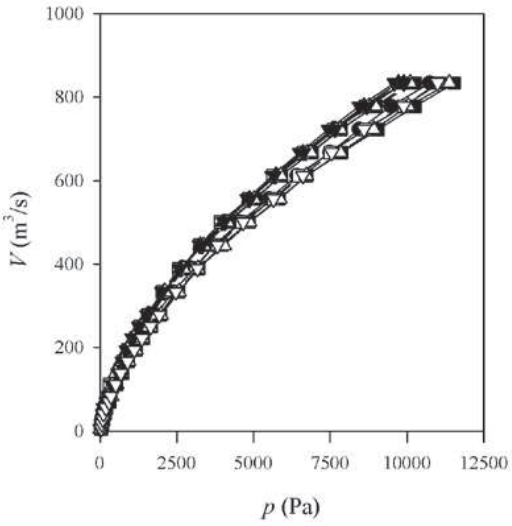
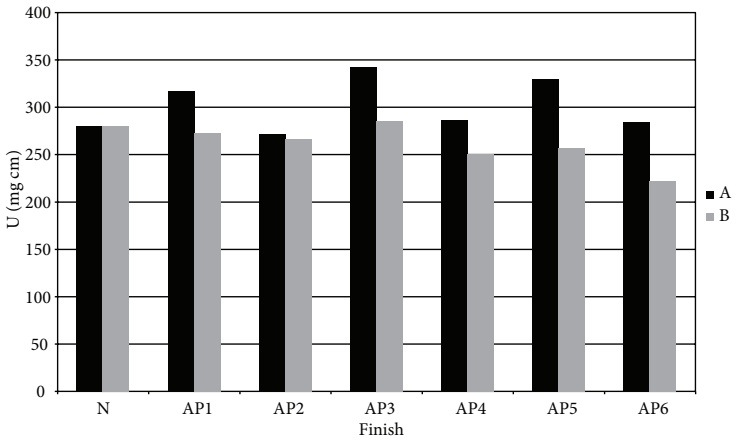


Slika 10: Volume rate, V, in dependence from pressure, p, through the untreated sample, N, and the samples treated by the finishes from AP1 to AP6.
–●–– N, –■–– AP1 without iSys MTX, –□–– AP1 with iSys MTX,–▲–– AP2 without iSys MTX, –Δ–– AP2 with iSys MTX, –▼–– AP3 without iSys MTX, –∇–– AP3 with iSys MTX, -■- - AP4 without iSys MTX, -□- - AP4 with iSys MTX, -▲- - AP5 without iSys MTX, -Δ- - AP5 with iSys MTX, -▼- - AP6 without iSys MTX, -∇- - AP6 with iSys MTX.

MTX. Znižanje zračne prepustnosti smo pripisali tvorbi polisiloksanskega filma na površini bombažne tkanine, ki je delno zaprl pore med nitmi osnove in votka tkanine in tako otežil pretok zraka skozi tkanino. Nekoliko drugačne rezultate pa smo dobili na podlagi meritev volumskega pretoka zraka, *V*, skozi suhe neapretirane in apretirane vzorce bombažne tkanine (slika 10). Iz njih je namreč razvidno, da je bil volumski pretok le malo odvisen od koncentra-



Slika 11: Bending rigidity, U, of the untreated sample, N, and the samples treated by the finishes from AP1 to AP6. A: without iSys MTX, B: with iSys MTX.

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cije Ag kot tudi od tega, ali je bilo v apreturi prisotno vezivo iSys MTX. Iz teh rezultatov nikakor ne moremo zaključiti, da bi dodatek veziva iSys MTX znižal volumski pretok zraka skozi suhe apretirane vzorce.
Z nanosom Ag se je togost tkanine, U_o, povečala, in to pri vseh njegovih koncentracijah (slika 11). Dodatek veziva iSys MTX je togost ponovno zmanjšal. Vzrok za to smo pripisali mehčalnemu učinku polisiloksanskega filma na površini bombažne tkanine.

4 Sklepi

Iz rezultatov raziskave je razvidno, da elementarno srebro velikost delcev nano dimenzij na bombažni tkanini zavre rast bakterije vrste *Escherichia coli*, vendar je bakterijska redukcija prenizka, da bi bilo protimikrobno delovanje učinkovito. Tudi z naraščajočo koncentracijo srebra na vlaknih se bakterijska redukcija ne povečuje in tudi pri najvišjih koncentracijah srebra ne preseže vrednosti 60 %. Prisotnost oksidne matrice sicer poveča koncentracijo srebra v apreturi, vendar se njegovo baktericidno delovanje s tem ne poveča. Nasprotno, celo zmanjša. Matrica tudi ne vpliva na povečanje pralne obstojnosti srebra na tkanini. Iz tega lahko sklepamo, da kombinacija elementarnega srebra in organske matrice ni smiselna za pripravo protimikrobne apreture. In to kljub njenim pozitivnim lastnostim v apreturi, kjer vpliva na povečanje omočljivosti, zmanjšanje padca beline in togosti tkanine v primerjavi z apreturo, kjer matrica ni prisotna.

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