Active Multifunctional Cotton Treated with Zeolite Nanoparticles

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Natural zeolites are aluminosilicate crystals with unique absorption and catalyst properties. In medicine they are attributed anticancerogen, antiallergic, antiseptic, antireumatic and other properties. They also exert a strong influence on blood circulation improvement. Addition of zeolite nanoparticles in different textile pretreatment and treatment phases is a novelty in textile finishing for multifunctional protection effects. Zeolites make a contribution to UV protection since they disperse UV radiation unlike other agents which absorb it and prevent their transmission. If zeolites are added to azalides in textile finishing, they increase their efficacious antimicrobial action. The paper describes cotton knitted fabric mercerized and bleached with addition of activated zeolite, clinoptilolite nanoparticles and treated with azalide to achieve multifunctional protection. Clinoptilolite was added into baths for cotton pretreatment, treatment and modification. Properties of the treated cotton were determined by international standards (EN, ISO, AS/NZS, AATCC).
Key words: *cotton, zeolite, multifunctional protection effects*

1. Introduction

High performance fabrics used for personal safety (medical textiles, protection and sport textiles) are today's guideline for textile development in Europe. Since clothing is the other skin of the human being and an appropriate border between environment and human body, it is an ideal tool for personal safety [1].

Healthy and active living has led to new textile technologies. Antimicrobial and UV protection agents resulting in sense of safety and well-being for manufacturers and consumers were developed rapidly. Antimicrobial treated materials provide freshness and safety, while materials for UV protection protect against harmful UV radiation. At first glance it seems rather simple to carry out this kind of finishing, but it is a problem to make it durable [2].

Addition of zeolite nanoparticles in different phases of pretreatment, treatment and modification results in a multifunctional protection.

1.1. Natural zeolite – clinoptilolite

Zeolites are hydrated natural and synthetic microporous crystals with defined structures containing AlO_4 and SiO_4 tetrahedra connected through oxygen atoms. They selectively adsorb water and exchange cations. They have a variety of uses such as adsorbents, ionic exchangers, catalysts and detergent builders in industry, agriculture, veterinary medicine, health care and environmental protection [3,4].

Natural zeolites are rock-forming, microporous silicate minerals. In terms of composition they are alumosilicates containing univalent or bivalent cations: Na^+, K^+, Ca^{2+}. They are formed by condensation of gases and vapors after volcanic eruptions and deposit as accumulations and rocks. There are about 276 types that can be found in oceans in huge amounts. Regarding their morphological structure there are three main kinds: fibrous, leafy and crystalline zeolites [3,5].

A mineral of natural zeolite, clinoptilolite, has a crystalline configuration, tetrahedron structure. It has a lattice structure with long channels comprising water molecules and alkaline earth ions. As they do not occupy fixed positions, these ions may shift within the lattice. In ionic form they can be easily released and exchanged without changing the character of crystal lattice, enabling clinoptilolite to have strong ion exchanges [3,4]. Clinoptilolite bonds heavy metals [6]. Many investigations indicate that clinoptilolite absorbs toxins and mould [7].

Its positive effect on the metabolism of living things has been confirmed in case of human application. Most recent research conducted over the last ten years or so prove its mechanisms of anticancerogenic and antimetastatic effect, strong mechanisms of antiviral activity and an exception less contribution to metabolic processes. Scientists define it as the most powerful natural imunostimulator and antioxidant. The essence of its effect is based on selective adsorption capacity, selective ion exchange, and regulation of the acid-based system, intercellular and intracellular space resulting in improving substance exchange at cell level [8-11].

There are numerous clinoptilolite deposits worldwide, the best known being in Cuba, Australia, USA and East and South European countries [12] (Russia – Siberia, Caucasus; Slovakia – Kosiče, Serbia – Vranje, Greece, Italy [4]). There are clinoptilolite deposits in Croatia in the area of Donje Jesenje near Krapina and Mursko Središće in Međimurje [13]. Zeolites are rarely used as found in nature, but they are subjected to mechanical and chemical treatments to improve their properties.

Tribomechanical activation of zeolite - clinoptilolite is the procedure of fine micronization into micro and nanoparticles, whereby a high activation of particles is done in a patented device (patent: PCT/1B99/00757) (Fig.1). The equipment for tribomechanical micronization and activation device (TMA equipment) consists of a box which is cooled by water and two rotor discs turned to each other. Each disc contains 3 to 7 concentric rings with specially designed elements of hard metal. The discs rotate into opposite directions with the same angular velocity. Source material is fed into the equipment through the central section of the rotor system by ventilating air stream. This is the reason why particles are accelerated due to a multiple change in running direction; they collide and rub against each other in short time intervals - at least three times in one thousandth of a second at angle from 8 to 15 degrees [12]. This does not change the chemical composition, but certain physical chemical properties are changed: increase in electrostatic charge, capacity of ion exchange, specific active surface and capacity of liquid absorption and water is released from lattice inside. It is relevant to note that the crystal ball cracks on the surface during the activation process, remaining active in its inner layer. Nanoparticles in one gram of the micronized clinoptilolite have a total surface of 50,000 m^2 and are interwoven with 50 million filter microchannels representing exceptionally powerful therapeutic microfilters. Well-known mechanisms of zeolite action and its action capacity are increased several times by this technological procedure.

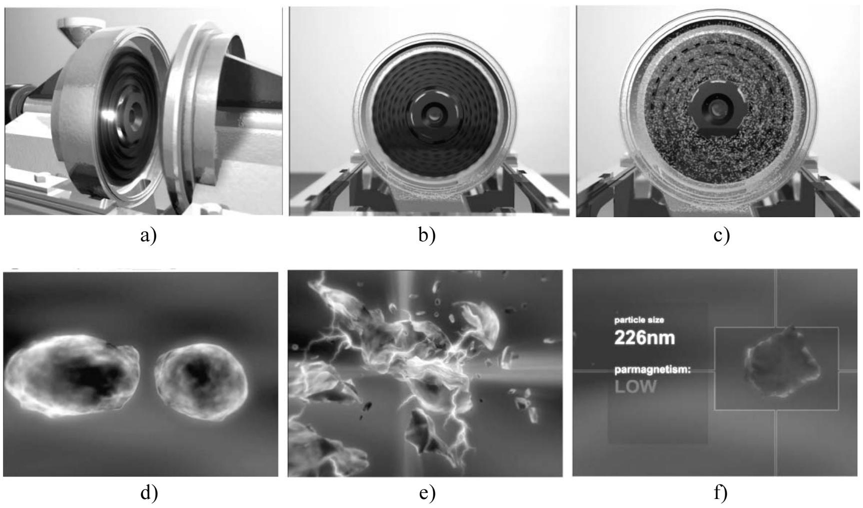


Fig.1 Tribomechanical activation: a) TMA equipment, b) TMA equipment before feeding nanoparticles, d) clinoptilolite particles during feeding, e) collision of particles at which micro and nanoparticles are formed, f) clinoptilolite nanoparticles [11]

Tribomechanically activated clinoptilolite is available on the market under the trade name Megamin®. Megamin® is a mineral preparation of natural origin. It consists of calcium-sodium-magnesium-alumosilicate and natural calcium and magnesium carbonate. It is prepared using a newly developed technology of mechanical activation in the conditions of centrifugal particle acceleration. The structure of the mineral preparation is lattice-like, the basic structure form is a crystal lattice, containing exchangeable alkaline earth cations: calcium, magnesium, sodium, potassium and crystal water.

The technology used for the micronization of basic ingredients Megamin® is newly prepared and unique in its effect on natural minerals. By its use biologically active nanoparticles are obtained which can move intercellularly, enter the cell and clean it up from harmful substances.

The particle surface of Megamin® is negatively charged. Thus, it becomes a powerful donator of electrons, whereby positively charged free radicals are neutralized. This makes it possible to use it for medical purposes, e.g. for cancer and diabetes healing [8-11, 14].

Megamin® is not a medicine, since it has failed essential and legally prescribed tests of proving effects and intoxicity, but investigations have shown that it is a strong antioxidant proved by TAS (Total Antioxidant Status). TAS is a test showing the state of the inner organism defense against a possible disease. Measurements were taken in 35 healthy persons, and in the first two weeks of taking Megamin® an average increase of TAS in these persons amounted to 6% [9, 14, 15].

The recent papers by Grancaric et al [2,11,16-20] showed that natural zeolites disperse UV radiation, increasing the efficiency of protection against this radiation by cotton and polyester fabrics.

1.2. UV protection

Geographical position, clouds, distance from the Earth's surface, dust, fog, smog and air pollution affect the quantity of UV radiation coming to the Earth's surface. Sun's UV radiation (UV radiation, UV-R, ranging from 100 to 400 nm) is life harmful of plants, animals and people. It may cause erythem, photo ageing, skin cancer, cataract, immune system deterioration etc. [16-23].

It is well-known that clothing provides a certain degree of UV protection. When UV radiation comes into contact with the surface of a textile material, some radiation portion is reflected (reflection), other portion is absorbed (absorption) and yet other passes through it (transmission). UV radiation is dependent on the type of fiber from which the fabric is made, fabric moisture content, fabric thickness and structure, fabric density, yarn fineness, dye content of the fiber, pigment addition in the polymer, type and concentration of the dyes used, optical brighteners, UV absorbers and the like [21-23].

1.3. Antimicrobial protection

Azalides are a class of antibiotics and have an efficiently antimicrobial effect. They are a subtype of macrolide antibiotics (antibiotics containing a lactonic ring with 11 - 19 carbon atoms and glycoside bond special sugars). Azithromycin is the best known azalide with trade names Zithromax® (Pfizer) and Sumamed® (Pliva). It is obtained from erythromycin by adding a nitrogen atom into the lactonic ring of A-erythromycin and forming a 15 member lactonic ring (Fig.2).

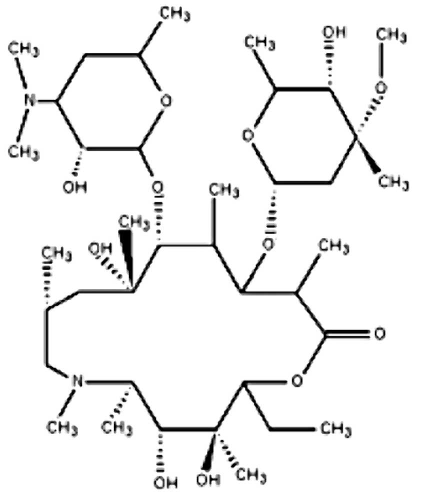


Fig.2 Azithromycin structure

Azithromycin is used to heal respiratory tract, soft tissues and genital infections. By inhibition of protein synthesis it affects the ability of bacteria to replicate and grow. They affect different Gram-positive, Gram-negative, anaerobic, intracellular and atypical microorganisms [24]. They affect pulmonary microorganisms *Chlamydia pneumoniae* and *Mycoplasma pneumoniae* quite well [25]. Gram-positive bacteria include plenty of well-known types such as *Bacillus, Listeria, Staphylococcus, Streptococcus*, *Enterococcus, and Clostridium*. The most important group consists of protobacteria *Escherichia coli, Salmonella, Pseudomonas, Moraxella, Helicobacter, Stenotrophomonas, Bdellovibrio*, bacteria of acetic acid, *Legionella*, and many others. Medically important Gram-negative cocci include three organisms causing many sexually transmissible diseases (*Neisseria gonorrhea*), meningitis (*Neisseria meningitidis*), and respiratory symptoms (*Moraxella catarrhalis*). Medically important Gram-negative bacilli include m any types. Some of them cause primary respiratory problems (*Hemophilus influenzae, Klebsiella pneumoniae, Legionella pneumophila, Pseudomonas aeruginosa*), primary urinary problems (*Escherichia coli, Proteus mirabilis, Enterobacter cloacae, Serattia marcescens*), and primary gastrointestinal problems (*Helcobacter pylori, Salmonella enteritidis, Salmonella typhi*). Using even a small concentration of azalide, an excellent antimicrobial and antibacterial protection is obtained in relation to other antimicrobial agents. Likewise, specific antimicrobial agents independently used show antimicrobial activity only on Gram-positive bacteria, while both agents in the bath containing azalide have an excellent effect on Gram-positive and Gram-negative bacteria thanks to the action of azalides. It is important to note that the antibacterial action of azalides continues even after washing the textile material [2].

This paper explores antimicrobial protection against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Klebsiella pneumoniae*) according to the modified AATCC method (AATCC TM 147-1998 [26] and AATCC TM 100-1999 [27]).

2. Experimental

2.1. Materials

Cotton knitted fabric was knitted on a Marchiso Jedi single knitting machine. Needle bed diameter is 660.4 mm (26"), machine gauge is E 24, and number of knitting systems is 62. Number of needles is 1944, while rotational speed of the needle bed is 18 rpm. Yarn count of the knitted fabric is 25 tex. Yarn twist level is 744 m^{-1}, yarn strength is 12.6 breaking kilometers. Total fabric width is 87 x 2 cm, surface mass is 123 g/m^2. Number of stitches in the wale direction is D_v 14 cm^{-1}, and number of stitches in the course direction is D_h 11 cm^{-1}.

Tribomechanically activated zeolite *(TMAZ)* - clinoptilolite particles activated and made by tribomechanical activation on the patented instrument manufactured by Tribomin d.o.o. Osijek. The origin of clinoptilolite is Kosiče, Slovakia. By X-ray diffractometry it was found that a TMAZ sample consists of about 80% clinoptilolite and the rest are zeolites montmorillonite and mordenite. Moisture at 105 °C amounted to the maximum of 6% [9]. The average particle size is 200 nm. Composition and physical chemical properties according to the analysis of ISEGA Forschungs- und Untersuchungs-gesellschaft mbH, Aschaffenburg, Germany [8] are given in Tab.1.

Azalide used in this work is a product from TNN development Ltd., China. It is broad spectrum antibiotic, first representative of a new subclass of macrolide antibiotics called azalides. Antimicrobial spectrum of this azalide includes different Gram-positive, Gram-negative, anaerobic, intracellular and atypical microorganisms. Because of the transport with white blood cells, it possesses a unique property - targeted activity at the site of infection. In infected tissues, it achieves high and sustained therapeutic concentrations that last five to seven days after the last dose. Because of that, administration of azalide is simple and short [28].

Tab.1 Composition and Physicochemical Properties of TMAZ analyzed by ISEGA Forschungs- und Untersuchungsgesellschaft mbH, Aschaffenburg, Germany [8]

Chemical composition	
Component	%
SiO_2	65,0-71,3
Al_2O_3	11,5-13,1
CaO	2,7-5,2
K_2O	2,2-3,4
Fe_2O_3	0,7-1,9
MgO	0,6-1,2
Na_2O	0,2-1,3
TiO_2	0,1-0,3
Si/Al rate	4,8-5,4
Empirical formula	
$(Ca,K_2,Na_2,Mg)_4Al_8Si_{40}O_{96}$ x $24H_2O$	
Physicomechanical properties	
Specific mass	2,2-2,5 g/cm^3
Porosity	32-40 %
Effective pore diameter	0,4 nm
Ion-exchanging capacity	mol/kg
Total	1,2-1,5
Ca^{2+}	0,64-0,98
Mg^{2+}	0,06-0,19
K^+	0,22-0,45
Na^+	0,01-0,19
Ion-exchanging selectivity	
$Cs>NH_4^+>Pb^{2+}>K^+>Na^+>Mg^{2+}>Ba^{2+}>Cu^{2+}>Zn^{2+}$	
Absorbed	
NH_3, hydrocarbons $C_1 – C_4$, CO_2, H_2S, SO_2, NO_x, aldehydes	
Toxicity	
Nontoxic according to US Code of Federal Regulations (21 CFR 82, Subpart C)	

2.2. Treatment procedures

The knitted fabric was mercerized, bleached and zeolite and azalide treated. Zeolite nanoparticles were added in different phases of pretreatment, treatment and modification.

Mercerization was carried out using 24% NaOH with addition of 8 g/l anion-active wetting agent Subitol MLF (Bezema) and a liquor ratio of 1:25 at a temperature of 18 °C and in a period of 120 s. It follows hot rinsing with distilled water, neutralization with 1% CH_3COOH, and a series of cold rinsing.

The activated zeolite was applied to the knitted fabric during mercerization when 5 g/l zeolite was added into the mercerizing liquor, and during the after-impregnation process in the padder with a squeezing effect of 100%.

Azalide was used to treat the fabric for antimicrobial protection in the exhaustion process on a Linitest apparatus (Original Hanau, Germany). It was treated with 3% azalide relative to fabric mass with 25% aqueous azalide solution and a period of 30 min at 60 °C, pH 6-7 and liquor ratio 1:20.

Specimen designations and treatments are given in Tab.2.

2.3. Test methods

Number of wale and course stitches on 10 cm was determined according to ISO 4921:2000 - Knitting - Basic concepts – Vocabulary

Tab.2 Specimen labels and treatments

Label	Description
R	Raw, untreated
RM	Raw, mercerized
RZ	Raw, zeolite impregnated
RMZ	Raw, mercerized, zeolite impregnated
RZM	Raw, mercerized with addition of zeolite into the mercerizing bath
B	Bleached
BM	Bleached, mercerized
BZ	Bleached, zeolite impregnated
BMZ	Bleached, mercerized, zeolite impregnated
BZM	Bleached, mercerized with addition of zeolite into the mercerizing bath
...A	...Azalide treated

Thickness of cotton knitted fabric was measured on the instrument for measuring thickness according to ISO 5084:1996 - Textiles - Determination of thickness of textiles and textile products.

Mass per unit area was determined according ISO 3801:1977 - Textiles - Woven fabrics - Determination of mass per unit length and mass per unit area.

Breaking force and elongation were determined on MesdanLab Strength Tester according to EN ISO 13934-1:1999 Textiles - Tensile properties of fabrics – Part 1: Determination of maximum force and elongation at maximum force using the strip method.

Scanning Electron Microscopy (SEM) - digital images were created at DTNW, Krefeld, Germany using FEI Quanta 200 Scanning Electron Microscope with 2000x magnification. The presented images were selected among 10 images taken at 7 different points on the fabric.

Degree of whiteness (CIE whiteness, W_{CIE}) and **yellowness index** (YI) of the cotton knitted fabric after treatment were processed on a Datacolor SF 600 PLUS CT spectrophotometer according to DIN 6167 Description of yellowing of practically white or practically colorless materials.

UV-protection ability was determined on a Varian Cary 50 Spectrophotometer. Although HRN EN 13758-1:2003 and HRN EN 13758-2: 2003 are available, the instrument does not have a software package for it, and UV protection was determined according to AS/NZS 4399:1996 Sun Protective Clothing: evaluation and classification. It is expressed via ultraviolet protection factor (**UPF**) indicating the ability of body protection by textile materials to prevent erythem [11,12,20]. UPF value is determined according to [20]:

$$\mathrm{UPF} = \frac{\sum_{\lambda=280}^{400} E(\lambda)\cdot\varepsilon(\lambda)\cdot\Delta\lambda}{\sum_{\lambda=280}^{400} E(\lambda)\cdot T(\lambda)\cdot\varepsilon(\lambda)\cdot\Delta\lambda} \quad (1)$$

Where is: $E(\lambda)$ - Sun's radiation, $\varepsilon(\lambda)$ - erythematous effect of the spectrum, $\Delta\lambda$ - wavelength interval in measuring, $T(\lambda)$ - spectrum permeability at a wavelength of λ.

Antimicrobial protection was determined by the modified method of two American test methods - AATCC TM 147-1998 *Antibacterial Activity Assessment of Textile Materials: Parallel Streak Method and AATC* TM 100-1999 *Antibacterial Finishes on Textile Materials: Assesment of.* AATCC TM 147-1998 is a qualitative, and AATCC TM 100-1999 is a quantitative method for the determination of antimicrobial activity of the material treated. Antimicrobial test on Gram-positive cocci - *Staphylococcus aureus* and on Gram-negative bacilli - *Klebsiella* was done at the City of Zagreb Public Health Institute.

The specimen tested has a circular form with a diameter of 24 mm. Microorganisms are inoculated in an 80 mm diameter Petri dish. A test specimen is inserted into the center, on the inoculated microorganisms. After a 24-hour incubation the specimen diameter is measured and the areas which were affected by the specimen. The difference between the specimen diameter and the diameter of the area affected by the specimen quantifies the effects of the textile on the microorganisms.

The results are expressed by factor *f*.

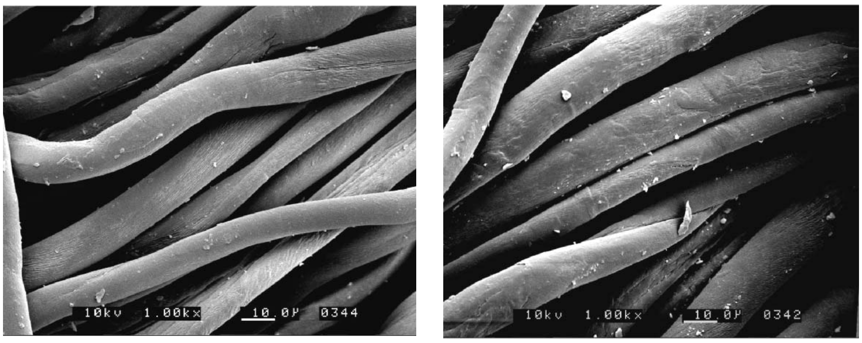
$$f = \frac{d_{treated}}{d_{untreated}} \quad (2)$$

Fastness to laundering was tested after 3 launderings according to ISO 105-C08/C09:2001 Textiles - Color fastness to domestic and commercial laundering using a non-phosphate reference, using ECE Non-Phosphate Test Detergent without optical brightener.

3. Results and discussion

To achieve multifunctional protection by knitted fabric for the purposes of this work, the knitted fabric was mercerized, bleached, nanoparticles of active clinoptilolite were added in different phases of pretreatment, treatment and modification (Fig.3), and treatment with an agent for antimicrobial protection - azalide - was carried out. The properties of such multifunctional cotton were determined in accordance with international standards (EN, ISO, AS/NZS, AATCC).

Digital SEM images of clinoptilolite-treated cotton knitted fabrics with 2000x magnification show that some of nanoparticles entered into spaces among fibres, other particles incorporated into the surface and yet other particles remained on the surface. The difference between the cotton knitted fabric after treated with zeolite (RMZ) in relation to the one with zeolite incorporated during mercerization (RZM) is apparent. In the RMZ fabric specimen



a) b)

Fig.3 SEM images (created at DNTW, Krefeld, Germany) of multifunctional zeolite-treated cotton knitted fabric: a) by mercerization (RZM), b) by impregnation (RMZ)

there is a bigger number of zeolite nanoparticles in interspaces and on the surface, while in the RZM specimen a part of nanoparticles remained incorporated within fibers during mercerization.

Tab.3 contains the measurement results of structure fabric parameters - number of wale and course stitches over 10 cm according to ISO 4921:2000, mass per unit area according to ISO 3801:1977 and fabric thickness according ISO 5084:1996.

In all wet treatments the knitted fabric shrinks because cotton swells in wet conditions and then it shrinks. The number of fabric courses and wales over 10 cm increases considerably, especially during mercerization. Thus, by mercerizing the cotton knitted fabric it comes to an increase in mass per unit area and fabric thickness. For this reason the mercerized specimens (RM and BM) show the highest values of increasing mass per unit area, almost 90%. The treatment with zeolite nanoparticles affects shrinkage and mass per unit area to a smaller extent, approximately additional 5%. Aftertreatment with azalide causes an increase in mass per unit area by additional 2%.

The measurement results for breaking force and elongation of the fabric were determined on MesdanLab Strength Tester according to EN ISO 13934-1 and are shown in Tab.4.

Tab.4 shows that aftertreatment reduces breaking force and strength of knitted fabric, respectively. Breaking strength of the knitted fabric is increased by mercerization. It is reduced slightly either by addition of zeolite clinoptilolite, or by after impregnation process, or by mercerization or after mercerization of cotton knitted fabric. Such minimum changes could be expected due to the incorporation of nanoparticles. Azalide treatment causes a

Tab.3 Number of wale and course stitches over 10 cm, mass per unit area and thickness of bleached and modified cotton knitted fabrics

Specimen	Number of course stitches		Number of wale stitches		Thickness		Surface mass
	[stitches/ 10 cm]	CV [%]	[stitches/ 10 cm]	CV [%]	[mm]	CV [%]	[g/m²]
R	110	1.08	140	0.85	0.60	0.55	123
RM	140	0.77	180	0.66	0.73	0.82	220
RZ	125	0.96	160	1.02	0.65	0.86	138
RZM	140	0.78	225	0.99	0.78	0.66	250
RMZ	145	0.73	205	0.47	0.76	0.74	227
RA	130	0.85	165	0.87	0.62	0.55	155
RMA	135	0.86	165	1.11	0.78	0.82	259
RZA	150	0.55	150	1.15	0.66	0.74	141
RZMA	140	0.77	215	0.78	0.73	1.03	204
RMZA	145	0.72	215	0.78	0.77	0.86	244
B	135	0.82	155	1.05	0.71	0.93	154
BM	145	0.73	190	0.74	0.74	0.77	218
BZ	140	0.82	155	0.78	0.72	0.74	160
BZM	140	0.85	205	0.74	0.76	1.03	230
BMZ	145	0.95	205	0.78	0.77	0.66	235
BA	160	0.65	135	0.82	0.69	0.82	184
BMA	165	0.70	145	0.74	0.79	0.95	240
BZA	150	0.66	145	0.82	0.73	0.86	202
BZMA	165	0.71	225	0.78	0.80	1.02	265
BMZA	165	0.69	215	1.08	0.80	0.55	260

Tab.4 Breaking force and elongation of raw, bleached and modified cotton knitted fabrics

Specimen	Breaking force		Elongation at break	
	F [N]	CV [%]	ε [%]	CV [%]
R	296	2.48	57.1	4.32
RM	416	6.14	85.3	16.96
RZ	377	13.41	62.1	6.77
RZM	390	16.35	90.2	10.43
RMZ	391	22.30	93.3	3.89
RA	350	10.34	66.0	11.37
RMA	425	16.21	89.7	12.43
RZA	372	19.23	68.0	12.55
RZMA	470	1.75	92.9	4.34
RMZA	472	10.52	94.0	12.90
B	284	8.14	50.5	3.20
BM	365	10.00	82.3	3.17
BZ	314	11.78	61.9	1.99
BZM	355	16.33	84.6	3.55
BMZ	357	19.97	83.5	4.38
BA	250	16.88	50.4	3.62
BMA	370	17.32	83.2	4.10
BZA	298	6.37	50.0	3.86
BZMA	375	11.20	92.0	4.21
BMZA	372	14.32	93.5	5.10

slight increase in strength. The strength results obtained represent positive signs of the treatment which did not change high effects of the mercerization, but on the contrary it improved them. A relatively high increase in strength (approx. 25% in relation to raw cotton) is part of these effects. Whiteness (CIE whiteness, W_{CIE}) and Yellowness Index (YI) of the cotton knitted fabric after treatment were determined on a Datacolor SF 600 PLUS CT spectrophotometer according to DIN 6167, and the results are shown in Fig.4 and 5.

Raw cotton contains foreign matters imparting yellowish shade so that its whiteness is low (W_R = 5.8). By boiling cotton fat, waxes, pectins, proteins and other organic substances of the primary cotton wall, affecting a remission increase from the knitted fabric and fabric whiteness, are removed. Since boiling does not result in satisfactory whiteness, cotton knitted fabrics are prebleached and bleached. Thus, bleached cotton knitted fabric has whiteness of W_B 76.9. Cotton mercerization changes micro and macro fiber structure, but its remission and whiteness change slightly to W_{RM} 14.3. Addition of zeolite nanoparticles during and after mercerization increases the whiteness of raw cotton. The treatment of bleached cotton with zeolite nanoparticles decreases whiteness at any rate since clinoptilollite is greenish yellow, and it shows its color on the fabric. The values of whiteness and yellowing do not practically change by azalide aftertreatment of raw cotton knitted fabrics, while an increase of whiteness in bleached fabrics is observable. Yellowing index, YI, decreases by analogy to an increase in whiteness. Raw cotton knitted fabric has the highest yellowing index because of pigments and foreign matters, and bleached cotton knitted fabrics have the lowest chemical index.

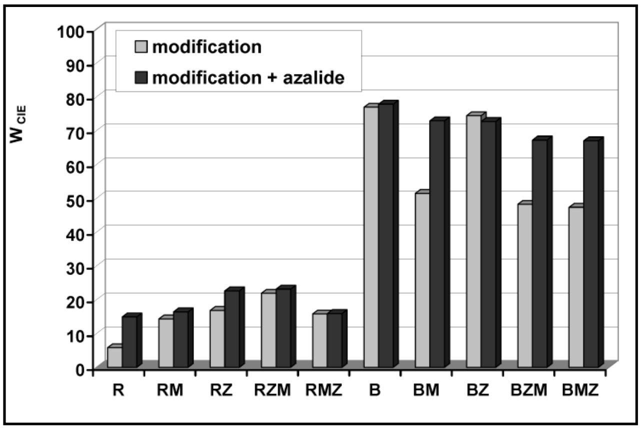


Fig.4 Whiteness (W_{CIE}) of raw, bleached and modified cotton knitted fabrics before and after azalide treatment

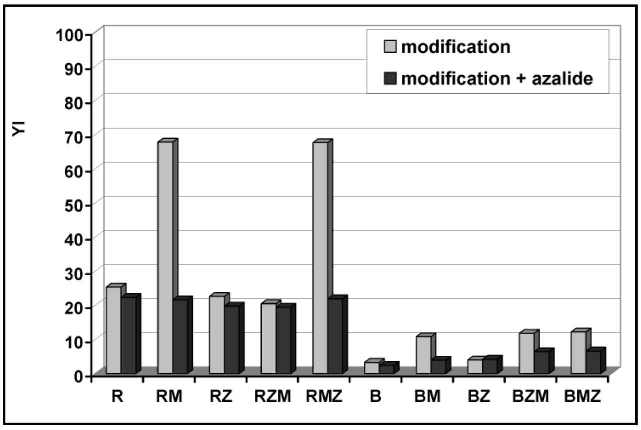


Fig.5 Yellowing index (YI) of raw, bleached and modified cotton knitted fabrics before and after azalide treatment

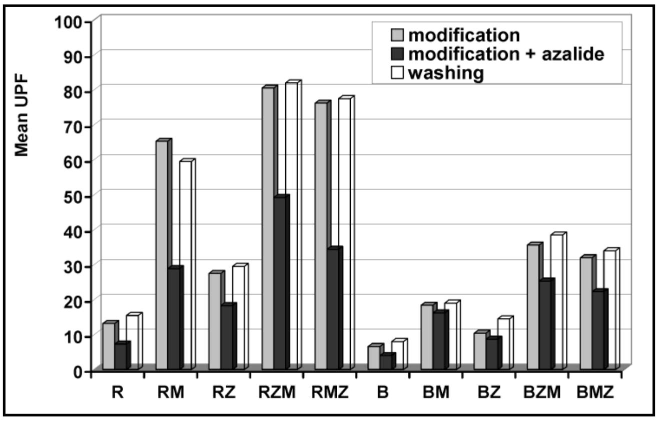


Fig.6 Average values of UPF for raw and bleached cotton knitted fabrics after modification, azalide aftertreatment and 3 washing cycles

UV protection ability by means of cotton knitted fabric - raw, bleached, modified and azalide treated, before and after 3 washing cycles - was determined on a Varian Cary 50 Spectrophotometer according to AS/NZS 4399:1996 and is expressed via ultraviolet protection factor (UPF). Table 6 shows the results.

According to Fig. 6 protection reduction by bleaching is observable, while protection by mercerization and treatment with zeolite nanoparticles and azalide increases in relation to raw knitted fabric. Although pretreatment led to fabric shrinkage, removal of foreign matters (pectins and pigments which absorb a small, but considerable portion of UV radiation) resulted in reducing UV protection. By mercerization cotton structure changes, which assists in the absorption of UV radiation and the remission from the surface of a lustrous fiber, causing the protection to increase to an excellent protection (UPF_{RM} = 65.02). Mercerization and treatment with zeolite clinoptilolite additionally increase UV protection, which is slightly more distinct on samples in the case of which zeolite was added into the mercerizing bath. By impregnation with zeolite nanoparticles protection increases considerably, and a very good of raw cotton is obtained (UPF_{RZ} = 27.54) and an excellent protection of mercerized cotton. By addition of zeolite during mercerization UV protection also increases to an excellent one (UPF_{RZM} = 80.51). It is caused by a partial shrinkage of knitted fabric as well as by an increase in mass per unit area because thus the transmission of UV radiation decreases. In addition, zeolite contributes to an additional dispersion of radiation, resulting in an increase in UV protection. In most cases an additional azalide treatment reduces UV protection, but it is still higher than in the raw sample. In case of adding zeolite particles during and after mercerization protection is very good and excellent, respectively (UPF_{RMZA} = 34.40; UPF_{RZMA} = 49.21). It is important to point out that the excellent UV protection achieved by

Tab.5 Antimicrobial activity of raw and bleached cotton knitted fabrics after modification, additional azalide treatment and 3 washing cycles to Gram-positive *Staphylococcus aureus* and Gram-negative *Klebsiella pneumoniae* bacteria

Specimen	*Staphylococus aureus*						*Klebsiella pneumoniae*					
	untreated		azalide treated		after 3 washing cycles		untreated		azalide treated		after 3 washing cycles	
	d [mm]	f	d [mm]	f	d [mm]	f	d [mm]	f	d [mm]	f	d [mm]	f
R	24	1.00	37	1.54	35	1.46	24	1.00	27	1.13	25	1.04
RM	24	1.00	39	1.62	37	1.54	24	1.00	30	1.25	29	1.21
RZ	24.5	1.02	44	1.83	42	1.75	24	1.00	39	1.62	35	1.46
RZM	33	1.38	47	1.95	45	1.88	24	1.00	39	1.62	34.5	1.44
RMZ	34.5	1.44	46	1.91	41	1.71	24	1.00	38.5	1.60	34.5	1.44
B	24	1.00	38	1.58	36	1.50	24	1.00	28	1.16	26	1.08
BM	24	1.00	38.5	1.60	37	1.54	24	1.00	28.5	1.18	26.5	1.10
BZ	24.5	1.02	39	1.62	37.5	1.56	24	1.00	29	1.20	27	1.13
BZM	33.5	1.40	48.5	2.02	46.5	1.94	24	1.00	42.5	1.77	39	1.62
BMZ	35	1.46	48	2.00	46	1.92	24	1.00	42	1.75	38	1.58

a) b) c)

Fig.7 Photos of the antimicrobial test: a) without protection, b) antimicrobial protection on Gram-positive *Staphyloccocus aureus* and c) antimicrobial protection on Gram-negative *Klebsiella pneumoniae*

treating raw cotton with zeolite still additionally increases by washing.

Although azalide has shown a slight reduction of UV protection, its high efficiency in antimicrobial protection has shown irreplaceable once more. The values measured distinctly indicate the blockade of microorganisms against the cotton knitted fabric. Tab.6 and Fig.7 show the results of an antimicrobial test using the modified method according to AATCC TM 147-1998 i AATCC TM 100-1999 on the action of Gram-positive, *Staphylococcus aureus,* and to Gram-negative, *Kleibsiella pneumoniae* bacteria.

Azalide treatment resulted in a high degree of antimicrobial protection, while knitted fabrics treated with zeolite provide antimicrobial protection only against Gram-positive *Staphylococcus aureus.* Adsorption surface increases by pretreatments, treatments and modification. Therefore, an increase in antimicrobial protection in each step of multifunctional finishing can be observed in this work. It is important to emphasize that addition of zeolite nanoparticles irrespective of whether by impregnation or during mercerization considerably increases adsorption surface, and antimicrobial protection is the highest by azalide treatment. It indicated a distinctly synergistic effect of zeolite clinoptilolite and azalide nanoparticles. After 3 washing cycles the azalide treated samples showed fastness.

4. Conclusion

Mercerization causes the cotton knitted fabric to shrink, resulting in an increase in mass per unit area and fabric thickness. The cotton knitted fabric treated with natural zeolite nanoparticles as well as an additional azalide treatment does not show a noticeable change in mass per unit area and fabric shrinkage.

Whiteness of the raw cotton fabric by zeolite treatment increases, while whiteness of the chemically bleached fabric decreases due to natural greenish yellow coloration of zeolite.

Azalide treatment does not change the values of whiteness and yellowness practically in all samples of the cotton knitted fabric. Yellowness decreases by analogy to an increase in whiteness.

Raw cotton knitted fabric does not provide UV protection. UV protection of the knitted fabric decreases by bleaching, while mercerization and treatment with zeolite nanoparticles considerably increase it. The cause of it is fabric shrinkage, whereby transmission of UV radiation decreases and radiation dispersion from the rough fabric surface where zeolite nanoparticles are adsorbed.

Azalide treatment decreases UV protection, but azalide is irreplaceable for antimicrobial protection of cotton. Nanoparticles of natural zeolite and azalide show a distinctively synergistic effect in antimicrobial protection of textiles.

Cotton knitted fabrics treated with zeolite and azalide are wash-fast.

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