

THE INFLUENCE OF ULTRASOUND POWER TO SURFACE FUNCTIONALIZATION OF POLYESTER FABRIC

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Abstract

Modification of textiles for achieving multifunctional materials is one of the guidance for future textile development in Europe. As highly hydrophobic synthetic material, polyester fabric from poly(ethylene-terphthalate) (PET), is not comfortable. Surface modifications such are aminolysis and alkaline hydrolysis result in better comfort and other fabric properties, but unfortunately, produce huge amounts of textile wastewater. Therefore, textile wet processes assisted by ultrasound and natural zeolite are researched. The main chemical effect of ultrasound is free radicals formation, which react with each other to form new molecules and radicals, or diffuse into surrounding and serve as oxidants. On the other hand, natural zeolites increase the active surface area, leading to better adsorption, and contribute to antimicrobial, UV, heat, flame and radioactive protection. In this paper, for better durability than achieved by thermosol procedure it was implemented on polyester fabric by high frequency ultrasound.

Keywords:

Polyester fabric, PET, high frequency ultrasound, natural zeolite

1. INTRODUCTION

Modification of textiles for achieving multifunctional materials is one of the guidance for future textile development in Europe. As highly hydrophobic synthetic material, polyester fabric from poly(ethylene-terphthalate), is not comfortable. Therefore, surface modifications such are hydrolysis and aminolysis are necessary for better comfort and other properties. Alkaline hydrolyses of polyester fabric causes modification to the surface of the hydrophobic fibers from

which the fabric is woven, which can improve comfort and other fabric properties [1-4]. It was the most common method of producing silk like polyester until appearance of new generation of polyester fabrics, which contains micro fibers, which have fineness under 1.0 dtex, the bulk and surface area of the normal fibers yarn. Produced textile fabrics are consequently softer and drape better than those made with standard yarn. However, micro fibers contain more oligomers and cause more unlevelness problems. One of the ways to solve this problem is new treatment using ethylenediamine (EDA). Ester-amine interchange reactions have also been researched and surface amine functionality results when diamines are used [5-7]. The use of EDA for short time in ambient conditions results in creation of both amine and carboxylic acid functional groups on the polyester fiber surface, not only carboxylic acid functional groups as in alkaline hydrolysis. The presence of two functional groups provides possibility for better finishing effects. Unfortunately, these conventional modifications (hydrolysis, aminolysis) produce huge amounts of textile wastewater [1-7].

The increasing demand for conservation of natural resources and environmental protection has forced researches to find alternatives to current technologies in order to reduce water consumption, increase energy efficiency and cut emissions of hazardous chemicals. Currently, textile wet processes assisted by ultrasound are of high interest for the textile industry [8]. Ultrasound assisted reactions involve several chemical and physical effects arising from interactions between ultrasound and water medium. The main chemical effect of ultrasound is free radicals formation, which either react with each other to form new molecules and radicals, or diffuse into surrounding and serve as oxidants [9].

In recent papers Grancaric et al. [7,10-14] have shown that the surface modification of textiles by natural zeolite (clinoptilolite) increases the active surface area. If added to azalides in textile finishing, increases the efficiency of antimicrobial action. Zeolite gives a contribution to protection from UV, heat and flame as well as radioactivity. In this paper, for better durability than achieved by thermosol procedure it was implemented on polyester fabric by ultrasound.

2. MATERIAL AND METHODS

Polyester fabric used in the present work was poly (ethylene-terephthalate), PET for summer cloth. It is satin woven fabric, previously heat set, with 60 g/m² weight. The satin PET fabric was woven of textured multifilament yarns (50 dtex, 16f) in warp and weft directions. Yarn is consisted of delustered fibers with trilobal cross section in warp and circular cross section in weft.

Since the ultrasound effects change with different frequency and power it was modified by ultrasound (US) changing the power of ultrasound (P = 30 W, 100 W, 140 W) on laboratory high frequency ultrasound equipment (Figure 1).



Figure 2 High frequency ultrasound equipment (University of Maribor)

Activated natural zeolite (Z) is clinoptilolite particles made by tribomechanical activation on the patented instrument manufactured by Tribomin d.o.o. Osijek. The origin of clinoptilolite used in this paper is Konica, Slovakia. By X-ray diffractometry it was found that the sample consists of about 80 % clinoptilolite and the rest are clay minerals montmorillonite and mordenite. Moisture content was investigated by heating to 105 °C the detected amount was maximum 6 wt % [15]. **The particle size is less than 200 nm.** Composition and physical chemical properties according to the analysis of ISEGA Forschungs- und Untersuchungsgesellschaft mbH, Aschaffenburg, German are given in Table 1 [7].

Table 1: Composition and physico-chemical properties of activated natural zeolite analysed by ISEGA Forschungs- und Untersuchungsgesellschaft GmbH, Aschaffenburg, Germany [7]

Chemical composition	
Component	%
SiO ₂	65,0-71,3
Al ₂ O ₃	11,5-13,1
CaO	2,7-5,2
K ₂ O	2,2-3,4
Fe ₂ O ₃	0,7-1,9
MgO	0,6-1,2
Na ₂ O	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) ₄ Al ₈ Si ₄₀ O ₉₆ x 24H ₂ O	
Physical properties	

Specific mass	2,2-2,5 g cm ⁻²
Porosity	32-40 %
Effective pore diameter	0,4 nm
Ion-exchanging capacity	mol kg ⁻¹
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 for selected ions	
	Cs>NH ₄ ⁺ >Pb ²⁺ >K ⁺ >Na ⁺ >Mg ²⁺ >Ba ²⁺ >Cu ²⁺ >Zn ²⁺
Absorbency	
	NH ₃ , hydrocarbons C ₁ . C ₄ , CO ₂ , H ₂ S, SO ₂ , NO _x , aldehydes
Toxicity	
	Nontoxic according to US Code of Federal Regulations (21 CFR 82, Subpart C)

The natural zeolite nanoparticles were implemented in ultrasound bath at frequency of 280 kHz, temperature of 25 °C for 1 h in distilled water without and with addition of activated natural zeolite nanoparticles (Z).

The characterization of surface and chemical composition of such treated polyester fabrics was performed applying instrumental methods - scanning electron microscopy (SEM) on FEI Quanta 200 Scanning Electron Microscope with magnification 2500x and Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) spectroscopy on Spectrum GX FT-IR (Perkin-Elmer).

The adsorption ability of optical brightener (OB) Uvitex ERN-P (Ciba) was determined through fabric whiteness (W_{CIE}) according to ISO 105-J02:1997 using remission spectrophotometer SF 600 PLUS CT (Datacolor) after treatment in optimal concentration of 0.5 % owf in stainless-steel bowls (Linitest, Original-Hanau) for 30 min at 120 °C.

The fabric UV protection was determined according to AS/NZS 4399:1996 Sun protective clothing - Evaluation and classification using Varian Cary 50 Spectrophotometer. The ultraviolet protection factor (UPF), which indicate the ability of body protection by textile materials to prevent eritem, was calculated according to eq. (1):

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

where $E(\lambda)$ is Solar radiation [$W m^{-2} nm^{-1}$]; $\varepsilon(\lambda)$ is relative erythemal spectral effectiveness; $T(\lambda)$ is spectrum permeability at wavelength λ and $\Delta\lambda$ is measured wavelength interval [nm].

3. RESULTS AND DISCUSSION

In this paper the influence of ultrasound power to surface functionalization of polyester fabric was investigated. After the ultrasound treatment with and without natural zeolite addition, the characterization of surface and chemical composition of such treated polyester fabrics was performed applying instrumental methods - scanning electron microscopy (SEM) (Figure 1) and FTIR-ATR spectroscopy (Figure 2).

From SEM micrographs shown in Figure 2 it is evident that ultrasound treatment cleared impurities from the surface of PET fabric (Fig 2c). Other significant changes are not noticeable. The difference between the nanoparticles implemented by ultrasound (Fig 2d) and by thermosol procedure (Fig 2b) is clearly visible. Natural zeolite nanoparticles implemented by thermosol generally remain on the fabric surface, while a good part of nanoparticles assisted by ultrasound penetrates in the pores of the fibers and are not visible on the surface any more.

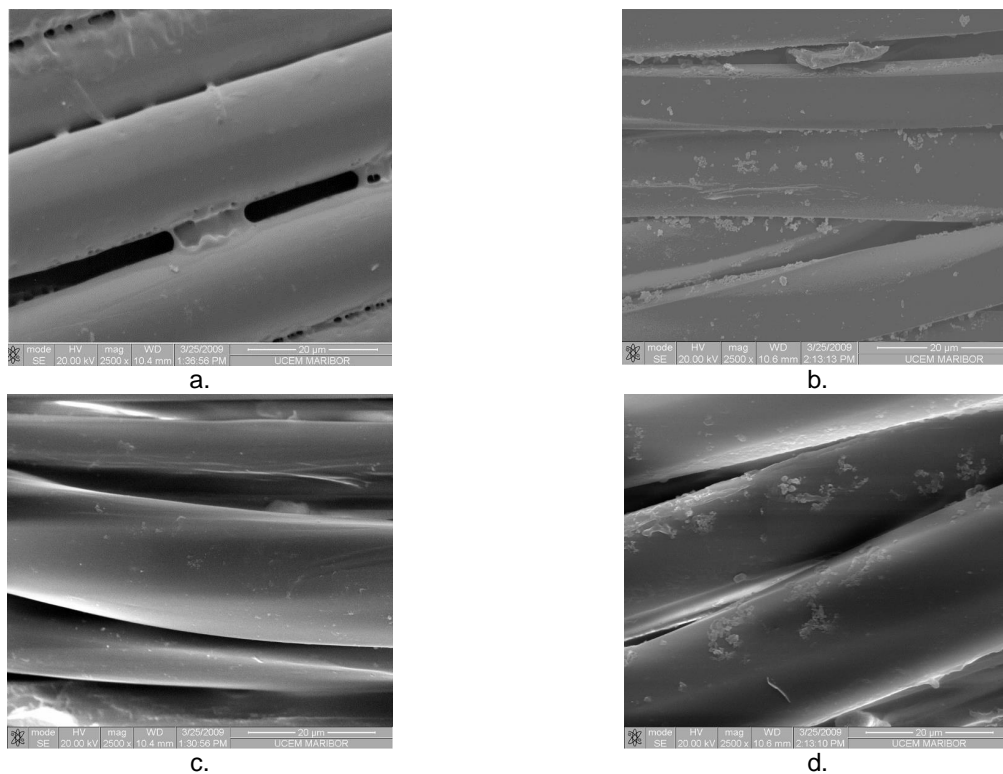
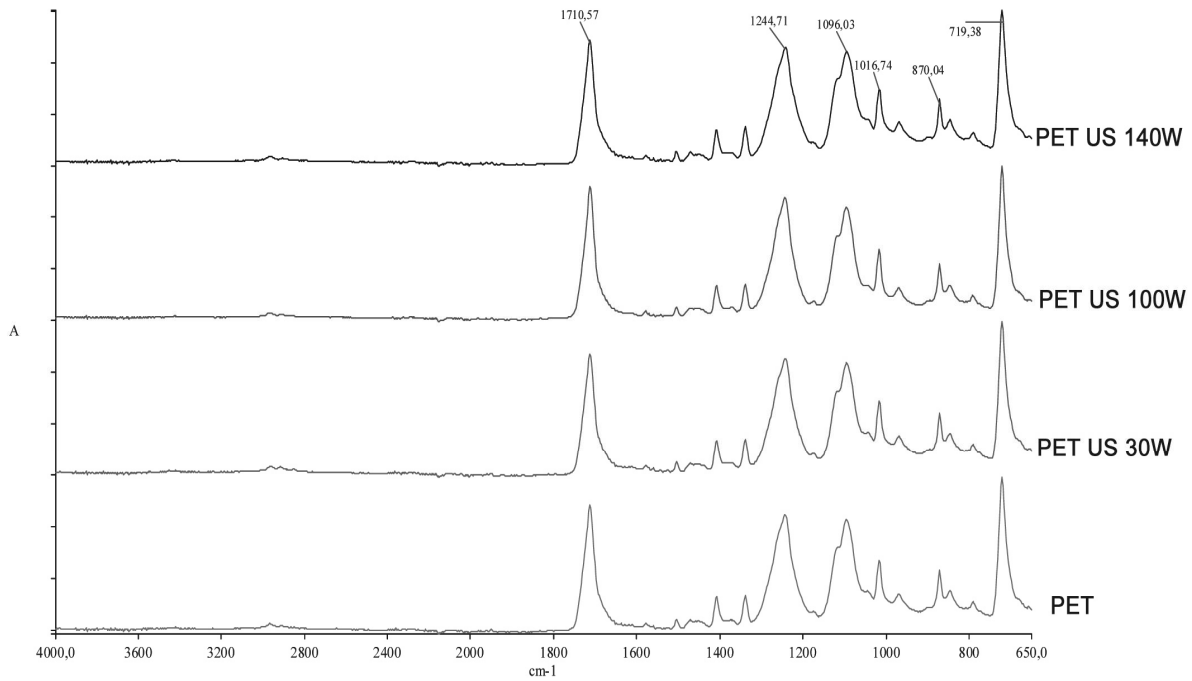


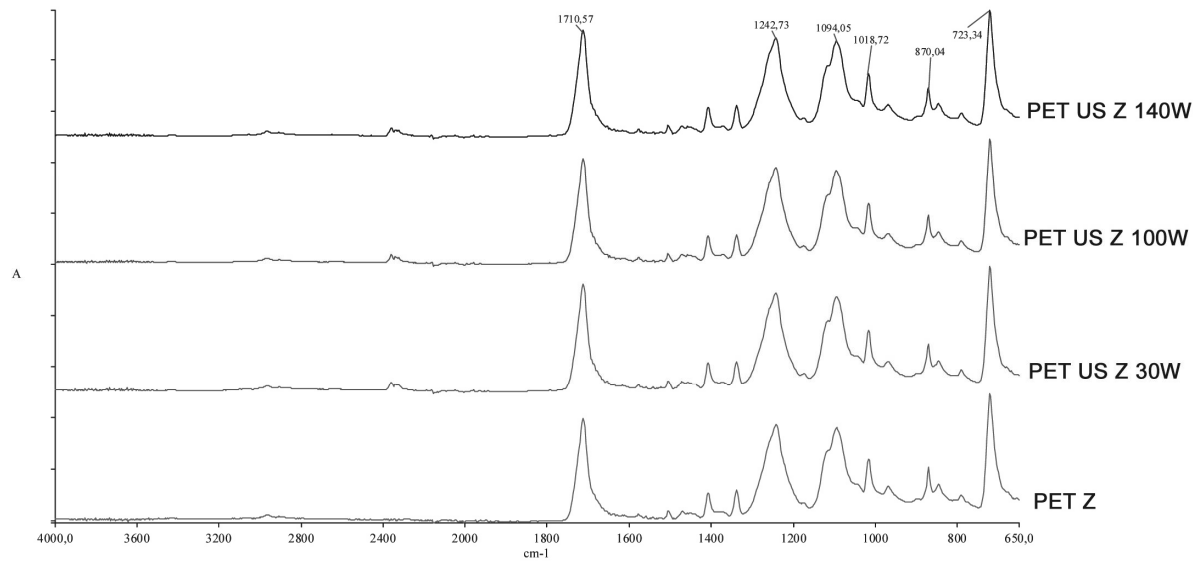
Figure 2 SEM micrographs of PET fiber with magnification 2500x - a. untreated fabric (PET) b. zeolite treated fabric (PET Z) c. ultrasound modified fabric (PET US) and d. ultrasound modified fabric with the zeolite addition (PET Z US)

From IR spectrums taken by Fourier Transform Infrared - Attenuated Total Reflectance Spectroscopy (FTIR-ATR) presented in Figure 3 it is evident that the significant change (detectable by IR) in chemical composition during the modification did not occur because all spectrum peaks are in the same position. On the other hand, it is evident that the transmission of IR spectra is significantly changed in ultrasound treatment with as well as without zeolite implementation. The

ultrasound treatment resulted in lower IR radiation transmission. Applying higher ultrasound power the effects are more pronounced.



a.



b.

Figure 3 Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) of PET fabric, a. untreated fabric and ultrasound treated applying power 30-100-140 W; b. zeolite treated fabric and ultrasound implemented zeolita applying power 30-100-140 W

Due to the extreme crystallinity polyester fibers, PET fabric absorbs small amounts of water, as well as other textile auxiliaries, such as optical brighteners, dyestuff etc. Therefore, the made garment of untreated fabric is uncomfortable. For this reason, the influence of ultrasound modification to adsorption ability was researched. The adsorption ability of optical brightener Uvitex ERN-P (Ciba) determined through fabric whiteness (W_{CIE}) is presented in Figure 4.

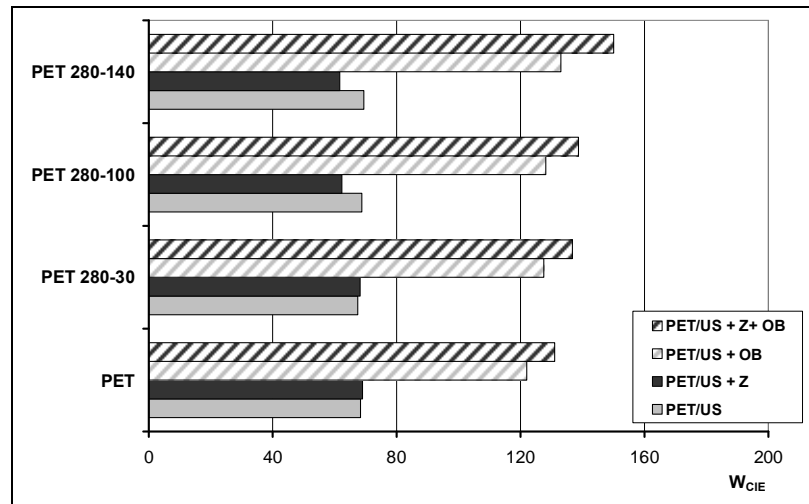


Figure 4 Absorption of optical brightener (OB) expressed through CIE whiteness (W_{CIE}) of PET fabrics

It is evident from Figure 4 that ultrasound treatment positively affects the whiteness of PET fabrics. The release of free radicals due to the effects of ultrasound causes a clean surface as indicated by the SEM micrograph (Fig 2c) increasing the basic fabric whiteness. In Figure 4 is an apparent significant increase in the adsorption of optical brighteners (degree of whiteness increased with 121 on the 139). The ultrasonic treatment leads to functionality of the surface which allows better adsorption. The ultrasound power emphasis these effects.

On the other hand, natural zeolite nanoparticles increase the surface area, and implementation onto PET fabric by ultrasound, increases adsorption ability. It should be noted that the implementation of zeolite nanoparticles by ultrasound resulted in remarkable adsorption of the optical brighteners in which it achieves a high degree of whiteness of the 156.

The fabric UV protection ability determined according to AS/NZS 4399:1996 expressed as ultraviolet protection factor (UPF) is presented in Figure 5.

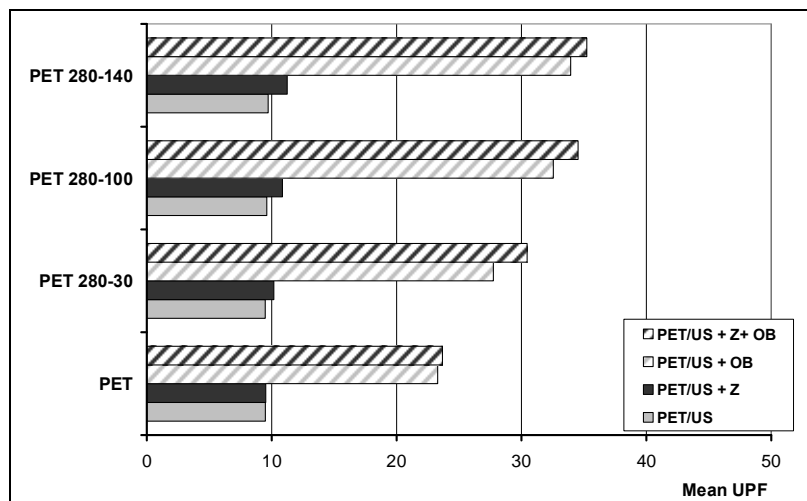


Figure 5 UV protection expressed through mean UPF of PET fabrics after ultrasound treatment and optical brightening

UPF values indicate how much longer the person can stay in the sun with the fabric covering the skin as compared with the uncovered skin to obtain same erythral response. Based on its aromatic backbone polyester fiber can absorb certain amounts of UV radiation, nevertheless the untreated fabric yields comparably low UV protection. Additionally, certain amounts of UV radiation are reflected by polyester multifilament. As a result the untreated PET fabric achieves a mean UPF value of 9.6 which it is not rateable for UV protection. Ultrasound treatment leads to cleaning of PET fabric, as well as fabric shrinkage what results in slightly higher UPF, which still do not achieve UV protection, but improve fabric aesthetic appearance. From Figure 6 it can be seen that the highest power leads to better UV protection.

By absorbing UV-A radiation optical bleached polyester fabrics transform this radiation to blue fluorescence not transmitting this range of radiation what leads to very good UV protection and expected high degree of whiteness, as well. Since the surface of PET fabric was activated by ultrasound it can absorb higher amount of optical brightener (FWA). It is evident that the higher ultrasound power in modification applied, the higher adsorption of optical brightener is; what results in very good UV protection.

Nanoparticles of activated natural zeolite on fabric surface scatter UV radiation resulting in higher UV protection. Increasing active surface area of fabric by zeolite implementation it absorbs higher amounts of FWAs. It is to point out that treatment with natural zeolite and UV absorber results in excellent UV protection. Additionally, ultrasound treatment, FWAs and zeolite shown synergism resulting in even higher UV protection. It is to point out that the UPF value increase with higher ultrasound power applied for PET fabric modification.

5. CONCLUSIONS

Modifications of poly(ethylene-terephthalate) fabric by ultrasound and nanoparticles of natural zeolite change the fabric surface properties. The change in chemical composition did not occur but it led to PET fabric functionalization.

The implementation of zeolite to polyester fabric is higher if the higher ultrasound power is applied. Therefore the fabric whiteness is slightly lower, but sorption of optical brightener is significantly higher what improves fabric aesthetic appearance yielding a better absorption of the surfaces in wet finishing and make these fabrics more comfortable.

Optical brightening of polyester fabric is necessary to achieve fabric whiteness as well as UV protection. Natural zeolite scatters the UV-R resulting in lower UV-A and UV-B transmission, increasing UV protection significantly, regardless the applying method.

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References

1. Zeroing H. S., Collins M. J.: Surface modification of Polyester by Alkaline Treatments, *Textile Progress*, 1989, Vol. 20, No. 2
2. Pfeifer H.: *Über den Abbau von Polyester fasern durch Hydrolyse und Aminolyse*, Westdeutscher Verlag, Köln, Germany, 1964
3. Gorraffa, A. M.: Caustic Treatment of Polyester Filament Fabrics, *AATCC Review* 1980, Vol. 12, No. 4, 83-87
4. Kallay N., Grancari , A. M., Tomi , M: Kinetics of Polyester Fibre Dissolution, *Text. Res. J.* 1990, Vol. 60, No. 11, 663-669
5. Bide, M. et al.: Bifunctional Surface Modification of Polyester, *AATCC Review* 2003, Vol. 3, No. 11, 24-28
6. Avny, Y., Rebenfeld, L.: Chemical modification of polyester fiber surfaces by amination reactions with multifunctional amines, *J. Appl. Polym. Sci*, 1986, Vol. 32, No. 3, 4009 . 4025
7. Grancari , A. M.; Tarbuk, A.: EDA Modified PET Fabric Treated with Activated Natural Zeolite Nanoparticles, *Materials Technology*, 2009, Vol. 24, No. 1; 58-63
8. Thakore K. A., Smith C.B., Clapp T.G.: Application of Ultrasound To Textile Wet Processing, *American Dyestuff Reporter* 79, 1990, 30-38
9. Vajnhandl, S., Majcen Le Marechal, A.: Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes, *Dyes and Pigments* 65, 2005, 89-101

10. Grancari , A.M., L. Markovi , A. Tarbuk: Active Multifunctional Cotton Treatment with Zeolite Nanoparticles, *Tekstil* 56, 2007, 543-553
11. Grancari , A. M., A. Tarbuk, I. Kova ek: Nanoparticles of Activated Natural Zeolite on Textiles for Protection and Therapy, *Chem. Ind. & Chem. Engineer. Quar.* 15, 2009, 201-208
12. Grancari , A. M., Prli , I. Tarbuk, A., Marovi , G.: Activated Natural Zeolites on Textiles - Ability to Protect from Radioactive Contamination; in *Defense Related Intelligent Textiles and Clothing for Ballistic and NBC (Nuclear, Biological, Chemical) Protection*; NATO Security through science series, Amsterdam: IOS Press, 2010
13. Grancaric, A. M., Tarbuk, A., Majcen le Marechal, A. Functionalization of PET Fabric by Ultrasound and Natural Zeolite, *Proc. Internat. Conf. Latest Advan. in High Tech Textiles and Textile Materials*, Gent, Ghent University, 2009, 219-224
14. Tarbuk, A., Grancaric, A. M., Majcen le Marechal, A. Natural Zeolite Nanoparticles Implemented by Ultrasound onto PET Fabric for Better UV Protection, *Proc. 15th Slo. Chem. Event*; Maribor, 2009, CD-ROM, 1-9
15. Ivkovi S. et al.: Dietary Supplementation with the Tribomechanically Activated Zeolite Clinoptilolite in Immunodeficiency, *Advances in Therapy* 21, 2004, 135-147