BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Tomul LVI (LX), Fasc. 4, 2010
Secţia
TEXTILE. PIELĂRIE

THE FABRIC HAND OF ANTIMICROBIAL PROTECTED COTTON FABRICS USING ANTIBIOTICS AND ANTISEPTICS[1]

BY

ANA MARIJA GRANCARIC, ANITA TARBUK and DARKO UJEVIC

Abstract. Healthy and active lifestyle has led in recent years to the rapid development of antimicrobial treatment. Such antimicrobial materials provide lasting freshness and a sense of security and well-being of consumers. At first glance it seems easy to achieve antimicrobial properties, but the persistence of such treatment is a bigger problem. Application of natural zeolite nanoparticles for antimicrobial protection has shown increased activity and synergism with some antimicrobial agents, *e.g.* azalide. On the other hand, azalides are not acceptable from dermatological or ethics view, because of resistance development.

This paper deals with the selection of optimal antimicrobial treatment which will provide protection against *Gram* positive (*Staphylococcus aureus*) and *Gram* negative (*Klebsiella pneumoniae*) bacteria, as well as fungi (*Candida albicans*). For this purpose, 100 % raw and bleached cotton knitted fabric was treated by exhaustion with natural zeolite nanoparticles and different antimicrobial agents – cationic surfactant, azalide and antiseptic. It is well known that the cationic surfactants significantly improve fabric hand, but the high concentrations of activated zeolite getting it worse. Therefore, the influence of these treatments on fabric hand (subjective and objective evaluated) was investigated.

Key words: antimicrobial protection, cotton knitted fabric, fabric hand, friction coefficient.

1. Introduction

Clothing and textile materials are carriers of microorganisms such as pathogenic and odor-generating bacteria, and mold fungi because of the adhesion of these organisms on fabric surface. Current vogue that promotes a healthier and active lifestyle led in last few years to rapid growth of antimicrobial finishes which results in textile material to impart durable freshness and a feeling of safety and wellbeing of consumers. At first glance it

[1] This is the full version of the paper, presented at ISKA 2010, Volume of Abstracts

seems simple to accomplish if you have good antimicrobial substance, but make it durable in usage is a greater problem [1],…,[4].

Antimicrobials are defined as the agents that either kill microorganisms (bactericidal) or simply inhibit their growth (bacteriostatic). Antimicrobial textile finishes must exhibit - effective control of bacteria, molds and fungi; selective activity towards undesirable microorganisms; absence of toxic effects for both the manufacturer and the consumer; durability of activity to laundering, dry cleaning, bleaching; applicability with no adverse effects on the fabric; acceptable moisture transport properties; compatibility with other finishing agents; and easy application, compatibility with common textile processing [4], [5].

Antiseptics are antimicrobial substances that are applied to living tissue/skin to reduce the possibility of infection, sepsis, or putrefaction. Antiseptics are generally distinguished from antibiotics by their ability to be transported through the lymphatic system to destroy bacteria within the body, and from disinfectants, which destroy microorganisms found on non-living objects. Some common antiseptics are Alcohols, Quaternary ammonium compounds, Boric acid, Hydrogen peroxide, Iodine - povidone, Octenidine dihydrochloride (Octenisept®), Phenol, Sodium chloride, Terpenes, etc. Every antiseptic, however good, is more or less toxic and irritating to a wounded surface and the over use of antiseptic and antibacterial agents might lead to an increase in dangerous, resistant strains of bacteria [5]. Azalides are subclass of macrolide antibiotics. Azithromycin, the most famous azalide with brand names Zithromax® (Pfizer) and Sumamed® (Pliva). It is used for the treatment of respiratory-tract, soft-tissue and genitourinary infections, what makes of great interest to research its antibacterial ability on textiles, *e.g.* as protection masks, for laundry, socks and underwear [6]. Good antimicrobial agents in textile application are proved to be the ones that include metals and metal salts; quaternary ammonium salts; N-Halamines (*e.g.* Triclosan), natural substances (*e.g.* chitosan) etc. Application of natural zeolite nanoparticles for antimicrobial protection has shown increased activity and synergism with some antimicrobial agents, *e.g.* azalide. On the other hand, azalides are not acceptable from dermatological or ethics view, because of resistance development [6],…,[8].

Natural zeolites are micro-porous hydrated crystals containing alumino-silicates with well- defined structures. Clinoptilolite is natural zeolite, having a cage-like structure, consisting of high portion of SiO_2 (60-67%) with characteristic pore and cavity structure. Therefore, it has unique adsorption, cation exchange, and catalytic properties. Micro and nanoparticles of natural zeolite were produced by tribomechanical processing in the patented machine so that their reactive ability and biological activity is exchanged several hundreds times. These activated natural zeolites are nontoxic substances, excellent for UV-R and microbes protection, for adsorption of proteins and small molecules such as glucose. It has strong anti-oxidative properties, acts as an immunoactivator and has decontamination effects. As an anti-oxidant it prevents forming of free radicals (FR) in human body. Therefore, clinoptilolite is used by cancer patients and patients with autoimmune diseases. Applied externally in powder form, it quickens the healing of wounds and surgical incisions. It is a proven bactericide and fungicide as well. Applied on textiles, activated natural zeolite increases surface area, and leads to better material adsorbency. Zeolite gives a contribution to UV protection by scattering UV radiation, as well as its flame retardancy [7], [8].

Hand of material is an important aesthetic and comfort characteristic, which an elusive quality of fabric. It is usually defined as "the subjective assessment of a textile material obtained from the sense of touch" [9] or as "the tactile sensation or impressions which arise when fabrics are touched, squeezed, rubbed or otherwise handled" [10]. A critical assessment of hand is usually relation between subjective assessment and objective measurement of eight physical properties – four related to bending, two to shearing and the other two, determined in this paper, coefficient of kinetic friction and drape coefficient, respectively. The KES (Kawabata Evaluation System) and FAST (Fabric Assurance by Simple Testing) instruments have reached a considerable acceptance, mainly by research institutions, but not as much in manufacturing environments since they are very expensive. Therefore, at the University of Minho, Portugal, FRICTORQ, fabric surface tester based on a new method of accessing coefficient of friction using a rotary principle and measuring torque, was developed and patented by Lima *et al.* [11],…,[15]. It shows good capabilities of accessing fabric friction as KES. It is well known that the cationic surfactants significantly improve fabric hand, but the high concentrations of activated zeolite getting it worse. Therefore, in this paper, the influence treatments with natural zeolite nanoparticles and different antimicrobial agents on fabric hand (subjective and objective evaluated) was investigated.

2. Material and Methods

The fabric used was chemically bleached 100% cotton circular weft single jersey or single-faced knitted fabric. It has mass per unit area of 130 g/m^2, 56 cm (22 inch) width in tubular form, and 11 whales/cm and 12 courses/cm. The knitted fabric was treated with nanoparticles of natural zeolite, antiseptics and azalide.

Natural zeolite nanoparticles were activated and made by tribomechanical activation. By X-ray diffractometry it was found that tribomechanically activated zeolite sample consists of about 80% clinoptilolite and the rest are zeolites montmorillonite and mordenite. The particle size is 80-250 nm [7]. The origin of clinoptilolite is Kosiče, Slovakia. The 5 g/l of activated zeolite nanoparticles was applied to fabrics in the after-impregnation process in the padder with a squeezing effect of 100%.

Octenidine dihydrochloride (Fig. 1*a* – Octenisept® (Schülke & Mayr GmbH)) is bis-(dihydropyridinyl)-decane derivative, which contains 0.1 g octenidinum and 2.0 g phenoxyethanolum in 100 ml [15]. The knitted fabrics were treated with 2,0% owf Octenisept® for antimicrobial activity in the exhaustion process on a Linitest apparatus (Original Hanau, Germany) for a period of 30 min at 60°C, pH 6-7 and liquor ratio 1:20. Hexadecyl-trimethyl ammonium chloride (Sigma), a cationic surfactant (Fig.1*b*), and azalide (Fig.1*c*) were applied in the same concentration, respectively.

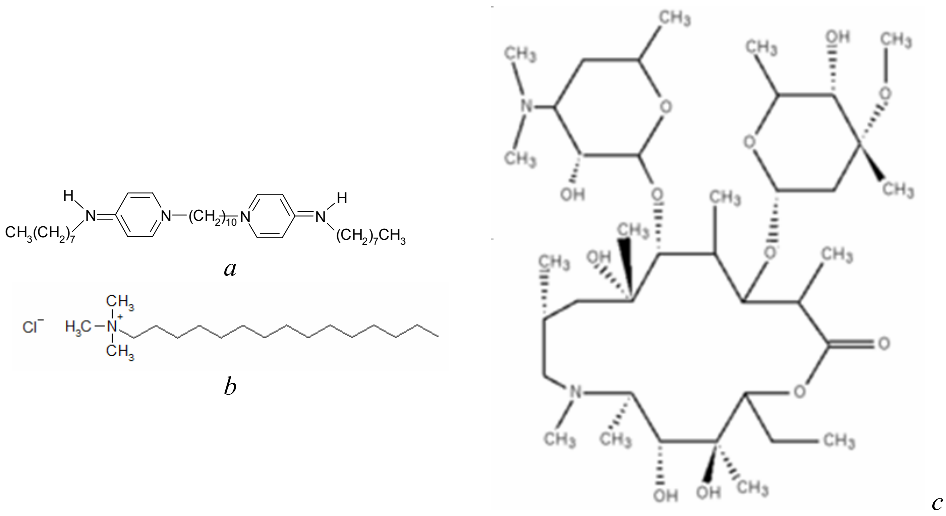


Fig. 1 – Structural formula of *a* − Octenidine dihydrochloride [15], b − Hexadecyl-trimethyl amonium chloride, *c* − Azalide (subclass of macrolide antibiotics).

The samples for testing are listed in Table 1.

Table 1
The Labels and Treatments of Test Samples

Label	Treatment
B	bleached cotton knitted fabric
B-Z	zeolite nanoparticles
B-HDTMAC	cationic surfactant (HDTMAC)
B-OCT	octenidine dihydrochloride (Octenisept)
B-AZI	azalide (azitromicine)

Antimicrobial protection against Gram positive (*Staphylococcus aureus*) and Gram negative (*Klebsiella pneumoniae*) organisms is determined according to EN ISO 20645:2004 - *Textile fabrics - Determination of antibacterial activity - Agar diffusion plate test*. Antifungal protection against the fungus (*Candida albicans*) was determined according to EN 14119:2003 - *Testing of textiles - Evaluation of the action of microfungi*. Both methods are based on the absence or presence of microbial growth in the contact zone between agar and specimen and on the eventual appearance of an inhibition zone. The results are expressed as the width of the inhibition zone, *H,* [mm].

Fabric hand was determined according to subjective and objective evaluation. For the subjective evaluation 10 evaluators performed subjective hand evaluation according to AATCC EP 5 [10] and ranked fabrics according the physical attributes of hand. For objective measurement of physical properties in this paper the fabric coefficient of kinetic friction using FRICTORQ and fabric drape coefficient according to ISO 9073-9:2008 - *Textiles – Test methods for the nonwovens – Part 9: Determination of drapability including drape coefficient, Method A* were determined.

For the measurement of dynamic or kinetic friction coefficient, μ_{kin}, a circular fabric sample of radius, *r*, is clamped and forced to rotate around a vertical axis at a constant angular velocity while a vertical load, *P*, is concentrically applied by a static upper body by means of three small contact sensors, placed in a circle at 120°. Friction coefficient is then proportional to the level of the dragging torque, *T,* measured on a high precision reaction torque transducer. Contact pressure of approximately 3.5 kPa is constant during the test. The torque signal is digitalized through an electronic interface and fed into a PC where dynamic or kinetic friction coefficient, μ_{kin}, is calculated according to [11]:

$$\mu_{kin} = \frac{T}{P \cdot r} \tag{1}$$

Fabric drape describes how the material falls or hangs over the 3-D form. It is the extent to which a fabric will deform when it is allowed to hang under its own weight. According to ISO 9073-9:2008, *Method A,* a circular specimen of the fabric being tested is held horizontally between smaller concentric discs and the exterior ring of fabric is allowed to drape into folds around the lower supporting disc. The shadow of draped fabric is cast from below onto ring of paper of known mass and of the same size as the unsupported part of the test fabric. The outline of the shadow is traced onto the paper ring, which is than cut along the trace. The mass of the inner part representing the shadow is determined. The drape coefficient was calculated according to (3) considering that m_{SA} is mass of the paper ring representing shadow, [g], and m_{PR} is mass of the paper ring, [g]:

$$D_{30} = \frac{m_{SA}}{m_{PR}} \cdot 100 \tag{2}$$

3. Results and Discussions

This paper deals with the influence of antimicrobial treatment with natural zeolite nanoparticles to hand of bleached cotton knitted fabric. The antimicrobial protection varies with antimicrobial agent applied. Therefore, firstly, the selection of antimicrobial agents (cationic surfactant, azalides and antiseptic) which provide optimum protection against Gram positive and Gram negative bacteria, and fungi was determined. The antimicrobial and antifungal activity of cotton knitted fabric treated with Octenisept® is as example presented in Fig.2. The results of antimicrobial activity of all cotton knitted fabrics against *Staphylococcus aureus* and *Klebsiella pneumoniae* according to EN ISO 20645:2004 and against the *Candida albicans* according to EN 14119:2003 expressed as inhibition zone (*H*) are presented in Table 2.

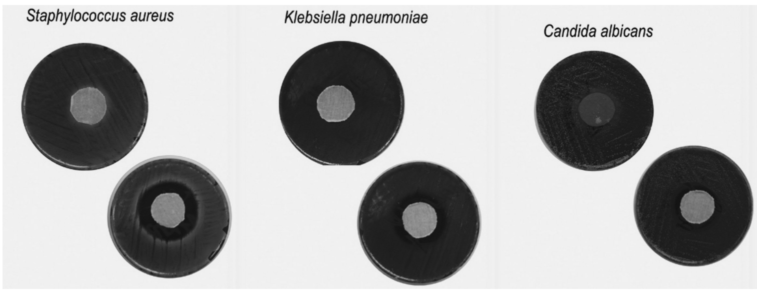


Fig. 2 – Antimicrobial and antifungal activity of untreated cotton knitted fabrics and treated with antiseptics.

According to the standards, excellent antimicrobial protection is for $H \geq 1$. The results of antimicrobial and antifungal activity shown in Table 2 indicate that all antimicrobial treatments regardless of applied agents resulted in antimicrobial protection. Antiseptic treatments, cationic surfactant HDTMAC and Octenisept®, resulted in a high degree of antimicrobial protection to both bacteria - Gram positive *Staphylococcus aureus* and Gram negative *Klebsiella pneumoniae*, as well as fungus *Candida albicans*; while treatment with antibiotics only provide antibacterial protection. Never the less, taking into account the extremely high value of inhibition zone, azalides are indispensable for antibacterial protection.

Table 2

Antimicrobial Activity of Cotton Fabrics (Diameter of Specimen d = 24 mm)

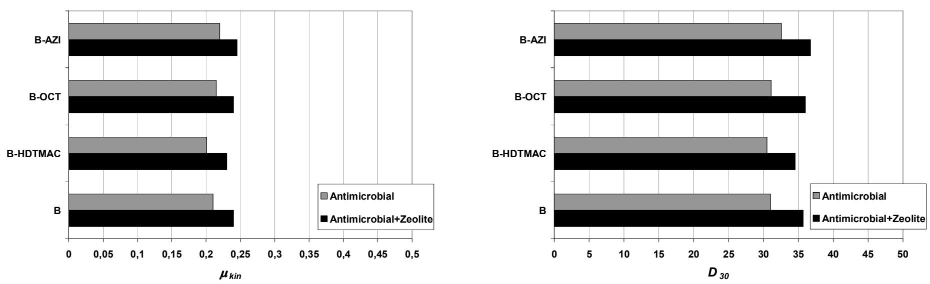
Fabric	*Staphylococcus aureus*		*Klebsiella pneumoniae*		*Candida albicans*	
	D, [mm]	*H*, [mm]	*D*, [mm]	*H*, [mm]	*D*, [mm]	*H*, [mm]
B	24.0	0	24.0	0	24.0	0
B-Z	24.5	0.25	24.0	0	24.0	0
B-HDTMAC	25.5	0.75	25.5	0.75	25.0	0.5
B-HDTMAC-Z	28.5	2.25	26.5	1.25	27.0	1.5
B-OCT	26.0	1.0	24.5	0.25	27.0	1.5
B-OCT-Z	29.0	2.5	25.5	0.75	29.5	2.75
B-AZI	38.0	7.0	27.0	1.5	24.0	0
B-AZI-Z	41.5	8.75	32.0	4.0	24.0	0

Knitted fabrics treated with zeolite provide antimicrobial protection only against Gram-positive bacteria *Staphylococcus aureus*. On the other hand, it is important to emphasize that addition of zeolite nanoparticles considerably increases adsorption surface area, as well resulting in higher antimicrobial protection after treatment. That indicates a distinctly synergistic effect of zeolite nanoparticles with antimicrobial agents.

Table 3
Fabric Hand Subjective Evaluation of Cotton Fabrics Through According to AATCC EP 5

Fabric	Attribute and rank			
	Compression	Bending	Shearing	Surface
B	soft	limp	firm	smooth
B-Z	little bit hard	little bit stiff	firm	rougher
B-HDTMAC	soft	limp	firm	smoother
B-HDTMAC-Z	little bit hard	little bit stiff	firm	smooth
B-OCT	soft	limp	firm	smoother
B-OCT-Z	little bit hard	little bit stiff	firm	smooth
B-AZI	soft	limp	firm	smooth
B-AZI-Z	little bit hard	little bit stiff	firm	rougher

As it was said above, fabric hand is associated with the aesthetic appearance and comfort of garments. The results of subjective evaluation performed according to AATCC EP 5 guidelines are presented in Table 3; and objective via two physical properties – kinetic friction coefficient, μ_{kin}, and drape coefficient, D_{30} presented in Fig. 3.



a *b*

Fig. 3 − Fabric hand objective evaluation of cotton fabrics. *a* − Friction, μ_{kin}, *b* − Drape coefficient, D_{30}.

From Table 3 it is quite evident the zeolite treatment effects fabric hand. All the evaluators distinctively separated all untreated fabrics from the zeolite treated ones regarding all physical attributes of fabric hand. Same result was obtained by objective measurement of fabric drape and friction. Zeolite nanoparticles penetrate into the cotton fabric, but certain amount remains on the fabric surface. Therefore, friction is higher and dynamic friction coefficient, μ_{kin}, increases with zeolite application. Never the less, all these fabric have μ_{kin} $\leq$ 0.25 what is wearable without any irritation of human skin, but their contribution to antimicrobial activity is indispensable. The evaluators ranked cotton fabric treated with HDTMAC (B-HDTMAC) as the smoothest and softest one; than follows the one treated with Octenisept® (B-OCT), what was to expect regarding their cationic surfactant base. That observation confirms the dynamic friction coefficient as well as drape coefficient.

4. Conclusions

Cotton fabrics treated with antiseptics provide vide broad of antimicrobial protection, while antibiotic treatment provides only antibacterial protection.

Nanoparticles of natural zeolite and antimicrobial agents show distinctively synergistic effect in antimicrobial protection of textile.

It is to recommend the application of antiseptics octenidin dihydrochloride (Octenisept ®) for antimicrobial protection which works on all types of microbes (Gram positive and Gram negative bacteria and fungi) improving the fabric hand at the same time.

Received: October 4, 2010

University of Zagreb, Faculty of Textile Technology,
Department of Textile Chemistry and Ecology
e-mail: amgranca@ttf.hr

R E F E R E N C E S

1. Sun G., Xu X., Textile Chemist and Colorist, **30**, *6*, 26−30 (1998).
2. Holme I., International Dyer, (Dec), 9−11 (2002).
3. Takai K., Ohtsuka T., Senda Y., Nakao M. *et al.*, Microbiol. Immunol., **46**, *2*, 75−81 (2002).
4. *** CLOTEFI, *New Multifunctional Textiles: Antimicrobial Treatments.* International Workshop “Intelligent Textile Structures – Application & Testing“, Thessaloniki, Greece (2005).
5. Grancarić A.M., Tarbuk A., Kovaček I., Knežević-Jonjić N., *Antimicrobial Protection of Cotton and Cotton/PES Fabrics Using Natural Zeolite and Antiseptics*. Proceedings of the 3rd Aachen-Dresden International Textile Conference, CD-ROM 1-7, Aachen, DWI & RWTH (2009).
6. Grancarić A.M., Tarbuk A., Kovaček I., Nagl A., *Antimicrobial Protection of Pretreated Cotton.* Proceedings of the 6th World Textile Conference AUTEX 2006, CD-ROM 1-6, Raleigh, USA (2006).
7. Grancarić A.M., Tarbuk A., Kovaček I., CI & CEQ, **15**, *4*, 203−210 (2009).
8. Grancarić A.M., Marković L., Tarbuk A., Tekstil **56**, *9*, 543−553 (2007).
9. Vigo T.L., *Textile Processing and Properties.* Elsevier, Amsterdam, Netherlands (1994).

10. * * * *AATCC Evaluation Procedure 5 – Fabric Hand: Guidelines for the Subjective Evaluation of*, AATCC Technical Manual, AATCC, (2007).
11. Lima M., Hes L., Martins J., *FRICTORQ, a Novel Fabric-to-Fabric Friction Tester: from Concept to Prototype.* Proceedings of 3rd International Conference on Advanced Engineering Design, Process Engineering Publisher (2003).
12. Lima M., Vasconcelos R., Cunha J., Martins J., Hes L., *FRICTORQ, Fabric Friction Tester: A Comparative Study with KES.* Book of Papers of 5th World Textile Conference AUTEX 2005, 802-808, Faculty of Mechanical Engineering, Maribor (2005).
13. Grancaric A.M., Tarbuk A., Lima M., *UV Protection of Summer Clothing by Natural Zeolite Treated Cotton – the Infulence on Fabric Hand.* Proceedings of 2nd ITMC 2009, 317−324, Casablanca, ESITH & ENSAIT (2009).
14. * * * Octenisept®, Schülke Product Information: Wound and muscous membrane disinfection, http://www.schuelkemayr.com/download/pdf/cint_len_Octenisept_ENG_59_prod.pdf; accessed 1st April 2009.
15. Grancaric A.M., Ujevic D., Tarbuk A., Brlobasic Sajatovic B, Tekstil, **58**, *10*, 529−536 (2009).

TUŞEUL MATERIALELOR DIN BUMBAC TRATATE ANTIMICROBIAL FOLOSIND ANTIBIOTICE ŞI ANTISEPTICE

(Rezumat)

Stilul de viață sănătos şi activ adoptat de populație în ultimii ani a dus la dezvoltarea rapidă a tratamentelor antimicrobiale. Astfel de materiale antimicrobiale sunt caracterizate de o prospețime îndelungată, oferind utililizatorilor senzația de siguranță şi de bine. La prima vedere, obținerea materialelor antimicrobiene este simplă, dar durata acestor tratamente ridică probleme. Utilizarea nanoparticulelor de zeoliți natuarli pentru protecția antimicrobiană a demonstrat o activitate crescută şi un sinergism cu anumiți agenți antimicrobieni, de exemplu azaliții. Pe de altă parte, azaliții nu sunt acceptabili din punct de vedere dermatologic, deoarece dezvoltă rezistență în timp.

Lucrarea prezintă alegerea tratamentului antimicrobial optim împotriva bacteriilor Gram pozitiv (*Staphylococcus aureus*) şi *Gram* negativ (*Klebsiella pneumoniae*), precum şi împotriva ciupercilor (*Candida albicans*). În acest scop, tricoturi din bumbac 100%, crude şi albite au fost tratate cu nanoparticule de zeolit natural şi alți agenți anitimicrobieni – surfactant cationic, azalit şi antiseptic. Se cunoaşte că surfactantul cationic îmbunătățeşte semnificativ tuşeul tricoturilor, în timp ce prezența zeolitului îl reduce. Din acest motiv s-a studiat influența acestor tratamente asupra tuşeului (prin investigare subiectivă şi obiectivă).