ANNALS
OF THE
UNIVERSITY OF ORADEA

FASCICLE OF TEXTILES, LEATHERWORK

VOLUME XIX, 2018

No. 2

ISSN 1843 – 813X

ANNALS
OF THE
UNIVERSITY OF ORADEA

FASCICLE OF TEXTILES, LEATHERWORK

VOLUME XIX, 2018

No. 2

This volume includes papers presented at International Scientific Conference "Innovative solutions for sustainable development of textiles and leather industry", 25th-26th of May 2018, Oradea, Romania

Contact and Editors' Address:
Liliana INDRIE,
UNIVERSITATEA DIN ORADEA,
FACULTATEA DE INGINERIE ENERGETICĂ ŞI MANAGEMENT INDUSTRIAL
DEPARTAMENTUL: TEXTILE- PIELĂRIE ŞI MANAGEMENT INDUSTRIAL
Str. B.St.Delavrancea nr. 4,
Oradea, 410058, Romania,
Tel.: 00-40-259-408448
E-mail : lindrie@uoradea.ro

Published by
Editura Universităţii din Oradea
Universitatea din Oradea, Str. Universităţii Nr. 1, 410087, Oradea, Bihor, Romania
P- ISSN 1843 – 813X
E - ISSN 2457-4880
CD- ISSN 2068 – 1070

Indexed in:

EBSCO-Textile Technology Complete
Directory of Open Access Journals (DOAJ)
Ulrich's Update - Periodicals Directory
Index Copernicus (ICV 2016: 81.40)

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CONTENTS

			Applied Science, Goztepe, Istanbul, Turkey	
5	**EFFECT OF BRASI-COLOR DYE ON UV PROTECTION OF BAMBOO KNITTED FABRICS**	**CHIRILA Laura[1], MITRAN Elena-Cornelia[1], DUMITRESCU Iuliana[1], PERDUM Elena[1], IORDACHE Ovidiu George[1], STEFANESCU Dana[2], PISLARU Mariana[2], MANCASI Iulian[3]**	[1]The National Research Development Institute for Textiles and Leather, Bucharest, Romania, Str. Lucretiu Patrascanu nr. 16, sector 3, 30508, Bucharest, Romania, [2]SC Tanex SRL, Sos. Bucuresti - Magurele, nr. 47B, 051432, Bucharest, Romania, [3]SC Majutex SRL, Bîrnova, Jud. Iași, 707035, Romania	**31**
6	**WASTE WATER ANALYSIS FROM A NEW GREEN PRETREATMENT OF COTTON FABRICS**	**DOCHIA Mihaela[1], GAVRILAȘ Simona[2], PUSTIANU Monica[3], MOISĂ Cristian[4], CHAMBRE Dorina[2]**	[1]"Aurel Vlaicu" University of Arad, Research Development Innovation in Technical and Natural Science Institute,Postal address, 310330, 2-4 Elena Dragoi Street, Arad, Romania [2]"Aurel Vlaicu" University of Arad, Faculty of Food Engineering, Tourism and Environmental Protection, Department of Technical and Natural Sciences, Postal address, 310330, 2-4 Elena Dragoi Street, Arad, Romania [3]"Aurel Vlaicu" University of Arad, Faculty of Engineering, Department of Automation, Industrial, Textile and Transportation Engineering, Postal address, 310330, 2-4 Elena Dragoi Street, Arad, Romania [4]Banat University of Agricultural Sciencies and Veterinary Medicine "King Michael I" of Romania, Postal address, 300645,	**37**

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

FUNCTIONALIZATION OF TEXTILE MATERIALS BY PLASMA TECHNOLOGY FOR METALLIC MICROPARTICLES DEPOSITION

AILENI Raluca Maria[1], RADULESCU Razvan Ion[1], CHIRIAC Laura[1]

[1] INCDTP, Research Department of Advanced Materials Investigation, Lucretiu Patrascanu 16, 030508 Bucharest, Romania

Corresponding author: Aileni, Raluca Maria, E-mail: raluca.aileni@certex.ro

Abstract: *In this paper we propose a method based on plasma technology, which does not cause damage of the fabric. In our work are described aspects regarding textile functionatization by plasma activation treatment for metallic deposition in order to obtain flexible electronics. By plasma activation the textile surface can be modified and can be obtained the optimal surface energy for additional treatments such as metallization by microparticles deposition for developing the electroconductive surfaces with great potential for use in sensors/actuators devices, EM shielding and with antistatic properties. Our work presents comparative aspects of the hydrophobic/hydrophilic surface obtained by plasma coating and used for metallization.*
The most used treatment for optimal surface energy preparate the textile surface for metallic deposition (print, lamination or padding) are based on the surface treatment such as plasma, inluding corona treatment and chemical treatment using classical techniques (padding).
The massive development of wireless communication systems and the miniaturization trend in electronics has generated a need for flexible wearable electronics based on conductive lightweight surfaces. The classical technology for metal deposition for electronics involves high temperature fabrication processes. Generally, the metal depossition in microfabrication processes, in semiconductors industry, is performed by chemical vapor deposition (CVD), electrodeposition and epitaxy.

Key words: *plasma technology, magnetron, electroconductive, metallic, textile*.

1. INTRODUCTION

On the microfabriaction industry is used the CVD techniques, electrodeposition and epitaxy. Unfortunately, the classical technology for metal deposition for electronics involves Si substrate, which is not flexible, and requires a high temperature fabrication processes [1].

The most used CVD techniques are LPCVD and PECVD and involve very high processing temperature (1000^0 C) in comparison with PVD (physical vapour deposition) techniques that require below temperatures ($200 \div 500^0$C) [2]. Therefore, both CVD and PVD techniques, involve temperatures enough high to cause damage to the fabric. The coating techniques based on vacuum deposition such as chemical vapor deposition (CVD) and physical vapor deposition (PVD). By CVD coating technology, a thin film obtained by chemical reaction between precursors. The inconvenient is that this technique requires a high-temperature medium. By PVD technique, the surface can be modified by evaporation and sputtering. Plasma technology for surface activation is requirement for metallic deposition on the textile surface [3] for small electronics (actuators/sensors) [4]. The plasma

technology is eco-friendly and dry technology that can be used for obtain functional surfaces with antibacterial, electrical, mechanical, hydrophobicity and water repellence characteristics improved.

Several treatments used for textile surface energy modeling include plasma treatments for obtain the hydrophilic or hydrophobic textiles for metallic deposition (print, lamination or padding) and chemical treatment using classical techniques (padding) [5].

2. EXPERIMENTAL PART AND DISCUSSIONS

The textile sample, cotton 100% with mass 401 g/m^2, was treated in plasma was used Teflon coating. After plasma treatment we observed the hydrophobic surface are partial stable in time (figure 1 and 2), but sufficiently stable in order to deposit an electro-conductive layer. In our previous experiments [6] by hydrophobization in plasma we obtained a material with good surface for metallization and by hidrophylization we try obtain the surface activation before classical hydrophobization treatment in order to reduce the chemicals consumption.

a. Afer 24 h *b. After 1 month*

Fig. 1. *Contact angle view for textile treated in plasma*

The hydrophobicity effect of the coated textile surfaces was analyzed by determining the water contact angle using the device VCA OPTIMA (figure 1) and spray rating tester (water resistance tester) James Heal (figure 2). The physico-chemical investigations for water resistance spray test were obtained using SR EN ISO 4920/2013 standard method and contact angle using ASTM D7490-08 standard method [6-7].

Fig. 2. *Spray test rating – James Heal*

After analysing the textile hydrophobization process in plasma we can conclude that this process affects drastically only the energy consumption (figure 3) and indirectly ozone layer dimension and clima changes, fossil fuels consumption and health by inspiration of the nocive gas waste.

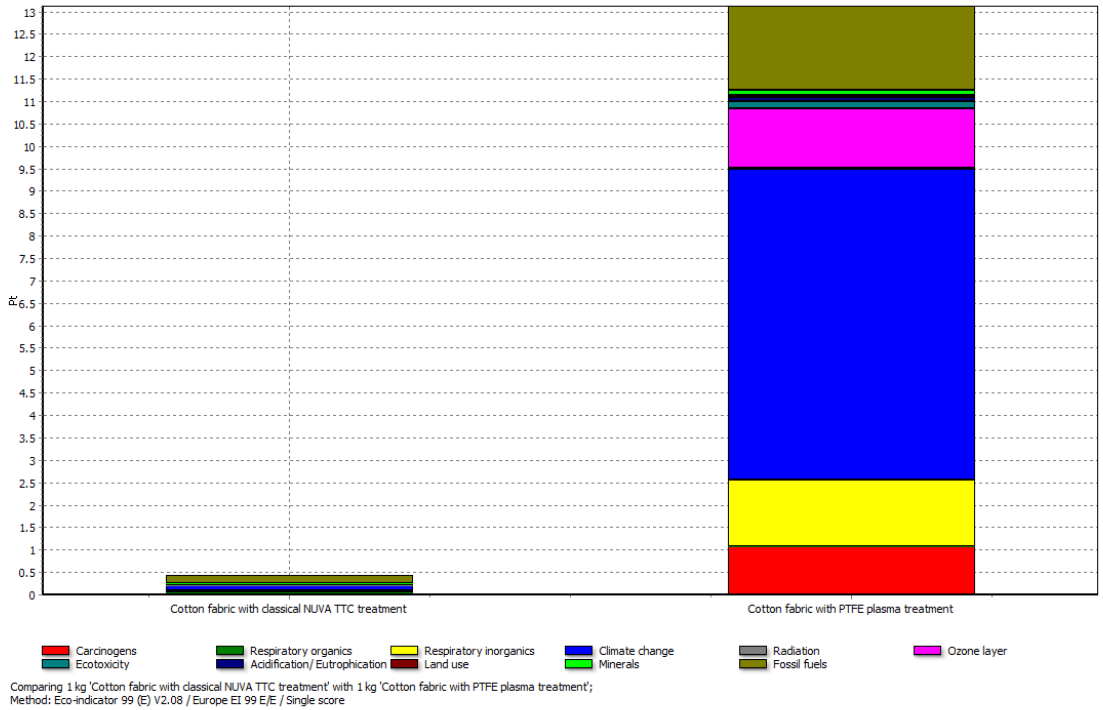


Fig.3. *Plasma hydrophobization impact*

Even if the plasma processes involves many harmful chemicals [8-11] and energy consumption, is still used in researches [12-14] and in industrial applications. For obtaining the textile with electrical or insulator properties it is very important to obtain dielectric surface, conductive surface and this involves, after plasma hydrophobization treatments, some deposition of the metallic powders [4].

4. CONCLUSIONS

There are some advantages of the using the water repellent treatment by plasma is that we can reduce to zero the environmental water waste and it is a clean procedure.
Unfortunately the plasma procedures are already reported as harmful to human health because of the chemicals used. But still, we can use this treatment for small piece treatment in order to obtain the conductive textiles [12].

The plasma treatment advantages are:

-Do not generate water waste;

-It generates reducing the carbon footprint;

-Reducing time for textile finishing;

The plasma treatment disadvantages are:

- High energy consumption;
- Potential hazard substantanced eliminated in the environments;
- Sofisticated equipment manufacturing;
- Increased cost with personal high qualified and equipment mentenance.

REFERENCES

[1] Y. C. Chang et al., "Study of deposition parameters on the RF magnetron sputtered ZnO films on Mo/SiNx/Si substrates" 2017 International Conference on Applied System Innovation (ICASI), Sapporo, 2017, pp. 988-990.

[2] J. H. Park, T. S. Sudarshan, "Chemical Vapor Deposition", ASM Internationl, 2001

[3] R. Bonadiman, M. Marques, G. Freitas and T. Reinikainen, "Evaluation of printing parameters and substrate treatmet over the quality of printed silver traces", 2008 second Electronics System-Integration Technology Conference, Greenwich, pp. 1343-1348, 2008.

[4] R. M. Aileni and L. Surdu, "Obtaining the optimal surface for electronic device deposition using nanotechnologies", 2014 International Symposium on Fundamentals of Electrical Engineering (ISFEE), Bucharest, pp. 1-4, 2014

[5] R. Bonadiman, M. Marques, G. Freitas and T. Reinikainen, "Evaluation of printing parameters and substrate treatmet over the quality of printed silver traces", 2008 2nd Electronics System-Integration Technology Conference, Greenwich, pp. 1343-1348, 2008.

[6] R. M. Aileni, V. Satulu, B. Mitu, L. Dincă, I. R. Radulescu, L. Surdu, "Textile surface hydrophobization by Plasma Vapor Deposition (PVD) using magnetron sputtering", Conferinţa Internationala TexTeh VIII, Bucuresti, Romania, 2017

[7] R. Shishoo, "Plasma technologies for textiles", CRC Press, 2007

[8] G. Benveniste and M. Perucca, "LCA comparative analysis of textile applications for oleophobic and hydrophobic properties", Public Report, ACTECO, 2007

[9] G. Buyle, "Nanoscale finishing of textiles via plasma treatment", Materials Technology, vol. 24, nr. 1, pp. 46-51, 2009

[10] J. T. Williams, "Waterproof and Water Repellent Textiles and Clothing", Elsevier, UK, 2018

[11] A. Fridman, "Plasma Chemistry", pp. 647-648, Chambridge University Press, USA, 2008

[12] B. O. Aronsson, J. Lausmaa, B. Kasemo, "Glow discharge plasma treatment for surface cleaning and modification of metallic biomaterials", J Biomed Mater Res. 1997 Apr;35(1):49-73.

[13] M. Caraiman, M. Neculaiasa, M. Ciocoiu, D. C. Radu, "Optimizarea tratamentelor in medii de plasma pentru fibrele de lana", a - X –a Conferinta Romana de Textile-Pielarie. Sectiunea a- XIII-a: Optimizari tehnologice si mijloace de investigatie, pag. 9-15, Iasi 1992

[14] M. Caraiman, M. Neculaiasa, M. Ciocoiu, D. C. Radu, "Modelarea matematica a procesului de tratare in medii de plasma pentru fire de lana", A X-a Conferinta Romana de Textile-Pielarie. Sectiunea a -XIII-a: Optimizari tehnologice si mijloace de investigatie, pag. 16-20, Iasi 1992. Marius CARAIMAN / Iasi 1999 Tratarea lânii în plasmă

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ANALYSING THE PHYSICAL AND MECHANICAL PROPERTIES OF CORE-SPUN YARNS

BALCI KILIC Gonca[1]

[1] Dokuz Eylül University, Faculty of Engineering, Department of Textile Engineering, 35397, İzmir, Turkey

Corresponding author: BALCI KILIC, Gonca, E-Mail: gonca.balci@deu.edu.tr

Abstract: *Core spun yarn is also named as complex, compound, composite or hybrid yarn can be defined as the combination of filament and staple fibres. A filament which is called core is covered by staple fibres called sheath. In this study, it was aimed to analyse physical and mechanical properties of ring core-spun and ring dual core-spun yarns. Moreover, conventional ring and OE-rotor yarns were used as reference materials for better assessment. For this purpose, unevenness and imperfections, hairiness, frictional properties and tensile properties of yarns were measured. It was observed that core and dual-core spun yarns have better unevenness and imperfections values than conventional ring and OE-rotor spun yarns. Also, friction coefficients of core and dual-core yarns for all surfaces (yarn, metal and ceramic) were found lower than the equivelant 100% cotton conventional ring and OE-rotor spun yarns. Results showed that ring yarns have the highest hairiness values and it was also found that there is no statistically significant difference between hairiness values of core-spun and dual-core yarns. When the breaking force and breaking elongation were examined, it was seen that dual-core yarns have the highest values whereas OE-rotor yarns have the lowest.*

Key words: *Core-spun yarn, dual-core yarn, ring spinning, OE-rotor spinning, yarn hairiness, yarn friction*

1. INTRODUCTION

Core-spun yarn can be defined as the combination of filament and staple fibres and it is also named as acomplex, compound, composite or hybrid yarn. For the production of core spun yarns, filaments are fed into the axis of the yarn as core and staples are used to cover filaments as sheath. In this kind of yarn structure, it is possible to get benefit of either performance and recovery properties of filaments or comfort and surface properties of staples. The history of core-spun production is back to 1950s, a few years after highly utilized filaments were discovered. At present, core spun yarn production is done in different spinning technologies such as friction spinning, rotor spinning, air-jet spinning and ring spinning. However, ring spinning technology is most widely used technologies for core spun yarn production.

After the wide range of usage of core-spun yarn, researches have been continued to improve core spun yarn properties. In 2000s dual core-spun yarn was introduced. To produce dual-core spun yarn, two individual filaments with different properties fed into the axis of yarn. In general, polyethylene terephthalate-based filaments are used for high tensile properties while polyurethane based filaments are used for high recovery properties in dual-core spun yarn production.

Core-spun yarns have been in the center of many researches with the superior features against staple or filament yarns. The vast majority part of these studies examine the physical and mechanical properties of core-spun yarns and fabrics produced from these yarns. The effects of

various parameters such as yarn linear density, yarn twist, core/sheath ratio, draft ratio, etc. were mostly studied [1, 2]. There are also many studies examine the electromagnetic shielding properties of fabrics produced from these yarns which are produced with electrically conductive filaments in the center of core-spun yarns [3, 4]. In recent years, many researchers have also focused on dual-core yarns produced using two different filaments in the core [5, 6].

Chakraborty and Chatterjee [7] examined the hairiness properties of silk-nylon core-spun yarns and they specified that core spun yarns have less number of protruding ends and loops than ring spun yarns. In another study, Tarafder and Chatterjee [8] analysed physical and mechanical properties of cotton covered nylon core-spun yarns. They stated that core spun yarns have better hairiness and abrasion resistance values than ring spun yarns. Jeddi et al. [9] compared the structural and mechanical properties of core-spun yarns with the 100% cotton ring spun yarns. They investigated the effect of yarn twist and pretension of the filament. Results showed that core-spun yarns have higher diameter, breaking strength and elongation and better unevenness and abrasion resistance than the equivelant 100% cotton conventional ring spun yarns. Babaarslan [10] examined that physical and mechanical properties of polyester/viscose staple and polyester/viscose core-spun yarns. It was pointed out that core positioning has a direct effect on the properties of the core-spun yarns and core-spun yarns have always higher hairiness than that of the staple yarn of the same fibers. Viswarajasekaran ve Raghunathan [11] analysed the physical properties of core-spun yarns. They remarked that tensile properties of core-spun yarns depend on core and sheath material, twist level and core/sheath ratio. They found that yarn irregularity decreases by reducing cotton content in the sheath and core-spun yarns have good tenacity and beraking extension as compared to yarns produced from conventional ring frame. Sue et al. [12] investigated the effect of draw ratio and feed-in angle on elastic recovery properties on core-spun yarns. They concluded that a higher feed-in angle provides a better cover effect and draw ratio of 3.5 yields better dynamic elastic recovery.

In this study, it was aimed to analyse and compare the physical and mechanical properties of conventional ring, OE-rotor and ring core-spun and ring dual core-spun yarns. For this purpose, unevenness and imperfections, hairiness, fricitonal properties and tensile properties of these yarns were measured and statistically analysed.

2. MATERIALS AND METHOD

In the study, 25 tex conventional ring, OE-rotor, ring core-spun and ring dual-core spun yarns were used. Properties of the yarns are given in Table 1.

Table 1: *Properties of the yarns*

Raw Material	**Spinning Technology**
Cotton	Ring
Cotton	OE-rotor
Sheath: Cotton, Core: Lycra (78 dtex)	Ring core-spun
Sheath: Cotton, Core: PBT (55 dtex), Core: Lycra (78 dtex)	Ring dual core-spun

Unevenness, imperfections and hairiness properties of yarns were measured by Uster Tester 5 at 400 m/min test speed. Breaking force (cN) and elongation (%) were measured by Instron 4411. Yarn-to-yarn, yarn-to-metal and yarn-to ceramic friction coefficient were tested by Lawson Hemphill (CTT) at 100 m/min test speed by using 25 cN input tension. Hairiness values (S1+2, S3) were also measured by Uster Zweigle Hairiness Tester 5 with 10 cN pretension.

3. RESULTS AND DISCUSSION

Physical and mechanical properties of ring, OE-rotor, core-spun and dual-core yarns were statistically analysed at α = 0.05 significance level using ANOVA and confidence interval graphs at 95% were illustrated.

3.1 Unevenness and Imperfections

Mean values of unevenness (CVm%), thin places (-50% /km), thick places (+50% /km) and neps (+200% /km) are given in Table 2. ANOVA results are given in Table 3.

Table 2: *Unevenness and imperfection values of yarns*

Spinning Tech.	CVm%	Thin Places -50%	Thick Places +50%	Neps +200%
Ring	14.46	1.5	207.5	256.5
OE-rotor	14.77	27.5	88.0	307.0
Core-spun	9.51	0.0	6.0	6.5
Dual-core	11.41	0.0	61.0	57.5

Table 3: *ANOVA results of unevenness and imperfections*

Parameters	Sum of Squares	Mean Square	F	Sig.
CVm%	95.292	31.764	616.745	0.000*
Thin places -50%	2741.250	913.750	27.455	0.000*
Thick places +50%	108528.438	36176.146	108.545	0.000*
Neps +200%	324753.438	108251.146	460.950	0.000*

* Statistically significant at α=0.05.

When the unevenness and imperfections values of the yarns were examined, it was seen that ring and OE-rotor spun yarns have higher values than both core-spun yarns and effect of spinning technology is statistically significant at α=0.05 (Table 3). Moreover, cotton/Lycra core-spun yarns have the lowest unevenness and imperfections values.

3.2 Hairiness

Yarn hairiness values (H, sH, S1+2 and S3) of ring, OE-rotor, core-spun and dual-core yarns and 95% confidence interval plots are given in Fig. 1.

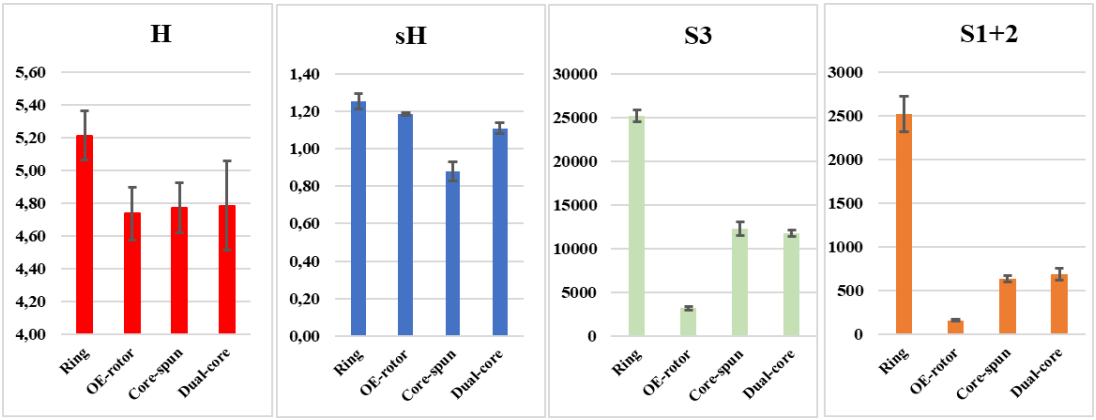


Fig. 1*: Hairiness values and confidence interval plots of yarns*

Statistical analyses for the effects of spinning technology on yarn hairiness values (H, sH, S3 and S1+2) showed that spinning technology is statistically important. It was seen that ring yarns have the highest values for all hairiness parameters. Furthermore, pairwise comparisons show that there is no statistically significant difference between hairiness values (H and S3) of core-spun and dual-core yarns (Table 4).

Table 4: *Pairwise comparison of hairiness*

Yarn Property	Spinning Technology	Mean Difference |I-J|	Standard Error	Sig.
H	Ring/OE-rotor	0.476	0.097	0.000*
	Ring/Core spun	0.440	0.097	0.000*
	Ring/Dual-core	0.428	0.097	0.000*
	OE-rotor/Core-spun	0.036	0.097	0.715
	OE-rotor/Dual-core	0.048	0.097	0.627
	Core-Spun/Dual-core	0.012	0.097	0.903
S3	Ring/OE-rotor	2358.200	55.981	0.000*
	Ring/Core spun	1887.600	55.981	0.000*
	Ring/Dual-core	1829.200	55.981	0.000*
	OE-rotor/Core-spun	470.600	55.981	0.000*
	OE-rotor/Dual-core	529.000	55.981	0.000*
	Core-Spun/Dual-core	58.400	55.981	0.312

* Statistically significant at α=0.05.

3.3 Frictional Properties

In order to examine frictional properties of yarns, yarn-to-yarn, yarn-to-metal and yarn-to-ceramic friction coefficients were measured by CTT. Friction coefficients and confidence interval plots for ring, OE-rotor, core and dual-core yarns are given in Fig. 2.

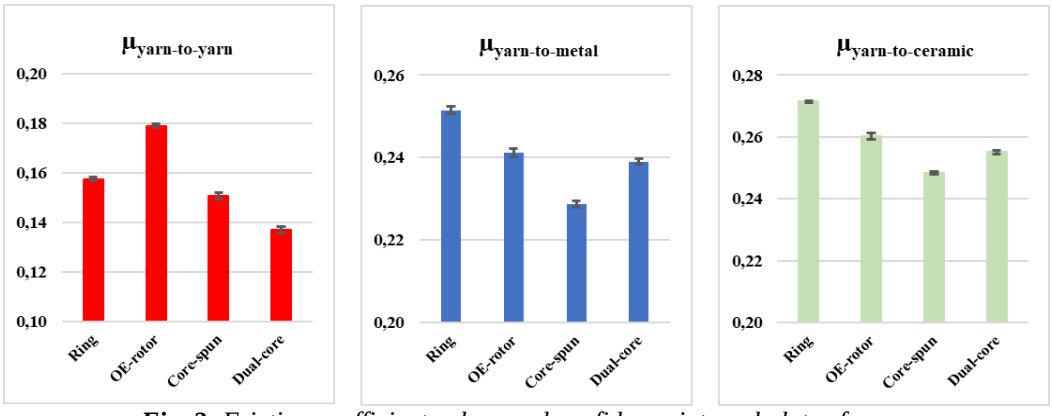


Fig. 2*: Friction coefficient values and confidence interval plots of yarns*

Yarn-to-metal and yarn-to-ceramic friction properties were calculated with Equation 1 (Capstan formula) and yarn-to-yarn friction properties were calculated with using Equation 2,

$$\mu = \frac{\ln(T_2 / T_1)}{4\pi(n-0.5)\sin\beta/2} \quad \textbf{(1)}$$

$$\mu = \frac{\ln(T_2 / T_1)}{\theta} \quad \textbf{(2)}$$

where, T_2 is output tension, T_1 is input tension, β is 35º (lower apex angle between two yarns), n is the number of wraps (n=3) and θ is the cumulative wrap angle (radian).

When a general evaluation is made, the effect of spinning technology on yarn frictional properties is found to be statistically significant. Comparing yarn frictional properties of ring, OE-rotor, core and dual-core yarns showed that friction coefficient values of core and dual-core yarns are the lowest for all surfaces (yarn, metal and ceramic) (Figure 2). Besides, it was observed that ring yarns have the highest yarn-to-metal and yarn-to-ceramic friction coefficient, OE-rotor yarns have the highest yarn-to-yarn friction coefficient. This situation in yarn-to-material (metal and ceramic) friction can be explained by higher hairiness of ring yarns. Furthermore, wrapped structure of OE-rotor yarns may be the reason of higher yarn-to-yarn friction coefficient.

3.4 Mechanical Properties

In order to compare mechanical properties of yarns, breaking load (cN) and breaking elongation (%) were measured.

Mean values of breaking load and breaking elongation are given in Table 5. ANOVA results showed that spinning technology is important either breaking load or breaking elongation (Table 6).

Table 5: *Breaking load and breaking elongation values of yarns*

Spinning Technology	Breaking load (cN)	Breaking elongation (%)
Ring	362.54	8.05
OE-rotor	259.08	7.92
Core-spun	349.22	10.14
Dual-core	393.66	16.23

Table 6: *ANOVA results of breaking load and breaking elongation*

Parameters	Sum of Squares	Mean Square	F	Sig.
Breaking load	50077.197	16692.399	166.763	0.000*
Breaking elongation	227.876	75.959	963.217	0.000*

* Statistically significant at α=0.05.

As the breaking strength and breaking elongation values are examined, it is observed that the yarn produced in OE-rotor technology has the lowest values whereas dual-core yarns have the highest (Table 5).

4. CONCLUSIONS

In this study, physical and mechanical properties of ring, OE-rotor, core-spun and dual-core yarns were examined. In experimental part of the study, unevenness and imperfections, hairiness, frictional properties and tensile properties of the yarns were measured. Based on statistical analyses, it was seen that the effect of spinning technology is important for physical and mechanical properties of all yarn types. The unevenness and imperfection values of core-spun and dual-core yarns have the lowest values. For hairiness values, core-spun and dual-core yarns have lower values than conventional ring yarns. Moreover, it was observed that there are no statistically significant

differences between H, S3 and S1+2 values for core-spun and dual-core yarns. When frictional properties of yarns were analysed, it was concluded that core-spun and dual-core yarns have the lowest friction coefficients for all surfaces (yarn, metal and ceramic). On the other hand, OE-rotor yarns have the highest yarn-to-yarn friction coefficient. Comparing breaking strength and breaking elongation values of yarns showed that OE-rotor yarns have the lowest values and dual-core yarns have the highest values.

REFERENCES

[1] M. B. Qadir, T. Hussain, M. Malik, F. Ahmad and S. H. Jeong, *"Effect of elastane linear density and draft ratio on the physical and mechanical properties of core-spun cotton yarns"*, Journal of the Textile Institute, vol. 105, no. 7, pp. 753-759, 2014.

[2] F. Marsal, D. Palet , M. Riera , A. Serra, L. Indrie and M. Ratiu, *" New development in the core yarns manufacture",* Annals of the University of Oradea. Fascicle of Textiles, Leatherwork, vol. XI, no. 2, pp. 86-89, 2010.

[3] D. Duran and H. Kadoğlu, *"Electromagnetic shielding characterization of conductive woven fabrics produced with silver-containing yarns",* Textile Research Journal, vol. 85 (10), pp. 1009-1021, 2015.

[4] R. Perumalraj and B. S. Dasaradan, *"Electromagnetic shielding effectiveness of copper core yarn knitted fabrics",* Indian Journal of Fibre & Textile Research, vol. 34, pp. 149-154, 2009.

[5] A. Telli, Y. Daşan, O. Babaarslan and S. Karaduman, *"Usage of Core and Dual-Core Yarns Containing Tungsten for Electromagnetic Shielding",* Advance Research in Textile Engineering, vol. 2(1), pp. 1013-1019.

[6] O.G. Ertaş, B. Z. Ünal and N. Çelik, *"Analyzing the effect of the elastane-containing dual-core weft yarn density on the denim fabric performance properties* Journal of the Textile Institute, vol. 107, no. 1, pp. 116-126, 2016.

[7] A. Chakraborty and S. M. Chatterjee, *"Influence on controlled pretension on hairiness of silk-nylon core-spun yarns",* Indian Journal of Fibre & Textile Research, vol. 19, pp. 12-16, 1994.

[8] N Tarafder and S. M. Chatterjee, *"Physical and mechanical properties of cotton covered nylon core yarns",* Indian Journal of Fibre & Textile Research, vol. 15, pp. 113-119, 1990.

[9] A.A. Jeddi, M. S. Johari and A.A. Merati, *"Study of the structural and physical properties of cotton-covered nylon filament core-spun yarns",* Journal of the Textile Institute, vol. 88, no. 1, pp. 12-20, 2014.

[10] O. Babaarslan, *"Method of producing a polyester/viscose core-spun yarn containing spandex using a modified ring spinning frame ",* Textile Research Journal, vol. 1 (4), pp. 367-371, 2001.

[11] V. Viswarajasekaran and K. Raghunatan, *"An investigation on the physical properties of core yarns",* Indian Journal of Fibre & Textile Research, vol. 31, pp. 298-301, 2006.

[12] C. I. Su, M. C. Maa and H. Y. Yang, *"Structure and performance of elastic core-spun yarn",* Textile Research Journal, vol. 74 (7), pp. 607-6010, 2004.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

AUTOMATIC CHARACTERIZATION OF NEEDLEPUNCHED FELTS BY CONTENT BASED IMAGE RETRIEVAL - CBIR

BELINO Nuno, NUNES Mário[2], FIADEIRO Paulo[3], ALEXANDRE Luis[4]

[1] University of Beira Interior, Textile Science and Technology Department, Rua Marquês D´Àvila e Bolama, 6200-001 - Covilhã – Portugal, belino@ubi.pt

[2] University of Beira Interior, Textile Science and Technology Department, Rua Marquês D´Àvila e Bolama, 6200-001 - Covilhã – Portugal, mnunes@ubi.pt

[3] University of Beira Interior, Physics Department, Rua Marquês D´Àvila e Bolama, 6200-001 - Covilhã – Portugal, fiadeiro@ubi.pt

[3] University of Beira Interior, Computer Science Department, Rua Marquês D´Àvila e Bolama, 6200-001 - Covilhã – Portugal, lfbaa@ubi.pt

Corresponding author: Belino, Nuno, belino@ubi.pt

Abstract: *The needled felts whose fibrous bats had been gotten by the classic carding process give us fabrics in which staple fibres follow a marked preferential direction of the machine workflow. This direction is named, as machine direction, main direction or MD and the perpendicular direction is known as cross direction or CD. In consequence of this fibre deposition, the mechanical properties of these products are different when submitted to longitudinal or transversal loads, with a much higher strength in the CD direction and a greater elongation in the MD direction. However, some technical applications of the nonwoven industry, such as filters, geotextiles, and some felts for the automotive industry demands equal mechanical properties along all their directions, particularly, an even MD:CD ratio. In order to introduce additional control in the production system and to achieve a final fabric with the desired behaviour, we envisioned an an automatic system for the pre-needling web drafting control. The management of the pre-needled felts drafting operation was made by an automatic inspection system based upon textural descriptors and content-based image retrieval, which assured optimal drafting conditions to attain a quasi-isotropic fiber distribution and an even MD:CD ratio. Our findings have shown that the comparison between collected images and reference images of the same product stored in the database - for the same feature vector and metric distance – is an excellent tool for the remote and continuous supervising of needlepunched felts quality.*

Key words: *Nonwovens, Needlepunched, Texture Analysis, Content Based Image Retrieval, Isotropy, MD:CD Ratio,*

1. INTRODUCTION

The fibre geometrical arrangement in a needled felt is primarily defined by the basic fibre web structure proceeding from the bat forming system. This special fibre arrangement should be understood as a three-dimensional system; however, this kind of analysis is very complex, and for the time being impossible. To create the opportunity of studying those materials, we will admit our felt structure with a neglectable thickness allowing a three-dimensional system to become a two-

dimensional planar structure. The needled felts whose fibrous bats had been gotten by the classic carding process give us fabrics in which staple fibres follow a marked preferential direction of the machine workflow [1,2]. This direction is named, as machine direction, main direction or MD. The perpendicular direction is designed as cross direction or CD. In consequence of this fibre deposition, the mechanical properties of these products are different when we applied longitudinal or transversal loads, with a much higher strength in the CD direction and a greater elongation in the MD direction.

Some technical applications of the nonwoven industry, such as filters, geotextiles, and some felts for the automotive industry requires equal mechanical properties along all their directions, particularly, an even MD:CD ratio. This need, compels us to introduce some modification in the production system to achieve a final fabric with the desired behaviour [3,4].

2. IMAGE AND TEXTURE ANALYSIS

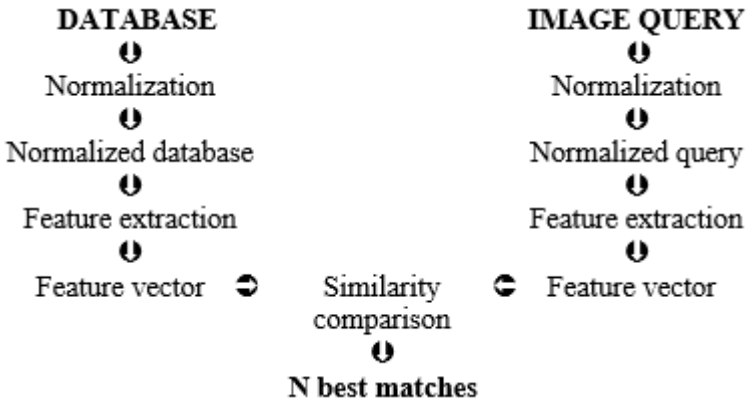
Image analysis deals with images and can be summarized as a set of techniques that convert object images in numbers and prepares this data to be processed by computer methods [5]. Texture analysis, is an essential concept of image analysis that deals with primitives or elements called texels, and this mean a contiguous set of pixels with some regional property or pattern. A texture feature is a numerical value, extracted from an object image, that gives us some information about the variation of grey levels distribution and variation on an image. Normally, texture feature is independent from his location, orientation, size and glow of the analysed object, as referred by Castelman K.N. (1996). From a statistical point of view, image textures are complicated pictorial patterns that can be defined by statistical models, in way to characterize these same patterns. According to Haralick et all [6], we have several approaches to measure and characterize image texture, that can be summarized in eight main techniques:

① - Autocorrelation function;
② - Optical transforms;
③ - Numerical transforms;
④ - Edge and contour detection;
⑤ - Structural analysis;
⑥ - Spatial grey level dependence method – Co-Occurrence matrixes method
⑦ - Run length method of grey levels;
⑧ - Autoregressive models.

According to the consulted bibliography, we found a prevalence of texture discrimination by the co-occurrence matrixes method in multiple researches works abroad many different fields. This technique gives us a high dimensional texture description and can be used for directly measure statistical distances between different textures. For this reason, we based our feature extraction on this methodology. This method places to evidence the space relations between the grey levels. Thus, as the grey levels are a function of the mass per unit area, we can accede to a characterization of the web structure. The probability of spatial grey level co-occurrence is a second order density probability, which can be defined by a matrix of relative frequencies *f(i,j)* with which two neighbouring pixels separated by a distance d on θ direction, occur on the image, one with grey level *i*, and the grey level *j*. Hence, for an image with N_G grey levels, the probability density functions can be written under the form of four squared matrices N_G X N_G for the 0º,45º,90º e 135º directions. Haralick, Shanmugan and Dienstein proposed 14 measures of textural features derived from the co-occurrence matrices, each one representing certain image properties. The textural descriptors selected and used in this research work were: First order entropy; Second order entropy; Energy or angular second moment; Homogeneity or inverse difference moment; Contrast and Correlation.

3. CONTENT BASED IMAGE RETRIEVAL

Content based image retrieval (CBIR) is a set of techniques which use visual content (pictorial content) to search images from an image database according to user interest [7]. In this work, instead of the exact matching, our system calculates the visual similarities between the query image and pattern images on a database. For this purpose, we used the Euclidian distance method, so as to get the distance between query image *i* and image *j* on the database, because each individual dimension is independent and have equal importance [8]. This metric is also widely spread and commonly used in image retrieval [9,10]. The image database consists of 4080 (256x256 sized 8 bit long) grey level images from standard pre-needled nonwoven and integrating, for each one of them, a feature vector with the textural descriptors based on first and second order statistics, and also their mechanical properties. For all and each acquired image on the experimental development, a feature vector is determined, and similarity comparison is made in accordance with the following schematic representation:



With this process, on a near future, we will be able to elaborate detailed quality reports for each felted roll produced, with the spatial localization, length and severity of the defects in accordance to a defined scale.

4. EXPERIMENTAL DEVELOPMENT

The experimental setup developed in this research work was comprised by the following elements:

1 – A Cosmatex nonwoven laboratorial line composed by a feeding/opener loader, card, cross-lapper and pre-needling/needling apparatus.

2 – An image analysis system composed by a Frame grabber DT3155 from Data Translation inc; 2 CCD_s Cohu model 2652-2000; Lenz system from Cosmicar – pentax; Monochromatic video monitor model TM923B from JVC, 1 PC for the drafting operation control and 1 PC for image acquisition and processing.

3 – A specifically devised pre-needled drafting prototype, conceived with 4 drafting zones between 5 drafting sets of cylinders and equipped with two CCD_s, one at the beginning of the process and another one at the end.

Ten experimental dynamometric tests for both axes (longitudinal and transverse directions), where made according to the following flow:

1 – Image acquisition of the dynamometric tests for both axes;
2 – Image pre-processing;
3 – Feature extraction;
4 – Similarity comparison;
5 – Data collecting and conclusions;

5. RESULTS

The obtained results are condensed in the following table and graphical representations.

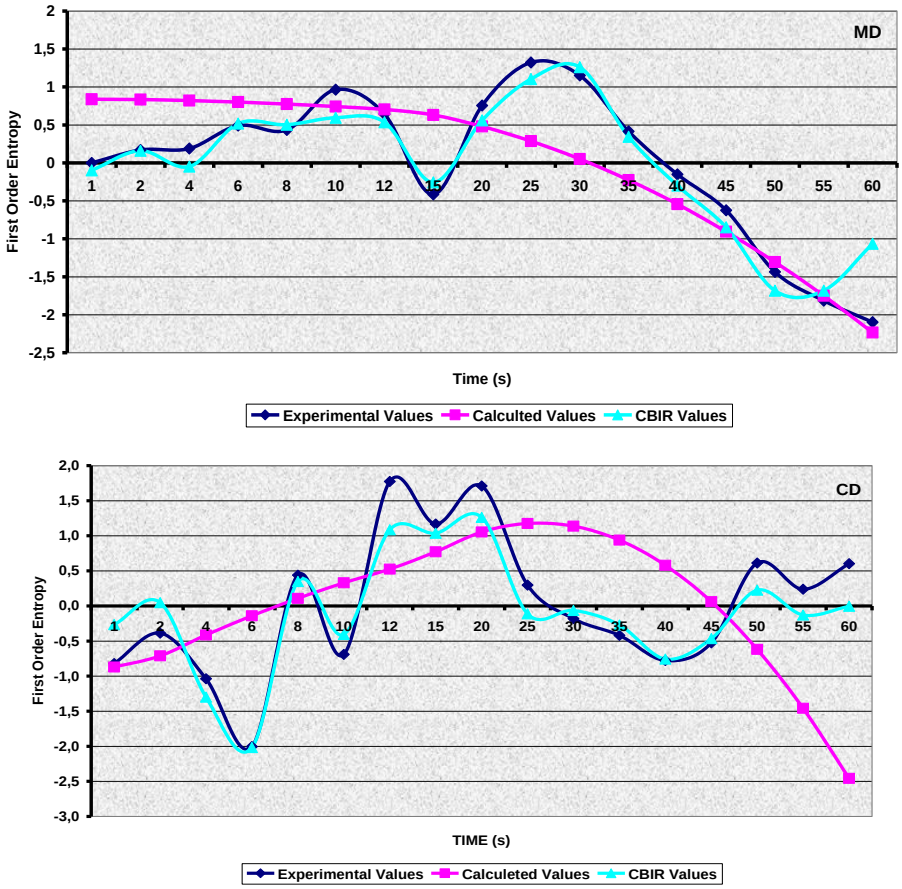


Fig1: *Graphical representation of first order entropy with all the studied models and for both axes.*

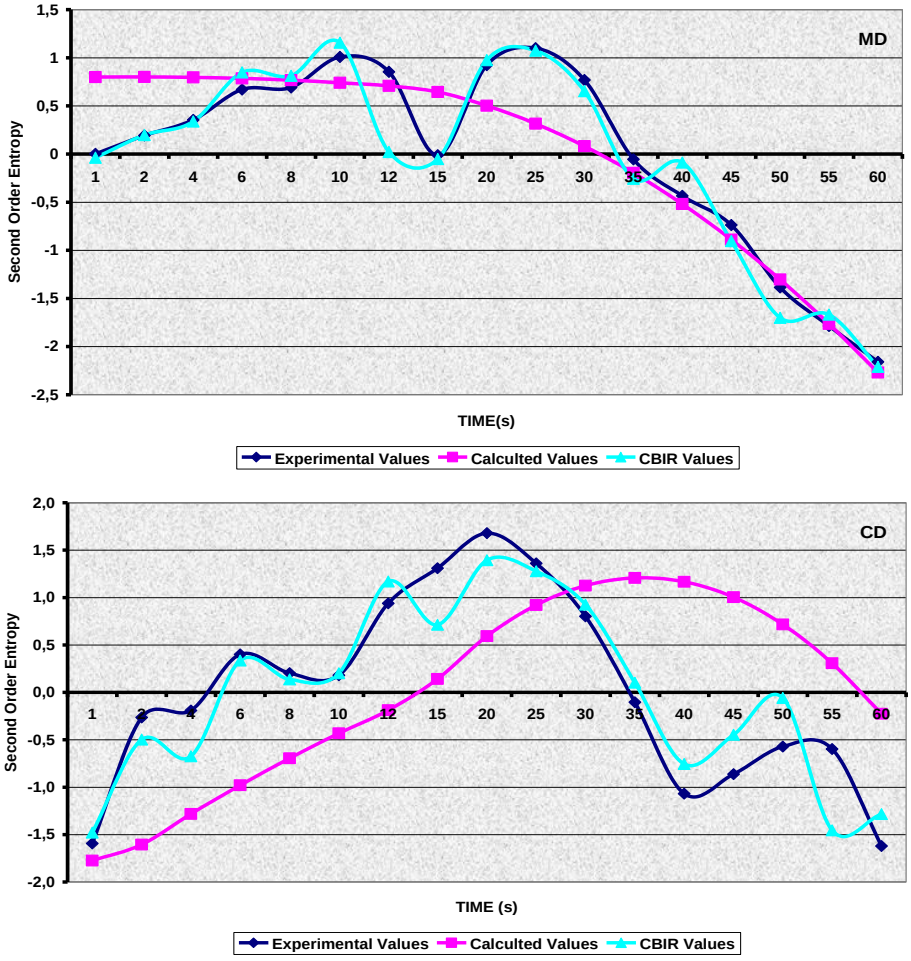


***Fig2**: Graphical representation of the average second order entropy with all the studied models and for both axes.*

***Table 1** – Correlation coefficients for all the studied models and or both axes.*

CORRELATION	EXPERIMENTAL VALUES X CALCULATED VALUES		EXPERIMENTAL VALUES X C.B.I.R. VALUES		C.B.I.R. VALUES X CALCULATED VALUES	
DIRECTION	**MD**	**CD**	**MD**	**CD**	**MD**	**CD**
Average First Order Entropy	0,8138	0,1385	0,9835	0,9431	0,7413	0,2104
Average Second Order Entropy	0,9037	0,2238	0,8828	0,9274	0,9684	0,3549
Average Energy	0,9244	0,4937	0,9656	0,9273	0,9278	0,6334
Average Contrast	0,5693	0,7436	0,9379	0,8789	0,4683	0,5427
Average Correlation	0,8908	0,9543	0,9387	0,8268	0,7806	0,8666
Average Homogeneity	0,8983	0,7642	0,9372	0,9664	0,9281	0,7610
Mechanical Strength	0,9997	0,9998	0,9855	0,9490	0,9860	0,9508

6. CONCLUSIONS

The comparison between collected images gathered with the new experimental tests and reference images of the same product in the database, for the same feature vector and metric distance, showed that, for all evaluated textural descriptor, CBIR method presents the higher correlation coefficients for both studied directions. All the textural descriptors exhibited greater proximity between experimental values and CBIR values than, comparatively, experimental values and calculated values for both studied directions. The calculated values and the experimental values are very similar. This may be due to imposed limitations of the carried out experimental set. However, CBIR method showed no significant deviations for this parameter and equal sensitivity. With this experimental framework and based on the collected information it is possible to affirm that the proposed technological solution based on CBIR methodology as great potential as a tool for quality control of the nonwoven pre-needled drafting process. It is particularly relevant the capabilities of queries formularization based on total or partial evaluated textural features associated with the main mechanical properties, which allows remote and continuous monotoring of production lines.

REFERENCES

[1] Mário F.N., "Novo Método de Controlo na Produção de Têxteis Técnicos", XX Seminário da APETT, Famalicão, 1999;

[2] Belino N.J.R., "Optimização de um sistema automático de controlo da isotropia de mantos pré-agulhados por análise de textura e recuperação de imagem baseada em conteúdo, PhD Thesis, UBI, 2006

[3] Tsai, P.P., "Theoretical and Experimental Investigation on the Relationship Between the Nonwoven Structure and the Web Properties", International Nonwovens Journal, Nº4. pp. 33-36,2002

[4] Hearle, J.W.S., Stevenson, P.J. "A Study of needled Fabrics, Part III: "The Anisotropy of Nonwoven Fabrics", Textile Research Journal, nº11, pp. 877-888, 1963

[5] Schalkoff, R., "Digital Image Processing and Computer Vision", John Wiley & Sons, Inc., 1989

[6] Haralick, R M., Shanmungam, K., Dinstein, I., "Textural Features for Image Classification", IEEE, Vol. 3, Nº. 6, pp. 610-621, 1973

[7] Baraldi, A., Parmigianni, F., "An Investigation of Textural Characteristics Associated with Grey-Level Co-occurrence Matrix Statistical Parameters", IEEE, Vol. 33, Nº. 2, pp. 195-199, 1995

[8] Moura, D. et Al., "Recuperação de Imagem Baseada em Conteúdo", Anais do IV Workshop de Tratamento de Imagem, NPDI/UFMG, pp. 101-109, 2003

[9] Aksoy, S., Textural Features for Image Database Retrieval", Msc Thesis, Seattle, Washington University, 1998

[10] Mitchel, O.R., Myers, C.R., Boyne, W., "A Maximum Measure for Image Texture Analysis", IEEE, Vol. 2, pp. 408-414, 1977.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A REVIEW ON SUN-PROTECTIVE CLOTHING

CANOGLU Suat [1], SUNTER EROGLU Nilsen[2], YUKSELOGLU S. Muge[1]

[1] Marmara University, Faculty of Technology, Department of Textile Engineering, Goztepe, Istanbul, Turkey

[2] Marmara University, Institute of Pure and Applied Science, Goztepe, Istanbul, Turkey

Corresponding author: Canoglu, Suat, E-mail: scanoglu@marmara.edu.tr

Abstract: *The sun is ultraviolet (UV) radiation source. Damage to skin cells from ultraviolet exposure can lead to the carcinogenic problem such as skin cancer. Clothes and protective agents in cosmetics could be supplied personal protection from UV radiations. The assessment of UV transmittance of clothing and the determination of the UV protection factor (UPF) is crucial for skin cancer. The pathogenesis of epithelial skin cancers causes effects in the human bodies such as squamous cell carcinoma (SCC) and basal cell carcinoma (BCC) and malignant melanoma (MM) could be prevented by suitable UV-protective clothing. UV protective clothes have some characteristic properties such as fiber type, yarn construction, fabric construction, fabric weight and thickness, coloring process, standards and presence of UV radiation absorbers. These parameters have a direct effect on the effectiveness of sun protection and consequently the risk of skin cancer. The increasing of skin cancer rates in past several decades has increased the interest sun-protective clothing. A lot of work has been done around the world on about sun-protective clothes. The aims of this review are to explain properties, standards, and applications of sun-protective clothes, change people's sun behavior and raise awareness for the use of adequate sun-protective clothing.*

Keywords: *Ultraviolet (UV), Ultraviolet Protection Factor (UPF), Sunlight, Absorber, Spectrophotometer*

1. INTRODUCTION

On Earth, the ultimate source of natural light is the Sun. The sunlight consists of infrared, visible light and ultraviolet (UV) radiation. UV radiations damage to skin cells and lead to the development of skin cancer. Sun-protective clothes could be supplied protection against the hazards of UV radiations. Various clothes parameters have an influence on the UPF (Ultraviolet Protection Factor) for being effective broadband protection against the sun. The measurement, properties and standards of UV radiation and UPF affects of clothing are important for the development and application of protective clothing. More detail (UV radiation and its health risks, sun-protective clothes etc.) is given in below sections and subsections of this paper.

2. UV RADIATION

UV radiation on with the wavelengths ranges from 200 to 400 nm, the span of wavelengths shorter than those of visible light but longer than x-rays (400-700 nm). UV radiation has three classifications for wavelengths: UVA (320 – 400 nm), UVB (280 – 320 nm), and UVC (200 – 280 nm) [1].

UVC has been blocked from reaching the Earth's surface by the stratospheric ozone layer. It could extinguish the harmful micro-organisms such as bacteria and viruses by destroying the genetic information in the DNA and use in germicidal lamps. The micro-organisms lose their reproductive capability and are destroyed. Wavelengths of the UVB radiation region are absorbed into the skin, it leads to health problems such as erythema, burns, persistent pigment darkening and so finally skin cancer. UVA has caused carcinogenic problems, speedly aging and wrinkling of the skin because including longer wavelengths than UVB and penetrating more deeply into the skin. UV radiation spectrum and its effects could be seen in Figure 1 [2-3].

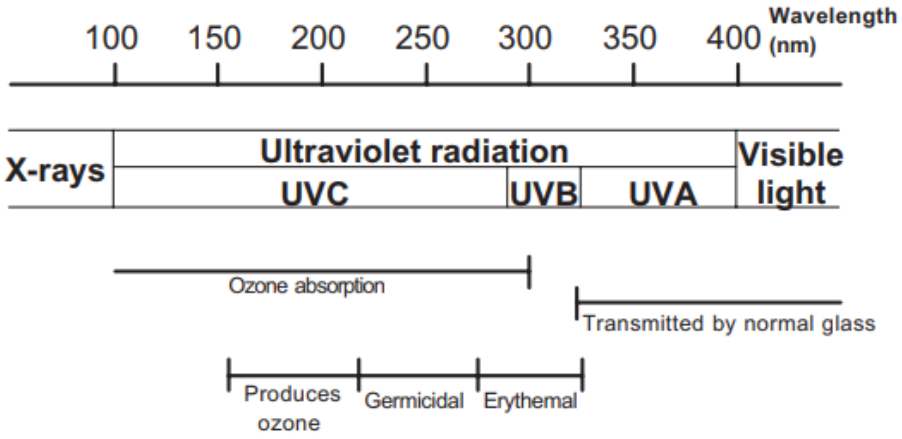


Fig. 1: *UV radiation spectrum and the chemical, physical and biological effects [2]*

3. HEALTHY RISKS OF UV RADIATION

Skin is the structure that will be most affected by cancer in the human body. Direct or indirect UV irradiation causes affect the pathogenesis of epithelial skin cancers such as squamous cell carcinoma (SCC) and basal cell carcinoma (BCC) and malignant melanoma (MM) [2]. Acute UV irradiation leads to DNA lesions such as pyrimidine dimers and (6-4) photoproducts. If they are not repaired, it could be caused to DNA mutations. This mutation must be prevented with DNA repair mechanisms [3].

UV protection against skin cancer has versatile tratments. Researchers have investigated about cell carcinoma on the groups which are beta carotene supplementation, another group sunscreen plus placebo tablets, beta carotene only or placebo only. None of the treatments caused to fall the incidence of BCC, but the incidence of SCC was dramatically lower in the sunscreen group than in the no-sunscreen group [3]. Especially, on white populations, the rising incidence rates of SCC and BCC are composed of increased sun exposure or exposure to ultraviolet (UV) light, increased outdoor activities, changes in clothing style, increased longevity, and ozone depletion [4].
MM is the most dangerous form of skin cancer because it may be developed when unrepaired DNA damage to skin cells. MM is caused by ultraviolet radiation from sunshine and triggered genetic defects. Malignant tumors derive from the pigment-producing melanocytes in the basal layer of the epidermis [5]. MM have different risk factors such as skin color, tendency to freckle, family history of melanoma, the presence of many naevi, increasing age and exposure to UV light [4]. Additionally, especially in childhood, the number of melanocytic nevi is associated with an increased risk of malignant melanoma [3].

Fig. 2: *Most Common Types of Skin Cancer [6]*

4. SUN-PROTECTIVE CLOTHES

Clothes and protective agents in cosmetics could be supplied personal protection from UV radiations. Fabrics provide protection against UV radiation, but it isn't enough to sufficient UV protection. Sunlight protective fabrics are evaluated by UV protection factor (UPF), which could be range from 15 to 24 for good protection, 25 to 39 for very good protection and 40 to 50 or more for excellent protection [7]. UPF factor can be measured with the spectrophotometer using an in vitro method. It collects both transmitted and scattered radiation with the aid of an integrating sphere positioned behind the textile sample [8] UV protective clothes must have some parameters such as UPF, fiber type, yarn construction, fabric construction, fabric weight and thickness, finishing process, coloration process, and presence of UV radiation absorbers [9]. Their protection effects represent with detail in Table 1.

Table 1: *Characteristics of Sun-Protective Clothes [10]*

Characteristic	**Good Protection**	**Poor Protection**
Fabric Construction	Tightly woven/knitted	Loosely woven/knitted
Fabric Weight	Heavy	Light
Type of Fiber	Wool, polyester	Cotton, silk, polyamide, polyacryl
Textile Color	Dark, bold	White, light, pastels
Moisture	Dry	Wet
Fit	Loose	Tight

4.1. Fiber and Yarn Parameters

It is affected of the base fibre material on the UV absorption causing the fluctuations up and down in the UV transmittance, but the UV reflectance trend is the same [11]. Polyester or polyester blends may be the most suitable fabric type for UV protection clothes because they provide relatively low UVB transmission probably due to a large conjugated system in the polymer chains. Bleached cotton and viscose rayon are transparent to UV so they can grant low portection to UV radiation [12].

Fine fibres in fabrics have both the high UV protection and good tactile comfort. The yarns with the fine fibre diameter, the large yarn linear density, low twist and large refractive index could supply the high UV protection [11].

4.2. Fabric Parameters

For fabric construction, both yarn-to-yarn spaces in the fabrics are smaller and less fabric's porosity results less UV radiation which is transmitted. For suitable fabric in UV protection must have fiber content and fabric construction, an increase in weight per unit area is associated with a decrease in fabric porosity and the spaces between the yarns could be smaller in a heavier textile, therefore less UV radiation is transmitted. Additionally, denser fabrics transmit less UV radiation and so fabric thickness is most useful in explaining differences in UV transmission [12]. Similarity, for the weight of the fabric, varies from 80 to 300 g/m^2, and this greatly affects the UPF [13].

The value of porosity in a good quality fabric is below 10% while that in a bad quality fabric may be above 30% [13]. The ideal fabric determined that the yarns which are completely opaque to ultraviolet radiation and the pores between the yarns are very small. Porosity of the ideal fabric as showen in equation 1 [14].

$$UPF = \frac{100}{Porosity\%} \quad (1)$$

4.3. Coloring Parameters

Generally, dark colors provide better UV protection due to increased UV absorption. UV absorbers are colorless compounds that absorb in the wavelength range 280-400 nm. Titan dioxide is frequently used as a UV blocking substance in fabrics. The absorptive and scattering properties of titan dioxide particles in the UVA wavelength range are different and depend mainly on the particle size and geometry [11]. UV-blocking treatment for cotton fabrics is used with the sol-gel method. A thin layer of titanium dioxide is formed on the surface of the treated cotton fabric, so it provides excellent UV-protection and this effect can be maintained after 50 washing [15]. The proportion of UVA wavelengths could be absorbed by the dye decreasing transmittance over part of the spectrum and increasing protection. Color depth affects both the absorption and the reflectivity of UV photons by the fabric with dye molecules and it has an important role [16].

4.4. Standardization of Sun-Protective Clothes

For determining UV protection in European Standards, European, draft standard prEN 13758-1, İt is used a spectrophotometric method with an integrating sphere. The method is used for clothing fabrics which are worn in close proximity to the skin but not on the skin. According to the method, UPF on clothing must be larger than 30 for being UV-protective. For determining UV protection in United Kingdom Standards, referred to as BS 7914 "Method of Test for Penetration of Erythemally Weighted Solar Ultraviolet Radiation Through Clothing Fabrics", it is used of a photospectrometer equipped with an integrating sphere. The first requirement of standard is the design of the clothing. Another requirement is a maximum UV penetration of 2.5%. This method is suitable for UV-protective apparel of children older than 6 months [17]. American Standarts have three categories for the testing and labeling of UV-protective textile products such as ASTM D 6544 "Standard Practice for the Preparation of Textiles Prior to UV Transmission Testing", AATCC 183 "Test Method for Transmittance or Blocking of Erythemally Weighted Ultraviolet Radiation Through Fabrics", and ASTM 6603 "Standard Guide to Labeling

of UV-protective Textiles" [18].

5. CONCLUSION

The sunlight consists of infrared, visible light and ultraviolet (UV) radiation. UV radiation has some carcinogenic properties on human skin. The use of sun-protective clothes can provide excellent protection against the hazards of sunlight. Sun-protective clothes play a significant role in the prevention of skin cancer. They depend on a number of parameters, including fibre material, yarn and fabric construction, type, weight, thickness, coloring processes, standardizations, and UV-absorbing substances additives. This paper could be useful to understanding parameters and raise awareness for the use of adequate sun-protective clothing.

REFERENCES

[1] Md Khan. Ershad, "*Application of textile technology for the prevention of uvr-induced skin cancer"*, Annals of the University of Oradea Fascicle of Textiles- Leatherwork Volume I, No. 2, pp.68-73,2010.

[2] Y. Matsumura and H. N. Ananthaswamy, "*Toxic effects of ultraviolet radiation on the skin"*, Toxicology and Applied Pharmacology 195, pp. 298 – 308,2004.

[3] R. Dummer and T. Maier," *UV Protection and Skin Cancer",* Recent Results in Cancer Research, Ed. R. Dummer F. O. Nestle G. Burg, Vol. 160, pp. 7-12, 2002.

[4] T.L. Dıepgen and V. Mahler, *"The epidemiology of skin cancer"*, British Journal of Dermatology, 146 (Suppl. 61): 1–6, 2002.

[5] Skin Cancer Foundation, (1.04.2018) [Online]. Available: https://www.skincancer.org/skin-cancer-information/melanoma

[6] Skin Cancer Foundation, (1.04.2018) [Online]. Available: https://www.skincancer.org/skin-cancer-information

[7] S. Hema, M. R. Neelam and S.J.S. Saroj, *"Combating Healthing Risks of Excessive UV Exposure Through Changes in Clothing Behavioral Practices"*, Indian Journal of Health and Wellbeing, 4(2), pp. 323-326, 2013.

[8] T. Gambichler, P. Altmeyer, and K. Hoffmann,*" Comparison of Methods: Determination of UV Protection of Clothing",* Recent Results in Cancer Research, Ed. R. Dummer F. O. Nestle G. Burg, Vol. 160, pp. 55-61, 2002.

[9] K. Senem and O. Gulay, *"An Investigation of UV Protection of Swimwear Fabrics"*, Textile Research Journal Vol 80(17), pp. 1811–1818, October 11, 2010.

[10] O. Uli and R. Hauke, "*Improving UV Protection by Clothing Recent Developments"*, Recent Results in Cancer Research, Ed. R. Dummer F. O. Nestle G. Burg, Vol. 160, pp. 62-69,2002.

[11] Y. Yao, H. Christopher, R.M. Keith, S. Lu and W, Xunga, "*Research on the İnfluence of Yarn Parameters on the Ultraviolet Protection of Yarns"*, The Journal of The Textile Institute, 1754-2340, 2016.

[12] G. Thilo, A. Peter and H. Klaus,*" Role of Clothes in Sun Protection",* Recent Results in Cancer Research, Ed. R. Dummer F. O. Nestle G. Burg, Vol. 160, pp. 15-25,2002.

[13] C. Jean-Pierre, *"Activities of CIE DIV-6 (Photobiology and Photochemistry) in UV Protection and Clothing*", Recent Results in Cancer Research, Ed. R. Dummer F. O. Nestle G. Burg, Vol. 160, pp. 48-61, 2002.

[14] B.R. Das,*" UV Radiation Protective Clothing"*, The Open Textile Journal, 2010 3, 14-21,2010.

[15] Y. W. H. Wong, C. W. M. Yuen, M. Y. S. Leung, S. K. A. Ku, and H. L. I. Lam, "*Selected Applications of Nanotechnology in Textiles"*, AUTEX Research Journal, Vol. No.-6(1), page 1-8, ISSN: 1470-9589,2006.

[16] C.A. Wilson, P.H. Gies, B.E. Niven, A. Mclenan and N.K. Bevin, "*The relationship between UV transmittance and colour visual description and instrumental measurement"*, Textile Research Journal, Vol. No.-78(2), page 128-13, ISSN: 0040-5175, 2008.

[17] J. Laperre and F. Foubert, *"European Standards for Protective Apparel Against UV Radiation"*, Recent Results in Cancer Research, Ed. R. Dummer F. O. Nestle G. Burg, Vol. 160, pp. 35-41,2002.

[18] K. 1. Hatch,*" American Standards for UV-Protective Textiles",* Recent Results in Cancer Research, Ed. R. Dummer F. O. Nestle G. Burg, Vol. 160, pp. 42-47, 2002.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EFFECT OF BRASI-COLOR DYE ON UV PROTECTION OF BAMBOO KNITTED FABRICS

CHIRILA Laura[1], MITRAN Elena-Cornelia[1], DUMITRESCU Iuliana[1], PERDUM Elena[1], IORDACHE Ovidiu George[1], STEFANESCU Dana[2], PISLARU Mariana[2], MANCASI Iulian[3]

[1]The National Research Development Institute for Textiles and Leather, Bucharest, Romania, Str. Lucretiu Patrascanu nr. 16, sector 3, 30508, Bucharest, Romania, E-Mail: iuliana.dumitrescu@certex.ro

[2]SC Tanex SRL, Str. Bucuresti - Magurele, nr. 47B, 051432, Bucharest, Romania, E-Mail: dana.stefanescu@tanex.ro

[3]SC Majutex SRL, Bîrnova, Jud. Iaşi, 707035, Romania, E-mail:office@majutex.ro

Corresponding author: Mitran Cornelia, E-mail: mitran.cornelia@certex.ro

Abstract: *Even natural dyes have several limitations such as high sensitivity to washing, light, pH, and low color strength and seasonal variation, their use is largely encouraged due to their renewability and multi-functional properties. In this study, 100% bamboo knitted fabric was dyed with Brasi-Color, a dyestuff extracted from brazilwood. The UV-VIS spectra demonstrate the presence of brazilin at pH 4 and of brazilein at pH 7 and 10. The molecular structure of the brazilein is changed at higher pH, due to deprotonation at the OH group of C3. The dyeing parameters and their effect on the dye exhaustion were investigated to optimize the dyeing method and to evaluate the ultraviolet protection factor (UPF). The optimal value was selected based on the highest degree of exhaustion, the dyeing uniformity and the highest color intensity. The maximum degree of exhaustion was achieved for 0.05% dye concentration, pH 7, 90 minutes dyeing at 90^{0}C. Even mean UPF, UVA and UVB transmission largely depends on process dyeing parameters, all the fabrics demonstrate an excellent UV protective effect (UPF >50+) and a very low transmission on both UVA and UVB region, being able to protect the human body against the harmful effects of UV rays.*

Key words*: Natural dye, brazilwood, UPF, UV-VIS spectra, exhaustion degree*

1. INTRODUCTION

Brazilin is the red pigment obtained from the heartwood of the tree Ceasalpinia sappan Linn. [1], used to dye textiles and prepare pigments and inks. Brazilin is colorless or pale yellow due separation of the two chromophores existing on the molecule. Under the influence of oxygen and light, brazilin is converted to brazilein due to the oxidation of one hydroxyl group to a carbonyl group. In brazilein, the quinone structure is conjugated with aromatic ring, acting as a chromophore absorbing at higher wavelengths. As all the natural dyes, brazilein is very sensitive to oxygen, temperature, pH, which modifies its chromophores. Therefore, it is necessary to optimize the dyeing process to avoid or minimize the photooxidation and to stabilize the fabric color.

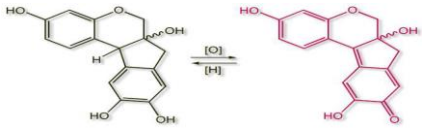


Fig. 1: *Brazilin (reduced form) and brazilein (oxidised form) [2]*

As studies [3] have demonstrated, brazilin and brazilein have anti-inflammatory, anti-bacterial, antineoplastic, antioxidant and UV protective effects [4]. The overexposure to UV rays may lead to keratosis and premature aging of the skin, cataracts and blindness, skin cancers [5]. The dyed clothes represent one of the most effective ways to protect the human body against the harmful effects of UV radiation. In this paper, a systemic approach of dyeing parameters of bamboo with dyes extracted from brazilwood was assessed to select the fabrics with high degree of UV protection.

2. MATERIALS AND METHODS

2.1. Materials

100% bamboo knitted fabric, 222g/m^2, 0.762mm thick, fabricated in INCDTP. Brasi-Color: dyestuff extracts of brazilwood, kindly provided by NIG Nahrungs - Ingenieurtechnik GmbH, Austria; Chemicals: CH_3COOH and Na_2CO_3 used for adjusting the pH.

2.2. Optimization of bamboo dyeing parameters

Optimization of dyeing parameters was performed to evaluate the appropiate conditions for the dyeing of bamboo fabric with Brasi-Color. It was considered as the optimal value, the value at which the highest degree of exhaustion was obtained and the fabric was uniformly dyed. In each optimization experiment, the values of the parameter to be optimized was varied while maintaining all other parameters constant, and the optimal value from the previous experiment was further used.

2.3. Characterization

The dyebath exhaustion was assessed by recording the absorbance of dyebath solutions before and after dyeing using UV- VIS- NIR spectrophotometer (Lambda 950, Perkin- Elmer, USA). The percentage of exhaustion was calculated with the equation (1):

$$E\% = 100 \times (A_i - A_f)/A_f \quad \textbf{(1)}$$

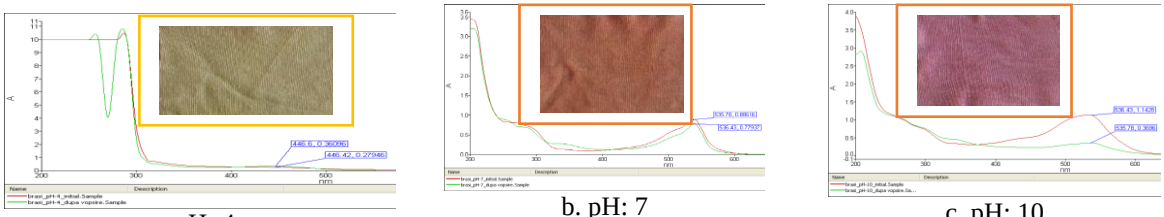
where, A_i and A_f are the concentrations of the dye bath before and after dyeing. The ultraviolet protection factor (UPF) of each dyed fabrics were measured on Carry 50 spectrophotometer (Varian, Australia) fitted with a specific accessory and dedicated software, according to AS/NZS 4399:1996 standard. Depending of UPF rating, the fabrics are classified as providing moderate (UPF 10 – 19), high (UPF 20 – 29), very high (UPF 30 – 49) and maximum (UPF > 50) protection [6].

3. EXPERIMENTAL

3.1. pH optimization

The bamboo fabrics were dyed with 0.1% Brasi Color at different pH(4, 7, 10) maintaining constant the temperature (80^{0}C), the dyeing time (60min.) and ratio M: L = 1: 60. The UV-Vis spectra were recorded on diluted solutions, dilution factor of 3:1 at pH 4 and 30:1 for pH 7 and 10. The optimal pH was considered that pH at which the highest degree of exhaustion was obtained, and the fabric has the highest color intensity and uniformity by visual evaluation.

The color, UV-VIS spectra and the degree of exhaustion are shown in the Figure 2 and Table 1.



a. pH: 4 b. pH: 7 c. pH: 10

Fig. 2: *The appearance of dyed fabrics and UV-VIS spectra of the Brasi Color dyeing baths: a. pH: 4; b. pH: 7; c. pH: 10; red line: initial dye bath, green line: dye bath after bamboo knit dyeing*

The studies [7] assigned to aqueous solution of brazilein, three major absorption bands at 446 nm (band I), 541 nm (band II) and 276 nm (band III). Band I was associated with the absorption of the cinnamoyl system, and band III with the absorption of benzoyl ring. At pH 4, the maximum absorption occurs at 446 nm (Fig. 2a), the acidic species, AH, displaying a faint yellow color. The peak at 446 nm is considered typical for the identification of brasilein [2] while the maximum absorption at 292 nm is characteristics for brazilin which, shows electronic transition shifted in blue region due to the sp3 carbon atom at C9[8]. A red shift of the maximum wavelength is recorded as the pH increases due to the changes in molecular structure of the brazilein were deprotonation at the OH group of C3 takes place [9]. At pH 7 (Fig. 2b) and 10 (Fig. 2c), the peak is shifted to 536nm (anionic form A^-), the absorption of the orange and violet solutions being largely intensified.

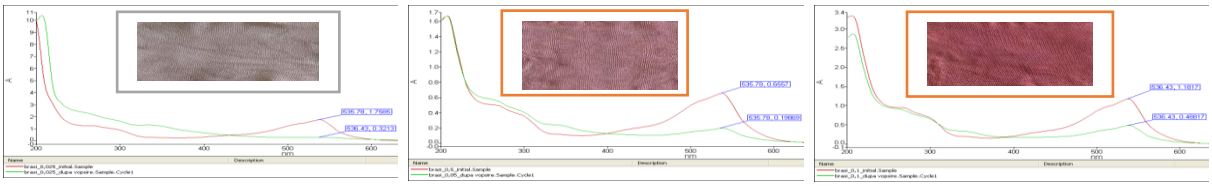
Table 1: *The exhaustion degree of 0.1% Brasi- Color solution at different pH*

pH	λ, nm	A_i	A_f	E, %	Color
4	446.5	0.28	0.36	-28.57	yellow
7	536	0.88	0.77	12.5	red-orange
10	540	1.14	0.37	67.54	move

The degree of exhaustion ((Table 1) increases with increases of the pH value of the dyeing bath from pH 4 to 10. The highest exhaustion degree is obtained at pH 10, but the uniformity and color intensity are higher at pH 7. More than that, as bamboo fabric is very sensitive at alkaline conditions, we have chosen pH 7 for the following experiments.

3.2. Optimization of the Brasi-Color concentration

The bamboo fabrics were dyed with different concentrations of Brasi Color, maintaining constant the former parameters. The UV-Vis spectra were recorded on diluted solutions, using a dilution factor of 6:1 for 0.025% Brasi-Color and 30:1 for 0.05% and 0.1% dye (Fig. 3 and Table 2).



0.025% BrasiColor 0.05% BrasiColor 0.1% BrasiColor

Fig. 3: *UV-Vis spectra of BrasiColor solutions before and after dyeing, pH 7*
Where: red: before dyeing; green: after dyeing

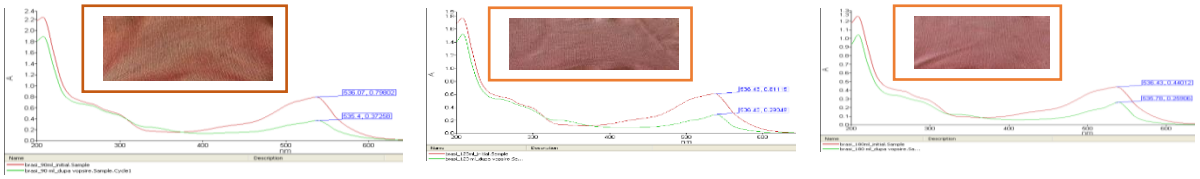
Table 2: *The exhaustion degree of Brasi Color dyebaths at different concentrations*

λ, nm	Dye concentration, %	A_i	A_f	E, %	Color
536	0.025	1.76	0.32	81.82	lavender
536	0.05	0.66	0.19	71.21	move
536	0.1	1.18	0.49	58.47	ruby

Increasing the dye concentration causes color intensification. The highest exhaustion degree is obtained at 0.025% dye concentration but the dyeing is relatively uneven and the color intensity is reduced. Therefore, 0.05% was chosen as the optimal dye concentration.

3.3. Optimization ratio textile material:dye solution

The bamboo fabrics were dyed at different ratio M:L maintaining constant the former parametrs. The effect of ratio material: dye solution on color intensity and degree of exhaustion of Brasi-Color of bamboo fabric is displayed in the Figure 4 and Table 3. The UV-VIS spectra were recorded on the initial and final dye solution with a dilution factor = 30:1.



a. **1:30** b. **1:40** c. **1:60**

Fig. 4: *UV-VIS spectra of dyeing baths: a. 1:30; b. 1:40; c. 1:60*

Table 3: *The exhaustion degree of Brasi-Color baths at different M:L ratio*

λ, nm	M:L	A_i	A_f	E, %
536	1:30	0.79	0.37	53.16
536	1:40	0.61	0.29	52.46
536	1:60	0.44	0.26	40.91

A wide variation shades is noticed at different M:L ratios determinated by the susceptibility to photo-oxidation and the inhomogeneity of the dye composition, which may consist of multiple components with different solubilities highly depending on solvent polarity, degree of polymerization of phenolics, interaction with other constituents and formation of insoluble complexes [10]. As the results show the highest degree of exhaustion was obtained at a ratio of 1:30 but the shade is very non-uniform. Consequently, a M:L of 1:40 was chosen for the next trial.

3.4. Optimization of dyeing time

The bamboo fabrics were dyed at for different durations under former constant dyeing parameters. The diluted solutions (DF = 30:1) of dye baths were recorded initially and after 45, 60 and 90 minutes of dyeing (Figure 5 and Table 4).

Table 4: *The exhausting degree of Brasicolor dyebaths at different dyeing time*

λ, nm	Time, min.	Ai	Af	E, %
536	45	0.49	0.38	22.45
536	60	0.49	0.33	32.65
536	90	0.49	0.28	**42.85**

As the dyeing time increases, the dye diffuses inside the fabrics until the dyeing equilibrium state is reached. As the results show, the maximum degree of exhaustion is attained after dyeing for 90minutes. Resuming, the optimum parameters to dye the cotton fabric are: pH 7, dyeing temperature: 80^0C, the BrasiColor concentration: 0.05% reported to the weight of fabric, fabric: dye solution = 1:40.

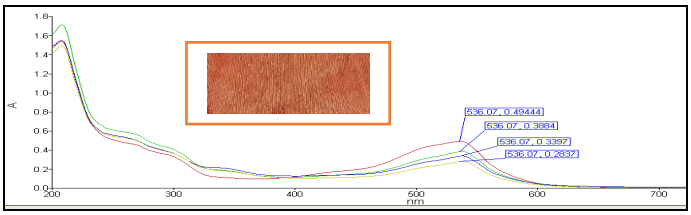


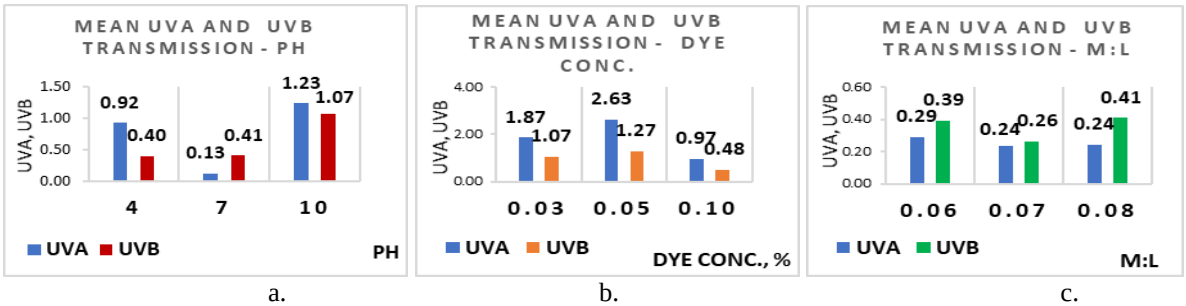
Fig. 5: *UV-VIS spectra of initial (red line) dye solutions and after 45 minutes (green line), 60 minutes (blue line), 90 minutes (yellow line)*

3.5. Ultraviolet protection factor (UPF) of dyed samples

UV protection provided by textile materials depends on various factors such as yarns type, fabric construction, porosity, density, moisture, type and concentration of applied dye. The results for each of the fabrics dyed in different conditions are displayed in the Table 5 and Figure 6.

Table 5: *UPF of the bamboo knit dyed with Brasi Color*

	Undyed knit	**Bamboo knit dyed with Brasi Color**									
		pH			**Dye concentration, %**			**M:L ratio**			**Time**
UPF values		pH 4	pH 7	pH 10	0.025	0.05	0.1	1:30	1:40	1:60	120min
Mean UPF	13.861	172.21	204.42	85.68	84.16	70.10	178.11	224.56	347.14	213.59	154.37
Mean UVA Transmission	9.623	0.924	0.129	1.232	1.868	2.633	0.966	0.289	0.237	0.244	0.717
Mean UVB Transmission	6.515	0.396	0.406	1.071	1.065	1.274	0.484	0.394	0.263	0.408	0.556
UPF calculate	13.204	144.76	173.52	66.62	71.95	54.84	148.25	194.28	288.83	191.71	143.05
UPF rating	**10**	**50+**	**50+**	**50+**	**50+**	**50**	**50+**	**50+**	**50+**	**50+**	**50+**



a. b. c.

Fig. 6: *Correlation of mean UVA and UVB transmission with dyeing parameters: a: UVA/UVB – pH; b. UVA/UVB –dye conc; c: UVA/UVB – material/dye solution ratio*

To minimize the harmful of ultraviolet radiation it is important that fabrics let to pass a minimum amount of UV rays, especially in the UV-B region. All the fabrics dyed at different pH have a low UV transmittance and a very high UPF value, being classified as excellent. Even mean UPF, UVA and UVB transmission largely depends on pH of dyeing, the lowest transmission of UVA rays is provided by the fabric dyed at pH 7. In the case of fabrics dyed at different

concentrations, the relative erythemal spectral efficiency is higher in the UV-B region compared to the UV-A region, responsible for the most UV harmful effects. Even at very low dye concentration (0.025%), the knitted fabric ensures an excellent protection (UPF 50). At 0.1% concentration, mean UVA transmission is 0.966 and UVB of 0.484, which is 2-3 times lower than that of the fabric dyed with the lowest dye concentrations. The mean UPF depends also, on the material: dyes solution ratio, the highest values being recorded for 1:40 ratio. As it is obviously from the UPF values, all the dyed fabrics are classified as having excellent UV protection (UPF values 50+). The best relative erythemal spectral effectiveness in the UV-B region is provided by the fabric dyed at the ratio 1:40.

4. CONCLUSIONS

Dyeing with natural dyes by the exhaust method is a difficult task due to non-homogeneity of dye composition and the large variation of color shade and intensity over a range of dyeing variables. The results of this study showed that simultaneous maximum exhaustion and intense color uniformity is not possible to be acquired in the case of natural dyes. Due to their strong absorption in UV domain, the dyed textile materials provide an excellent protection to UV radiation.

Acknowledgments: This study was supported by UEFISCDI through the project No. 55/2017 – UV-SHIELD in the frame of PN III Program, EUREKA Traditional projects.

REFERENCES

[1] E. S. B. Ferreira, A.N. Hulme, H. McNab, and A. Quye, "*The natural constituents of historical textile dyes*", in Chemical Society Reviews, vol. 33, pp 329-336, 2004.

[2] D. Cardon, in "*Natural Dyes. Sources, Tradition, Technology and Science"*, London: Archetype Publications, 2007, XXI, p 778.

[3] L. Y. Tao, J.Y. Li, J.Y. Zhang , "*Brazilein, a compound isolated from Caesalpinia sappan Linn., induced growth inhibition in breast cancer cells via involvement of GSK-3β/β-Catenin/cyclin D1 pathway*", in Chemico-biological interactions, vol. 206, pp. *1-5*, 2013.

[4] D. Grifoni, L. Bacci, G. Zipoli, L. Albanese, F. Sabatini, *"The role of natural dyes in the UV protection of fabrics made of vegetable fibres"*, Dyes Pigments volume 91, pp 279-285, 2011.

[5] https://www.epa.gov/sunsafety/health-effects-uv-radiation, accessed 29 March 2018.

[6] M. M. Alam, M. T. Islam, *"A Review on Ultraviolet Protection of Textiles"*, International Journal of Engineering Technology Science and Research IJETSR, vol 4 (8), pp 2394 – 3386, 2017.

[7] K. Wongsooksin , S. Rattanaphani, M. Tangsathitkulchai , V. Rattanaphani , and J. Barnard Bremner, *"An Al(III) Complex with the Plant Dye Brazilein From Ceasalpinia sappan Linn"*, Suranaree J. Sci. Technol., volume 15 (2), pp 159-165, 2008.

[8] N. P. Nirmal, M.S. Rajput, R.G.S.V. Prasad, M. Ahmad, *"Brazilin from Caesalpinia sappan heartwood and its pharmacological activities: A review"*, Asian Pacific Journal of Tropical Medicine, vol. 8(6), pp 421–430, 2015.

[9] V. K. Sinsawasdi, *"Sappan wood water extract: Evaluation of color properties, functional properties, and toxicity"*, http://ufdc.ufl.edu/UFE0043348/00001, accessed 29.03. 2018.

[10] R. J. Robbins. "Phenolic acids in foods: an overview of analytical methodology*"*, J Agri Food Chem 51(10), pp 2866-2887, 2003.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

WASTE WATER ANALYSIS FROM A NEW GREEN PRETREATMENT OF COTTON FABRICS

DOCHIA Mihaela[1], GAVRILAȘ Simona[2], PUSTIANU Monica[3], MOISĂ Cristian[4], CHAMBRE Dorina[2]

[1]"Aurel Vlaicu" University of Arad, Research Development Innovation in Technical and Natural Science Institute, Postal address, 310330, 2-4 Elena Dragoi Street, Arad, Romania, E-Mail: dochiamihaela@yahoo.com

[2]"Aurel Vlaicu" University of Arad, Faculty of Food Engineering, Tourism and Environmental Protection, Department of Technical and Natural Sciences, Postal address, 310330, 2-4 Elena Dragoi Street, Arad, Romania, E-Mail: simona2213@yahoo.com

[3]"Aurel Vlaicu" University of Arad, Faculty of Engineering, Department of Automation, Industrial, Textile and Transportation Engineering, Postal address, 310330, 2-4 Elena Dragoi Street, Arad, Romania, E-Mail: pustianumonica@yahoo.com

[4]Banat University of Agricultural Sciencies and Veterinary Medicine "King Michael I" of Romania, Postal address, 300645, 119 Aradului Street, Timișoara, Romania, E-mail: moisa.cristian@yahoo.com

Corresponding author: Gavrilaș, Simona, E-mail: simona2213@yahoo.com

Abstract: *In the current context of sustainable development and environmental protection, finding and applying green technologies for textile finishing of cellulosic materials is a priority, being among the main objectives of current researches. Bioscouring treatment is one of the green processes for treating cellulosic textile materials that has successfully replaced classic alkaline treatment. Waste waters resulting from bio preparation are considered biodegradable and with low toxicity unlike alkaline treatment. An analysis and characterization of residual waters from the finishing processes is necessary in order to establish optimal parameters for disposal and low environmental impact, for reducing costs of waste water treatment and for efficient recovery and re-used. The paper presents a characterization of water resulted from a new bioscouring treatment of cotton fabrics using a commercial enzymatic product in ultrasound with sodium citrate as a chelating agent in comparison with bioscouring treatment were EDTA was and alkaline classical treatment. The main quality indicators of the residual waters analyzed were: pH, turbidity, conductivity, TSD, salinity, dry residue, total oxygen dissolved and chemical oxygen demand (COD-CCOMn). After analyzing the obtained data, similar values were observed for the two enzymatic treatments except the pH value which was lower for the process were EDTA was used, requiring a slight correction. For classical alkaline treatment, the obtained values exceeded the allowed limits for almost all analyzed parameters.*

Key words: *cotton fabrics, new green pretreatment, residual water, turbidity, TDS, chemical oxygen demand*

1. INTRODUCTION

Textile industry is a large water consumer, many of the technological steps involving wet processes. Such process is that of scouring which removes different impurities (wax, pectin and organic acids, minerals) from the natural fibres. In this situation the wastewaters have high

temperature and contain large quantities of alkali with negative impact on the environment. An alternative is represented by bioscouring treatment which involves the use of pectinase to depolymerise and demethylate the pectin structure and release the cellulose active groups to properly interact with the whitening or dyeing agent in the following technological processes.

The tendency in our days is to obtain reusable waste waters with low toxicity. Waste waters resulted from cotton fabrics processing have a high content of salts and total dissolved solids, and also large amount of different types of dyes [1]. The treatment for the waste waters could be expensive. Although many recent researches have as main object the establishment of new methods to treat the waste waters from textile industry with the possibility of the reusing, it is preferable to decrease the chemicals used in the specific technological steps. One proposed method considers oxygen based procedure [2]. Studies in domain consider being efficient from economical and ecological point of view to integrate waste water in new technological step due to the fact that a high quantity of alkaline compounds remain in the treatment baths. It had been demonstrated that the quality of the fabrics presents a small improvement in such conditions [3].

There are attempts to reduce the values of the solid suspension and chemical oxygen demand of the waters resulted from cotton pretreatments by chemical methods. Utilisation of aluminium sulphate in optimum quantity could reduce almost to half the level of chemical oxygen demand and only to 15 % the solid state [4]. Even if this treatment shows promising result it implies the use of chemical compounds. The quantity of chemical compounds presented in the waste waters could be successfully decrease by using enzymatic treatments. Many researches focus on pectinases, their role being to hydrolyse the pectic wall presented in the first layer of the cotton fibres to release more reactive groups.

In the conventional alkaline scouring treatment, all the pectin is removed. It was also demonstrated that the structure of the cotton fibres are damaged. Compared with this hard chemical treatment, the enzymatic one is less harsh, removing the pectin to an optimum degree, the fibres resulted being characterised by mild surface and optimum strength retention [5]. Along with the fact the cotton fibres are less dameged during an enzymatic scouring procees, the costs and consumption of chemical is reduced, and the scouring baths have biodegradable characteristics [6].

It had been proven that good results are obtained also by using mixture of different types of enzymes, pectinases, cellulases and proteases [7].

2. EXPERIMENTAL PART

2.1 Materials

- 100 % cotton fabric characterised by: width (150 ± 3 cm), weight (200 ± 10 g/m^2), warp of 100 % cotton yarn with Nm 25/2 and weft of 100 % cotton yarn with Nm 25/1.
- Pectinolytic product Beisol PRO, the surfactant Denimcol Wash RGN supplyed by CHT Bezema Company.
- Sodium citrate, sodium hydroxide, sodium carbonate, sodium bisulfite, sodium silicate purchased from Sigma-Aldrich.
- Sulfolen 148 (S-148, alkyl polyglicol ether) from Rotta Company.
- The residual water resulted from the enzymatic pretreatments and alkaline one.

2.2 Methods

2.2.1 Pretreatments of the cotton fabric

The 100 % cotton fabric was subjected to tree types of pretreatments: two enzymatic treatments where the complexing agents were EDTA or sodium citrate and one alkaline treatment. Prior to the pretreatments, the samples were washed in order to eliminate dust and other impurities.

The procedure was done by using an AATCC Launder Ömeter, M228-AA model from SDL Atlas Company-USA. The following step was the conditioning of the samples which was made in an oven from Caloris Grup Romania.

All enzymatic treatments were done using pectinolytic product Beisol PRO (which consists of a mixture of enzymes) in water at a 20:1 liquid to goods ratio and a temperature of 55 ^{0}C. The enzyme concentration was varied between 1-3 % o.w.f (over weight fiber) at different action time (15 to 55 minutes). As auxiliary reagents, 2 g/L EDTA or sodium citrate (complexing agents) and 0.5 % Denimcol Wash RGN (surfactant) were used. The bioscouring treatments were conducted at 45 kHz in an ultrasound bath Elmasonic X-tra basic 2500 from Elma Company, Germany.

The alkaline treatment used for comparison was done at 100 ^{o}C for 1 hour in AATCC Launder Ömeter with 10 g/L sodium hydroxide, 5 g/L sodium carbonate, 1 g/L sodium bisulfite, 2 g/L sodium silicate and 2 g/L Sulfolen 148 (S-148, alkyl polyglicol ether) as a wetting agent.

In **Fig. 1** are presented the steps of the green pretreatments (with enzymes and sodium citrate or EDTA).

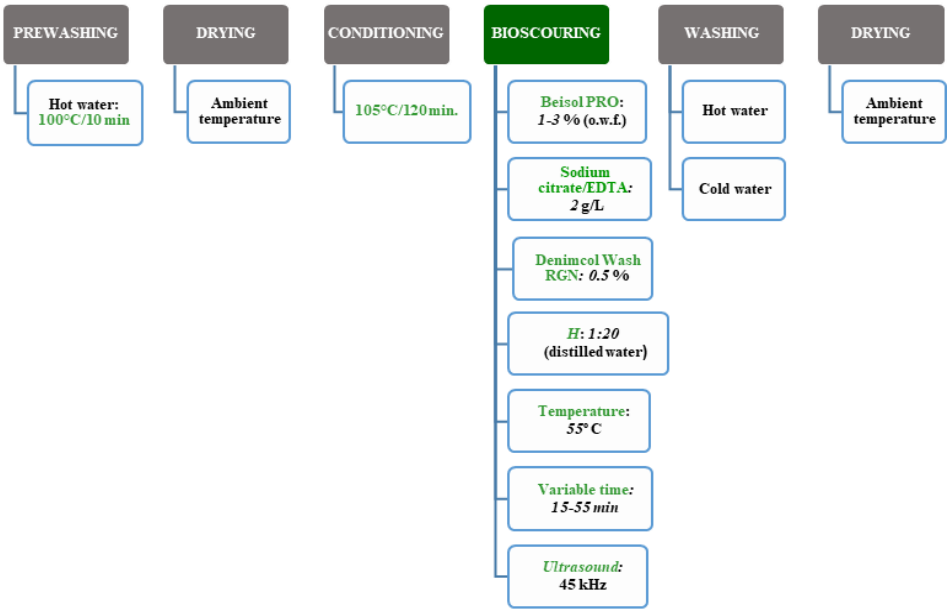


***Fig. 1**: The steps of the green pretreatments of the cotton fabric*

2.2.2 Testing and analysis of the waste water

The main quality indicators of the residual waters analyzed were: pH, TDS (total dissolved solids), salinity, conductivity, total dissolved oxygen, turbidity, dry residue, and chemical oxygen demand (CCOMn). The pH, TDS, salinity, conductivity and total dissolved oxygen were determined by using a WTW multi-parameter INOLAB MULTI 740. For measuring the turbidity a HI 88713 Turbidimeter from HANNA Instruments was used. The dry residue was gravimetric determined as difference in mass before and after the drying process. The water samples were evaporated in a Pura 14 water bath from Julabo, Germany and dried at (105 ± 5) °C to constant mass in an oven from Caloris Grup [8]. The chemical oxygen demand was done using the titration method with $KMnO_4$ as described by R. Ballance [9].

3. RESULTS AND DISCUSSIONS

It is important to study all characteristics of the textile effluents to improve environmental performance and also to sustain considerable quality of the individual companies. The physico-chemical parameters of waste water resulted from all tree type of pretreatments have been analyzed.

The acidic and basic nature of the effluents can be identified by pH value. The toxicity of waste water increases due to variations of the pH. Hence low or high strength of the pH in effluent can affect the quality of clean water and alters the rate of biological reaction with survival of various microorganisms. The strength of the pH also alters the soil permeability which results in contaminating underground water resources. As a result it is necessary to evaluate the waste waters with respect to pH value then it can be neutralized with acidic or basic solution. In **Fig. 2** the pH and salinity values for the enzymatic pretreatments are presented.

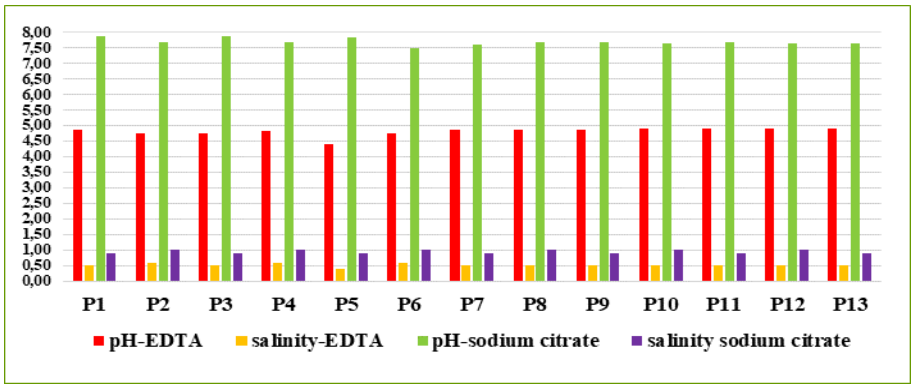


***Fig. 2**: The pH and salinity of the waste waters from the green pretreatments of the cotton fabric*

It can be noticed that the pH of waste water resulted from the enzymatic treatments were sodium citrate was used is almost neutral in comparison with EDTA were the pH values are below 5, requiring a slight correction. As for salinity, this shows higher values for sodium citrate treatments.

Generally textile industries shows higher TDS value than the other industries mainly due to the fixing, bleaching and dyeing agents used for fabric processing on different stages. The high TDS value of water is not recommended for drinking and irrigation purposes as it may cause salinity problem. **Fig. 3** shows the obtained values for TDS and conductivity in the case of the two green pretreatments. Both TDS and conductivity have similar values for both types of pretreatment within the admissible limits.

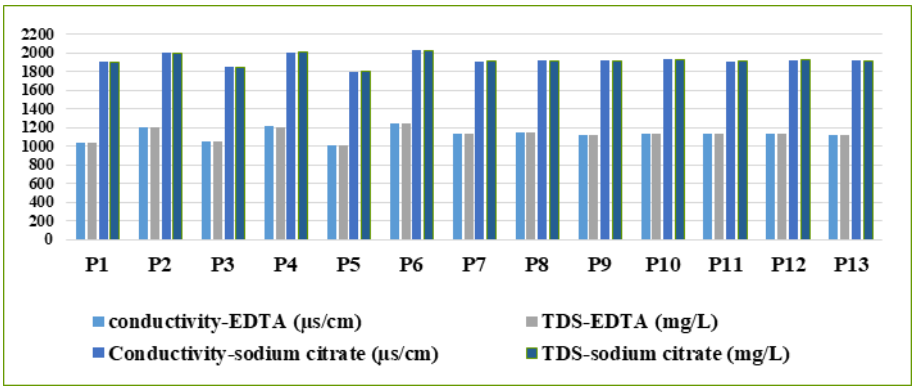


***Fig. 3**: The TDS and conductivity of the waste waters from the green pretreatments of the cotton fabric*

From **Fig. 4** the maximum COD values (CCOMn) were recorded for treatments were EDTA was used with higher values for P6-P13 samples. Ussualy, organic strength of the effluent can be identified by COD values. Increases in COD can be due to detergents, softeners, non biodegradable chemicals, etc. Higher concentration of COD in water implies toxic conditions and the presence of biologically resistant organic substances. Hence the effluent is incompatible for the survival of water living organisms due to the reduction of DO content.

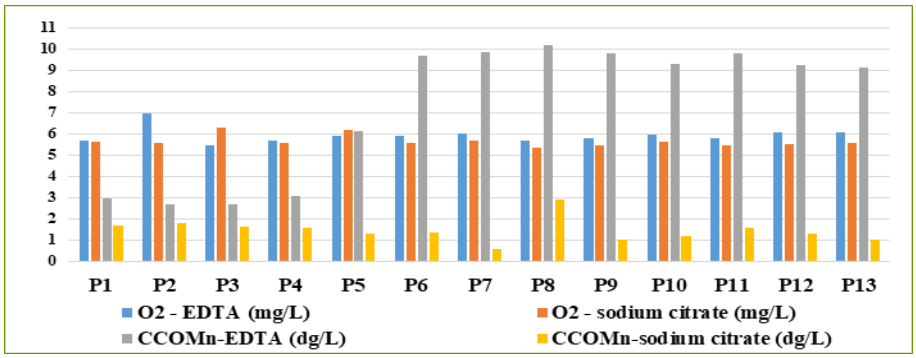


***Fig. 4**: The COD (CCOMn) and O_2 values of the waste waters from the green pretreatments of the cotton fabric*

The turbidity an dry residue are presented in **Fig. 5**. Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particles. The values for turbidity were recorded in the interval 1.7 - 3 NTU for sodium citrate and 1.0 – 2.2 NTU for EDTA which were been found to be in the BIS limit. A higher turbidity prevents the penetration of sunlight and oxygen transfer process and as result, the process of photosynthesis is hindered. Thus turbidity should be measured and treated carefully before waste water final disposal. The dry residue values are the same for both biocouring treatment within the admissible limits.

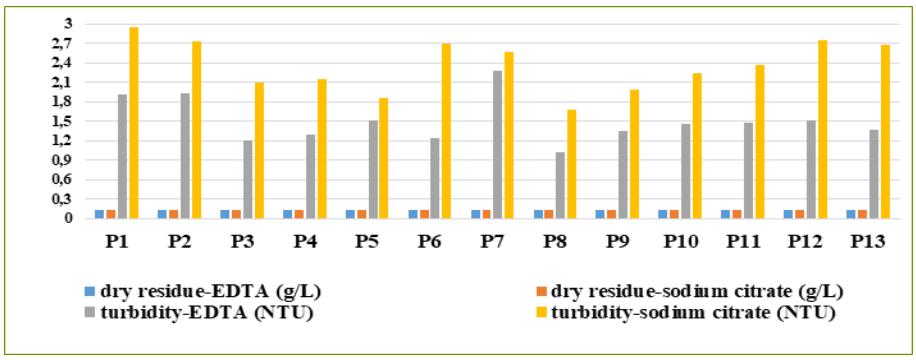


***Fig. 5**: The dry residue and turbidity of the waste waters from the green pretreatments of the cotton fabric*

Table 1 presents all parameters of the waste water from the clasical alkaline treatment. As it can be seen, for all measurements, the obtained values exceed admissible limits.

***Table 1**: The waste water parameters from the clasical alkaline treatment*

Conventional alkaline treatment	pH	Salinity	Conductivity (µs/cm)	TDS (mg/L)	Dry residue (g/L)	Turbidity (NTU)	O_2 (mg/L)	CCOMn (mg/L)
	12.70	32.50	39000	39000	2.313	72	3.53	13000

4. CONCLUSION

The present study clearly enlightens the physico-chemical parameters of the waste water resulted from tree type of pretreatment of cotton fabrics, which is useful to analyze the nature and types of pollutant concentration present in the effluent. Based on the obtained experimental data it is concluded that for enzymatic pretreatments (EDTA or sodium citrate) all the parameters are in the limits given by BIS except the pH for treatments were EDTA was used. We can not say the same thing in the case of classic alkaline treatment were higher values were obtained for all analyses. A constant monitoring of water quality is necessary to avoid further dreadful conditions. The effluents which are toxic in nature are needed imperative treatment before disposal on water bodies to create less pollution and a eco-friendly environment.

ACKNOWLEDGEMENTS

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-1370,

REFERENCES

[1] C. R. Holkar, A.J. Jadhav, D.V. Pinjari, N.M. Mahamuni, A.B. Pandit, "*A critical review on textile wastewater treatments: Possible approaches*", J. Environ. Manage., 182, 2016, pp. 351-366.

[2] L. Bilińska, M. Gmurek, S. Ledakowicz, "*Textile wastewater treatment by AOPs for brine reuse*", Process Saf. Environ., 109, 2017, pp. 420-428.

[3] Y. Zhang, S. Shao, W. Yu, F. Yang, X. Xu, "*Study on Recycling Alkali from the Wastewater of Textile Mercerization Process by Nanofiltration*", *IERI Proc*., 9, 2014, pp. 71-76.

[4] A. Shaid, Md.S. Showkat, Md.A. Hannan, M.A.R.Bhuiyan, "*Direct Reusing of Textile Wastewater in Scouring-Bleaching of Cotton Goods Devoid of Any Treatment",* Int. J. Eng. Research Develop., 5, 2013, pp. 45-54.

[5] A.I. Hafez, M.A. Khedr, H. Ali, R. Sabry, "*Characterization and pretreatment of dyeing wastewater from the cotton and polyester textile industry in Egypt*". Desalin. Water Treat., 30, 2011, pp. 37-43, DOI: 10.5004/dwt.2011.1520.

[6] K. Mojsov, "*Bioscouring and bleaching process of cotton fabrics an opportunity of saving water and energy*". The Journal of The Textile Institute, 2015 http://dx.doi.org/10.1080/00405000.2015.1070603.

[7] E. Karapinar, M.O. Sariisik, "*Scouring of Cotton with Cellulases, Pectinases and Proteases*". Fibres Tex. Eas. Eur., 12, 2004, pp. 79-82.

[8] DS 204:1980 (in compliance with SFS 3008, NS 4764, and SS 028113); "*Determination of total residue and total fixed residue in water, sludge and sediment*".

[9] R. Ballance, Chapter 7-"*Physical and chemical analyses, Water Quality Monitoring-A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes*". Edited by Bartram J. and Ballance R. UNEP/WHO ISBN 0 419 22320 7 (Hbk) 0 419 21730 4 (Pbk), 199.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PIGMENT PRINTING OF COTTON FABRICS WITH CYCLODEXTRIN AND BIFUNCTIONAL REACTIVE DYE

ERKAN Gökhan[1], ŞENGÜL Kemal[1], AKKAŞ Münevver[1], BÜYÜKPOYRAZ Sinem[1]

[1]Dokuz Eylül University, Faculty of Engineering, Textile Engineering Department, Tınaztepe yerleşkesi Buca, 35397, İzmir, Turkey, gökhan.erkan@deu.edu.tr

Corresponding author: Erkan, Gökhan, E-mail: gokhan.erkan@deu.edu.tr

Abstract: *Beta-cyclodextrin, which has seven glucopyranose units, have ability to make inclusion complexes with the appropriate molecules that are called guest molecules. The inclusion complex occurs in the apolar cavity of beta-cyclodextrin therefore guest molecules should have the appropriate apolar groups and molecular size. Cyclodextrins can change the some properties of guest molecules, such as solubility, thermal behavior etc. Beta-cyclodextrin, has been preferred to use in various textile applications, such as insecticide, cosmetics, pharmaceutical agents, antibacterial agents, odour applications, and in dyeing as an auxiliary agent. However, a few studies are done using cyclodextrins in printing. Printing of pigment dyes with reactive printing paste using beta-cyclodextrin was investigated in this work. By this purpose, in the first step inclusion complexes were obtained by kneading method at various weight ratios of beta-cyclodextrin and pigments. Inclusion complexes were printed on cotton fabric by flat screen printing with using alginate based reactive printing paste. In the second step, pigments were printed by pigment printing paste with and without of cyclodextrin Reactive dye also was printed with and without cyclodextrin. Colorimetric values, colour strength fastness properties and stiffness peculiarities were investigated. The optimum complex forming weight ratio was found 1:2 for red, blue and mixture of pigments, and 1:3 for yellow pigment from colorimetric and colour strength values. Crocking fastness were improved by addition of inclusion complexes.*

Key words: *Fastness, Printing, Inclusion complex, Colour strength, CIEL*a*b**

1. INTRODUCTION

Beta-cyclodextrin, which has seven glucopyranose units, has been preferred to use in various textile applications [1]. Many investigations were performed for dyeing process due to its capability to form inclusion complexes with common textile dyes. Especially cyclodextrins are studied as additive in dyeing of cotton [2], [3]. and emulsifier in washing process [3], [4]. Unfortunately, a few studies are performed in printing of textiles. Knittel, Buschmann & Schollmeyer (1996), investigate the usage of derivatives cyclodextrin to be alternative to urea. They investigate the viscosity of printing paste and dye fixation and found that monochlortriazinyl derivative of beta-cyclodextrin improves the dye fixation [5]. The effect of monochlortriazinyl derivative of beta-cyclodextrin on rheological behaviours, colour strength and fastness properties is investigated [6]. Monochlortriazinyl derivative of beta-cyclodextrin is used in printing of wool/polyester fabrics. First the fabrics are modified by cyclodextrin derivative and then are printed by paste of disperse dye [7].

As well known reactive dyes have reactive groups, which reacts with hydroxyl groups of cellulose macromolecules. The reactive dyeing or printing are performed at basic conditions, however besides reaction between hydroxyl of cellulose and reactive group, reactive groups can react with hydroxyl groups of water molecules. Bifunctional reactive dyes have been introduced owing to avoid of reaction between water and reactive groups. Bifunctional reactive dye was used as a bridge between cyclodextrin and cellulose [8].

Printing of pigment dyes with reactive printing paste was investigated in this work. By this purpose, in the first step inclusion complexes were obtained by kneading method at various weight ratios of beta-cyclodextrin and pigments. Inclusion complexes were printed on cotton fabric by flat screen printing with using alginate based reactive printing paste. In the second step, pigments were printed by pigment printing paste with and without of cyclodextrin Reactive dye also was printed with and without cyclodextrin. Colorimetric values, colour strength fastness properties and stiffness peculiarities were investigated.

2. EXPERIMENTAL

2.1 Materials

Commercial beta-cyclodextrin Periplex CDP (β-CD) was supplied by Dr. Petry Textile Auxiliaries (Turkey). Three pigment dyes (Lyosperse Yellow M3G liq-CI Pigment Yellow 17, Lyosperse Red 2BN liq-CI Pigment Red 146, Lyosperse Blue G liq-CI Pigment Blue15:3) and a bifunctional reactive dye (Novacron Orange PH-3R-CI Reaktive Orange 131) (Huntsmann) were used. Alginate based Lyoprint RD-HT (Huntsman) for reactive printing and polyacrilic acid derivative (PTF) for pigment printing were used as thickener. (Table 1) All chemicals were commercial grade and used without any purification. Methanol (merck) and purified water were used for kneading process of inclusion complexes. All printing process achieved by using soft water.

2.2 Methods

Kneading process was performed according to Taneri et al. (2003) [9]. Kneaded products were prepared in three pigments: β-CD weight ratios (1:1, 1:2 and 1:3). After preparation of complexes, they introduced into reactive printing paste. Reactive dye also was printed alone and with addition of β-CD in 1:1 weight ratio. Fixation of printed goods was achieved by steaming at 102 ^{o}C for 10 minutes. Washing-off procedures are in order of 2 cold rinses, 2 hot wash at 90 ^{o}C for 10 minutes with 1 g/l Eriopon R (Huntsman) dispersant, warm rinse, cold rinse, neutralize to pH 7 and finally a cold rinse.

Table 1. *Printing pastes reciepes*

Reactive Printing Paste Recipe			**Pigment Printing Paste Recipe**	
Ingredient	Amount (g)		Ingredient	Amount
Lyoprint RD-HT	25		Ammonia (ml)	20
Urea	100		PTF (g)	30
Chelating agent	4	Paste A	Binder (g)	60
Sodium carbonate	4		Water (g)	X
Sodium bicarbonate	28		Total (g)	1000
Calgon T	4		Emulsifier (ml)	10
Ludigol	12	Paste B	White Sprit (g)	150
Water	X		Urea (g)	20
Total	1000		Paste A (g)	Y
			Total (g)	1000

Printing paste of pigment dyes was prepared according to recipes for reactive and pigment printing, which were given in Table 1. Pigment dyes were printed alone and with addition of β-CD in 1:1 weight ratio. Fixation of printed goods was achieved by thermofixation at 140 ^{o}C for 4 minutes. After printing a cold washing-off procedure was employed.

Colorimetric values (CIE L*a*b*C*H) of printed fabrics were measured by Minolta 3600D spectrophotometer (D65, specular included, 10^{o}). To determine the colour strength, K/S values at the wavelength of maximum absorption were calculated from the formula (Kubelka-Munk) by using spectrophotometer (Minolta -3600D). Washing fastness tests were carried out according to ISO 105-.C06 method of A1S. Crocking fastness was measured according to ISO 105-X12. Stiffness of printed fabrics was determined according to TS 1409 by using flexometer.

3. RESULTS and DISCUSSION

3.1. CIE L*a*b*C*H values

Colorimetric values of printed fabrics are shown in Table 2. Highest L* (lightness) value was obtained in the case of 1:3 weight ratio, when blue pigment was examined. Chroma, a* and b* values were increased with increasing of weight ratio. Thus the printings of 1:3 pigment: cyclodextrin weight ratio was more vivid and had red and yellow shades. However this fact can be due to using reactive dye as a bridge between the cyclodextrin and cellulose. In the case of yellow pigment, there were no differences between weight ratios of cyclodextrins. This fact can be attributed to yellow shades of both pigment and reactive dyestuff. Lightness and b* values of red pigment was increased with weight ratio. Increasing of yellowness can denote the existence of complex between reactive dyestuff and cyclodextrin. 1:2 weight ratio of red pigment gave highest red values at greenness-redness axis of colour space. Trichromic mixture of pigments, reactive dye and cyclodextrin were also printed to cotton fabrics. Lightness values of mixture printings were not significantly different, however vividness of fabrics were changed. The highest chroma value was observed at 1:2 weight ratio. Dullest shade was observed at 1:3 weight ratio. Hue that is more reddish was observed in the case of 1:2 weight ratio. It can be said that the colorimetric values of mixture printings were dominated by red pigment.

To understand the effect of cyclodextrin on reactive dyestuff, printing of reactive dyestuff and 1:1 cyclodextrin: reactive dyestuff mixture was also applied. All colorimetric values, except lightness value, increased with cyclodextrin addition. Of course cyclodextrin is not only forming complexes with pigments. Also, it can make complexes with non-polar groups of suitable substances. Thereby cyclodextrin can form complexes with both hydrolyzed and non-hydrolyzed reactive dyestuff. Cyclodextrin increased the Yellowness of fabrics increased because of fixation of more reactive dyestuff. Also more reddish and vivid hues were observed with the addition of cyclodextrin.

Printing with printing paste was also investigated. Lightness value of yellow pigment decreased with addition of cyclodextrin. Contrary lightness values of other pigments increased with cyclodextrin. Yellowness of yellow pigment increased with cyclodextrin due to complex between pigment and cyclodextrin. In the case of red pigment, a* values slightly increased with addition of cyclodextrin.

3.2. Colour Strength

Colour strength of printings was observed by K/S values. The highest K/S values were observed at 1:2 weight ratio for red, blue and mixture printings. For the yellow pigment, the highest K/S value was observed at 1:3 weight ratio. Colour strength values were compatible with colorimetric values. Thereby it can be concluded that the optimum complex forming weight ratio

was 1:2 for red, blue and mixture of pigments, and 1:3 for yellow pigment. Addition of cyclodextrin increased colour strength of reactive dye. It can be inferred that cyclodextrin may form complex with both hydrolyzed and non-hydrolyzed reactive dyestuff. Thus colour strength of cyclodextrin added printings were higher than the absence of cyclodextrin. K/S values decreased with cyclodextrin addition in the case of pigment printing.

3.3. Fastness Properties

Fastness properties of printed fabrics depicts in Table 3. In spite of good bleeding properties, colour change values were very poor at reactive printings of pigments, except yellow pigment. Good colour change values of yellow pigment were observed due to colour of reactive dyestuff. Very low bleeding properties obtained for pigment printing paste with cyclodextrin.

Table 2. *Colourimetric and K/S Values*

Printing Paste	Colour	Dye:β-CD Ratio	L*	a*	b*	C*	H	K/S
Reactive Printing Paste	Blue	1:1	53.074	3.486	27.580	27.799	82.791	53.108
		1:2	53.763	2.983	27.949	28.108	83.909	51.857
		1:3	57.219	11.529	37.358	39.097	82.849	57.576
	Yellow	1:1	69.572	33.045	55.542	64.629	59.249	52.285
		1:2	68.066	34.762	56.269	66.141	58.293	57.189
		1:3	68.825	34.116	55.395	65.158	58.373	53.448
	Red	1:1	60.422	40.939	45.218	60.997	47.843	60.288
		1:2	62.045	41.357	47.804	63.211	49.136	60.843
		1:3	64.449	36.966	50.831	62.851	53.974	58.548
	Trichromatic	1:1	63.570	24.519	44.407	50.727	61.095	49.317
		1:2	63.154	25.43	45.927	52.497	61.027	53.527
		1:3	63.743	21.968	41.136	46.634	61.896	45.043
	Reactive	-	72.617	28.212	42.413	50.939	56.369	29.209
		1:1	69.020	34.400	56.766	66.376	58.785	56.400
Pigment Printing Paste	Blue	-	37.699	10.966	38.739	40.261	254.195	15.812
		1:1	42.986	13.640	38.350	40.704	250.422	11.078
	Yellow	-	87.072	2.226	96.640	96.665	1.320	13.023
		1:1	86.190	0.938	98.262	98.266	0.547	12.667
	Red	-	40.939	59.116	22.368	63.206	20.725	14.922
		1:1	45.872	59.991	18.511	62.782	17.149	11.166

Colour fastness to crocking is the characteristic property of pigment printing. If the Table 3 examine, pigment printing pastes had very poor wet crocking fastness. Approximately 1 point increase was observed for kneading method to complex formation and their printing with reactive dyestuff. Highest wet crocking fastnesses were obtained at mixture of pigments as well as reactive dyes. Moderate dry crocking fastnesses were obtained for pigments. Good dry crocking fastnesses were observed for reactive dyestuffs, which were expected.

***Table 3**. Fastness Properties*

Printing Paste	Colour	Dye:β-CD Ratio	Colour change	Washing Bleeding						Crocking	
				Wo	PAC	PES	PA	Co	CA	Wet	Dry
Reactive Printing Paste	Blue	1:1	1	4-5	5	4-5	4-5	5	5	2-3	3
		1:2	1	4-5	4	4	4	4-5	5	2-3	3-4
		1:3	1	5	5	5	4-5	4-5	5	3-4	4
	Yellow	1:1	2-3	4-5	4-5	4-5	5	5	5	2-3	4
		1:2	4	4-5	4-5	5	4-5	4-5	5	3	3-4
		1:3	4-5	5	5	5	5	5	5	3	3-4
	Red	1:1	2	4-5	5	5	4-5	5	5	2-3	3-4
		1:2	2-3	4-5	4-5	4-5	4-5	4-5	4-5	2-3	3-4
		1:3	2-3	4-5	4-5	4-5	4-5	4-5	4-5	3-4	4
	Trichromatic	1:1	4	4	4	4-5	4	4-5	3-4	3-4	4-5
		1:2	2	4-5	4-5	4-5	4	4	4-5	4	4-5
		1:3	3	5	5	4-5	4-5	5	5	4-5	4-5
	Reactive	-	2-3	4-5	4-5	4	4	4-5	4-5	4-5	4-5
		1:1	3	5	5	5	4-5	4-5	5	4-5	4-5
Pigment Printing Paste	Blue	-	4	4-5	4-5	3-4	4	4-5	4-5	2	3-4
		1:1	3	2	2	2	2-3	2	2-3	2-3	3-4
	Yellow	-	4-5	4-5	4-5	4-5	4-5	4-5	4-5	2	3-4
		1:1	3-4	1-2	1-2	2	2	1-2	1-2	1-2	3-4
	Red	-	4	4	4	4	4-5	4	4-5	2	3-4
		1:1	3	1-2	1-2	1-2	2	1-2	1-2	1-2	3-4

3.4. Bending Properties

Fig. 1 shows bending properties of inclusion complexes with reactive printing paste. Bending values were varying between 17.2 and 13.3. Fig. 2 depicts effect of cyclodextrin addition on bending properties of both pigment and reactive printing pastes. Bending properties were enhanced by addition of cyclodextrin in the case of pigment printing paste. However cyclodextrin did not change the handle properties of reactive printing.

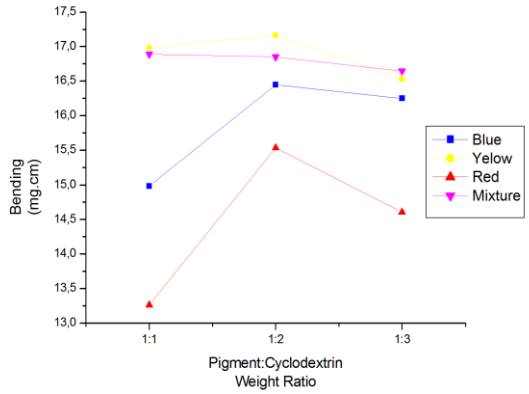


Fig. 1. *Bending Properties of Reactive Printing Paste*

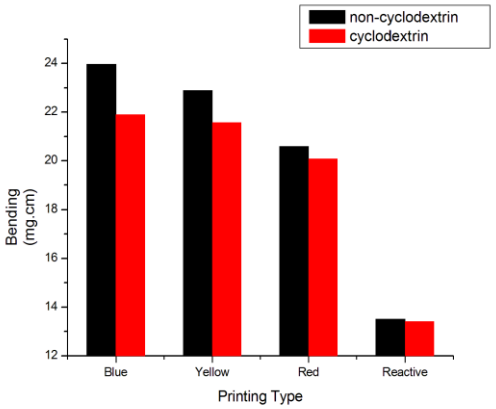


Fig. 2. *Bending Properties of Pigment Printing Paste*

5. CONCLUSIONS

It can be concluded that the optimum complex forming weight ratio was 1:2 for red, blue and mixture of pigments, and 1:3 for yellow pigment from colorimetric and colour strength values. Colour fastness to wet crocking and water spotting values were improved by inclusion complexes. Bending properties were enhanced by addition of cyclodextrin. By looking all the data it can be said that cyclodextrins can be used with bifunctional reactive dyestuff at printing of pigments.

REFERENCES

[1] J. Szejtli, *"Cyclodextrins in the textile industry,"* Starch/Staerke, vol. 55, pp. 191-196, 2003.

[2] U. Denter, E. Schollmeyer, *"Bestimmung der farbstoff-aufnahme beim trichromen färben von baumwolle,"* Textilveredlung, vol. 29, pp. 288-291, 1994.

[3] A. Cireli, B. Yurdakul, *"Application of cyclodextrin to the textile dyeing and washing processes,"* J. Appl. Polym. Sci., vol. 100, pp. 208-218, 2006.

[4] E. Franco, M. Ferrándiz, L. M. Pérez, S. Moldovan, E. Nuñez, J. A. Gabaldón, P. Cosma, P. Fini, E. Perez, M. Ferrándiz, *"Cyclodextrins to recover textile dyes in waste water,"* Annals of The University of Oradea Fascicle of Textiles, Leatherwork, vol. XVI, pp. 31-34, 2015.

[5] D. Knittel, H. J. Buschmann, E. Schollmeyer, *"Beiträge zum reaktivdrucksubtitution von harnstoff,"* Textilveredlung, vol. 31, pp. 153-157, 1996.

[6] A. A. Hebeish, A. A.Ragheb, S. H. Nassar, E. E. Allam, J. I. Abd El Thalouth, *"Technological evaluation of reactive cyclodextrin in cotton printing with reactive and natural dyes,"* J. Appl. Polym. Sci., vol. 102, pp. 338–347, 2006.

[7] N. A. Ibrahim, E. M. R. El-Zairy, *"Union disperse printing and UV-protecting of wool/polyester blend using a reactive β-cyclodextrin,"*Carbohyd. Polym., vol. 76, pp. 244–249, 2009.

[8] W. Chao-Xia, C. Shui-Lin, *"Anchoring -cyclodextrin to retain fragrances on cotton by means of heterobifunctional reactive dyes,"* Color. Technol., vol. 120, pp. 14-18, 2004.

[9] F. Taneri, T. Güneri, Z. Aigner, M. Kata, *"Influence of cyclodextrin complexation on the physicochemical and biopharmaceutical properties of ketoconazole,"* J. Incl. Phenom. Macro., vol. 47, pp. 15–23, 2003.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PERFORMANCE EVALUATION OF A CIRCULAR WEFT KNITTING MACHINE THROUGH OBSERVATION OF YARN INPUT TENSION: A CASE STUDY

HOSSAIN A.K.M Mobarok[1], ALI Abu Rayhan Md.[2]

[1]Ahsanullah University of Science and Technology, Faculty of Engineering, Department of Textile Engineering, 1208 Dhaka, Bangladesh, E-mail: mobarok@aust.edu, mobarok_textech@yahoo.com

[2]Bangladesh University of Engineering and Technology, Faculty of Mechanical Engineering, Department of Mechanical Engineering, 1000 Dhaka, Bangladesh, E-mail: armali@me.buet.ac.bd

Corresponding author: Hossain, A.K.M.Mobarok, E-mail: mobarok@aust.edu, mobarok_textech@yahoo.com

Abstract: *This paper presents a noble approach to assess the performance of a modern knitting machine through monitoring of running yarn tension during operational hours. An industrial circular weft knitting machine having positive storage feed system was observed, as a case study, in this research for its performance evaluation. A total of 16 different production runs- each for a machine running period of 30 seconds [equivalent to the time required for more than 05 revolutions of the needle bed or machine at 10.5 rev. /min.] were analyzed. Highest tension-peak value for each second was identified through MLT Wesco Yarn Tension and Rate Meter and associated PC software. Run charts were built-up with these selected tension values by a statistical software, i.e. Minitab and the p-values were checked to identify special cause variations. It was found that most of the production runs showed no non-random pattern in the tension values based on an alpha value (significance level) of 0.05, representing absence of special cause variations and thus disclosing quite satisfactory machine performance. However, the production run with non-random pattern was investigated through cause-effect diagram. The presence of astronomical data point was also evaluated. The findings here also indicated no direct machine-related cause regarding such variation or pattern in yarn input tension.*

Key words: *Knitting, Yarn Input Tension (YIT), Run Chart, Special Cause Variation, p-Value*

1. INTRODUCTION

The knowledge of how well a knitting machine is working during production is very important for a knitter. This information allows scheduling all plans and necessary actions required for improved productivity and quality in a manufacturing plant [1]. According to Catarino as cited by Catarino et al. [2] yarn input tension in a modern circular weft knitting machine can be used as a valuable resource of information concerning in particular the knitting process, and in more general term, the overall behavior of the knitting machine, since YIT directly reflects the influence of the different mechanisms involved in the production of the knitted fabric.

The analysis of yarn input tension reveals that it should be basically a fairly well-shaped sinusoidal waveform, with a frequency equivalent to the time elapsed between each loop formation [3]. However, there are all other mechanisms involved in the production of the knitted structure that will induce other harmonics and thus change the shape of the YIT waveform [3]. Nevertheless, YIT is considered as one of the most important parameters for weft knitting industry and its inspection allows the detection of several problems during production [4].

When some abnormality occurs in the knitting process it will always be reflected in the YIT [2] which is a reflection of the whole knitting process for a given yarn feeder [5]. Through the YIT waveform it is possible to identify the appearance of a fault, which is represented by a sudden increase/decrease in the force, determine eccentricities of the feeding system, which are represented with sinusoidal waveform, determine abnormalities that can degenerate in fault [1]. However, any abnormality resulting from machine performance will produce some kind of periodic behavior as almost all moving parts depend on one main engine and their movement is almost always circular [3].

The simple inspection of YIT waveform allows the detection of faults and malfunctions of knitting machines. However, the representation on graphics of the entire YIT from a feeder and inspection of YIT waveform may lead to erroneous judgment in an industrial environment as YIT fluctuates due to yarn irregularity, dust and other situations which do not constitute a fault [1]. Instead, it would be very useful to deal with any particular state of YIT (like average or peak) to evaluate the whole process of loop formation thus enabling the detection of abnormalities and possible cause diagnosis. Statistical quality tools, like run charts, may be deployed to fulfill the above purpose.

2. RUN CHART

A run chart is a graphical display of data over time or a time series chart of data. It can reveal evidence of special cause variation those creates recognizable patterns. Therefore, it may be used as a quick test of system performance.

When statistical software like Minitab is used to create a run chart, it plots individual observations in the order they were collected and draws a horizontal reference line at the median. Four basic patterns of non-randomness are detected by run chart [6], i.e. mixture, cluster, oscillating and trend, which are sometimes termed as special cause variations as shown in figure 1.

(i) (ii) (iii) (iv)

Fig. 1: *Non-random patterns as identified by a run chart-(i) Mixture (ii) Clusters (iii) Oscillation and (iv)Trend* [6]

Moreover, astronomical data points [7] are also detected on a run chart through noticeable shift from the median. Consequently, all the possible causes responsible for non-randomness may be evaluated to judge the performance of the machine.

3. METHODOLOGY

3.1 Monitoring of Knitted Fabric Production through Yarn Input Tension

The test machine is a multifeeder industrial circular knitting machine (Orizio, Johnan) of 24 gauge and 26 inch diameter. To evaluate its performance run charts were built with the help of highest tension values recorded at a particular feeder for a fixed QAP, i.e. yarn delivery setting, which occurred at each second for a machine running period of 30 seconds. YIT waveform was obtained through MLT Wesco PC software (figure 2). Advanced memory mode with zoom option of this program was used to discover secondwise graphical shape of YIT (figure 3) - thanks to Memminger-IRO.

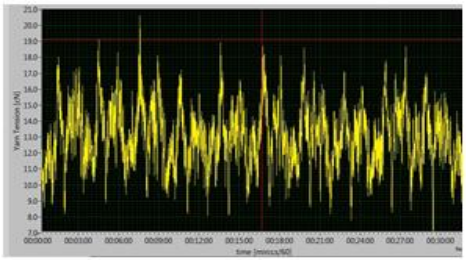


Fig.2: *A typical YIT wave form (for 30 sec)*

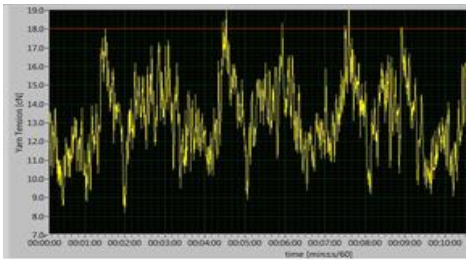


Fig. 3: *A typical YIT wave form (for 10 sec)*

A total of 16 production runs producing plain jersey fabrics with spun polyester and cotton yarns were evaluated. Two different counts (as measured experimentally) were used for each type of yarn at four different cam setting points. All other machine settings were kept constant. The machine rpm of 10.5 indicates more than 5 revolutions of the needle bed in the chosen run time. Average temperature and relative humidity recorded during the experimental hours were around 29°C and 67% respectively.

3.2 Interpretation of Run Charts

Tension values for each process were plotted through run charts in the order that they were collected. The run chart built through Minitab (version 17.1.0) also calculates p-values for different special cause variations. These are presented in table 1. The p-value is a probability that measures the evidence against the null hypothesis. The null hypothesis is that there exists no non-randomness pattern in the data. A p-value that is less than the specified level of significance indicates a tendency for non-randomness or special cause variation. Usually a significance level (denoted as α or alpha) of 0.05 works well. A significance level of 0.05 indicates a 5% risk of concluding that a nonrandom pattern exists when the data are actually randomly distributed. If the p-value is less than or equal to the significance level, the null hypothesis can be rejected and it can be concluded that the data are not randomly distributed [8].

Table 1: *Summarized results for different run charts obtained through Minitab software*

Run No.	Yarn	Cam setting Point	p-value for clustering	p-value for mixtures	p-value for trends	p-value for oscillation	Special Cause Variation/Non Randomness type (If any)	Presence of astronomical data point (if any)
01	23.62 Tex Spun Polyester	0.7	0.500	0.500	0.974	0.026	Oscillation	--
02	23.62 Tex Spun Polyester	0.6	0.874	0.126	0.559	0.441	--	--
03	23.62 Tex Spun Polyester	0.5	0.771	0.229	0.228	0.772	--	--
04	23.62 Tex Spun Polyester	0.4	0.771	0.229	0.383	0.617	--	Yes
05	20.36 Tex Spun Polyester	0.7	0.500	0.500	0.559	0.441	--	--
06	20.36 Tex Spun Polyester	0.6	0.655	0.345	0.559	0.441	--	--
07	20.36 Tex Spun Polyester	0.5	0.645	0.355	0.117	0.883	--	--
08	20.36 Tex Spun Polyester	0.4	0.510	0.490	0.383	0.617	--	--

09	19.92 Tex Cotton	0.7	0.931	0.069	0.383	0.617	--	--
10	19.92 Tex Cotton	0.6	0.229	0.771	0.724	0.276	--	--
11	19.92 Tex Cotton	0.5	0.936	0.064	0.383	0.617	--	--
12	19.92 Tex Cotton	0.4	0.645	0.355	0.383	0.617	--	--
13	15.22 Tex Cotton	0.7	0.500	0.500	0.383	0.617	--	--
14	15.22 Tex Cotton	0.6	0.931	0.069	0.383	0.617	--	--
15	15.22 Tex Cotton	0.5	0.510	0.490	0.724	0.276	--	--
16	15.22 Tex Cotton	0.4	0.229	0.771	0.228	0.772	--	--

4. RESULTS AND DISCUSSION

Production Run No. 2-3 & 5-16

Here in every case the p-values for clustering, mixtures, trends and oscillation are all greater than α-value of 0.05. So, presence of special cause variation or non-randomness is absent for these production runs.

Production Run No. 1

The p-value for oscillation is less than α-value of 0.05, indicating that the process is not steady. It can be found in figures 4 & 5.

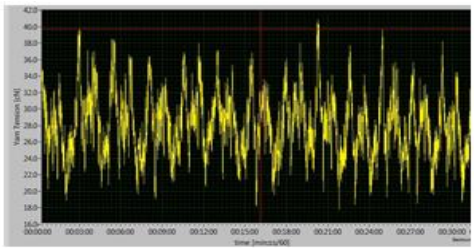


Fig. 4: *YIT waveform obtained for knitting production with 23.62 Tex Spun Polyester at cam setting 0.7*

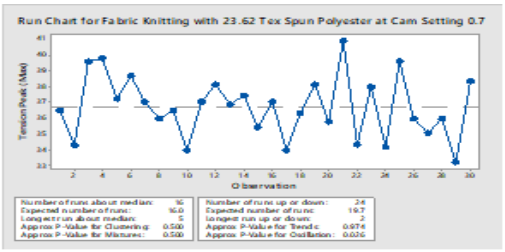


Fig. 5: *Run chart for production run no.01(30 sec)*

Fluctuation in maximum yarn input tension may be attributed to periodic variation of yarn delivery rate from the feed wheel. The cause-effect diagram (figure 6) for oscillation in yarn tension on a knitting machine may be depicted as:

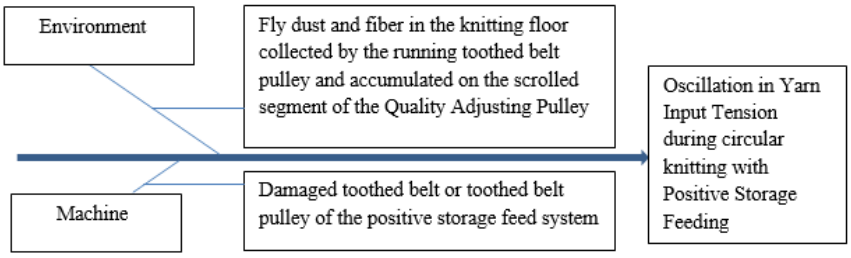


Fig. 6: *A cause-effect diagram for oscillating yarn input tension in a circular weft knitting machine with positive storage feeding*

In this particular case it was found that fluff deposition around the scrolled segments of quality pulley (figures 7 & 8) built non-uniform diameter, which in turn introduced some kind of periodic variation in yarn delivery from the feed wheel.

Fig. 7: *Quality Adjusting Pulley (QAP)-Top view*

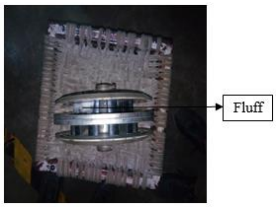


Fig. 8: *Fluff deposition inside QAP*

As the machine speed and cam setting remained same, such variation in yarn delivery resulted oscillation in tension peaks.

Production Run No. 4

Here the p-values for clustering, mixtures, trends and oscillation are all greater than α-value of 0.05. So, presence of special cause variation or non-randomness is absent here. However, observation no. 19 may be judged as an astronomical data point. It seems to be fleeting -a one-time occurrence of a special cause (figures 9 & 10)

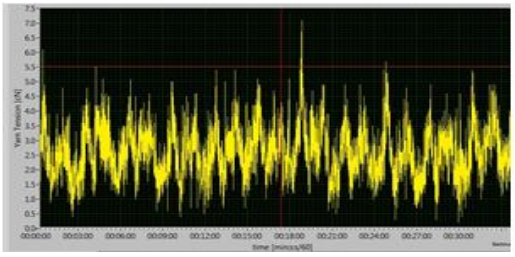


Figure 9: *YIT waveform obtained for knitting with 23.62 Tex Spun Polyester at cam setting 0.4*

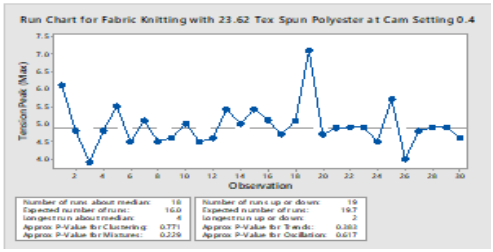


Figure 10: *Run chart for production run no.04 (1st 30 sec)*

To find out whether it comes back again or not - another run chart (figure 11), built with tension peak values for next 30 seconds, was examined.

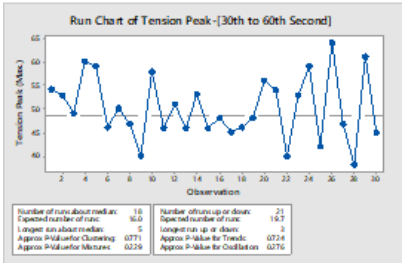


Figure 11: *Run chart for production run no. 04 (31st to 60th second)*

On the 2nd run chart built for fabric knitting with 23.62 Tex spun polyester at cam setting 0.4, the presence of any astronomical data point is not prominent. So, the sudden large shift of tension peak value at a particular observation on figure 5 was caused by a fleeting special cause -it was there and then it was gone.

5. CONCLUSION

The monitoring of performance of an industrial knitting machine is crucial for order planning and scheduling from both production and quality related aspects. Performance evaluation is also significant to find out any flaw of the running machine. In this research work an industrial knitting machine of an export-oriented knitting factory of Bangladesh was selected for its performance evaluation. The aim was mainly concentrated on discovering machine related flaws that could hamper its performance, ultimately the process performance. It was found that non-random patterns were absent in more than 85% of the evaluated production runs based on an alpha level (significance level) of 0.05. However the production run with special cause variation was due to environmental rather than machine related cause. Astronomical data point observed in another production run was of fleeting nature rather than periodical. Therefore the said knitting machine was quite flawless during the experimental production hours. Additionally IMR charts (Individuals-Moving Range Charts) may be consulted to get the complete information on the behavior of the overall processes.

ACKNOWLEDGEMENT

The authors are indebted to the Department of Mechanical Engineering of Bangladesh University of Engineering and Technology for sponsoring the work and to Padma PolyCotton Knit Fabrics Limited, Dhaka for providing access to its restricted manufacturing zone for carrying out the research work.

REFERENCES

[1] Catarino, A. P., Rocha, A. M., Monteiro, J. L. & Soares, F., "*A system for knitting process monitoring and fault detection on weft circular knitting machine*", presented at the World Textile Conference – 4th AUTEX Conference, Roubaix, France, 2004.

[2] Catarino, A. P., Rocha, A. M., Monteiro, J. L. & Soares, F. "*A new system for monitoring and analysis of the knitting process*", presented at the Mechatronics, 2004. ICM'04. Proceedings of the IEEE International Conference on, pp. 415-420, Istanbul, Turkey, 2004.

[3] Catarino, A. P., Rocha, A. M., Monteiro, J. L. & Soares, F., "*Knitting process surveillance using time and frequency analysis"*, presented at the Industrial Electronics, 2005.ISIE 2005. Proceedings of the IEEE International Symposium on, Volume: 4, Dubrovnik, Croatia, 2005.

[4] Catarino, A. P., Rocha, A. M., Monteiro, J. L. & Soares, F., "*Surveillance and control of the yarn input tension on circular weft knitting machines: new approaches*", presented at the Industrial Technology, 2004. IEEE ICIT '04. 2004 IEEE International Conference on, Hammamet, Tunisia, 2004.

[5] De Araújo, M., Catarino, A. and Hong, H., "*Process control for total quality in circular knitting*," AUTEX Research Journal, vol.: 1, no.: 1, pp.21-29, 1999.

[6] Run chart basics, https://support.minitab.com/en-us/minitab/18/help-and-how-to/quality-and-process-improvement/quality-tools/supporting-topics/run-chart-basics/, access date 27.12.2017

[7] MEASUREMENT: Interpreting Run Charts, http://qualitycompass.hqontario.ca/Documents/EN/Interpreting%20Run%20Charts.pdf, access date 27.12.2017

[8] All statistics and graphs for Run Chart, https://support.minitab.com/en-us/minitab/18/help-and-how-to/quality-and-process-improvement/quality-tools/how-to/run-chart/interpret-the-results/all-statistics-and-graphs/, access date 27.12.2017

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE SOFTWARE APPLICATION FOR MATHEMATICAL MODELLING OF TECHNOLOGICAL PROCESS IN TEXTILE INDUSTRY

IROVAN Marcela[1],TUTUNARU Irina[1], FARIMA Daniela[2], CIOCOIU Mihai[2]

[1] Technical University of Moldova, Faculty of Textiles and Poligraphy, blvd Stefan cel Mare si Sfant, 168, MD 2004, Chișinău, Republic of Moldova
E-Mail: marcela.irovan@gmail.com

[2]"Gheorghe Asachi" Technical University, Iasi, Romania

Corresponding author: IROVAN Marcela, E-mail: marcela.irovan@gmail.com

Abstract: *This paper presents a statistical processing program of the experimental data by a program a second degree central composite rotatable in order to obtain a mathematical model and the graphic representation thereof. The paper presents a software application, designed so that it can be used by any individual, without requiring specific knowledge of computer, because every step is accompanied by messages in clear. The application is used by students in the last year of study, by PhD. students and researchers, because it appeals to the deep knowledge of textile technology and mathematical statistics. In the first stage will select, after specific criteria, the values of those technological parameters that influence the outcome of the analyzed process, which are input values for OPTEX application (the acronym of expression OPTIMIZATION OF TEXTILE). Like output values, may be hourly production, yield, etc. The application generates a second degree mathematical relationship, which has in the right part of the equal sign, the technological parameters, denoted by x, accompanied by numerical coefficients and in the left part of the same sign, the result of the analyzed process, denoted by y. The application executes automatically the significance analysis of numerical coefficients and checks the veracity of the mathematical model. It is eliminated from relation, those coefficients whose values are insignificant. The accuracy of new model is show through a clear message and also is displayed the correct form of the mathematical relation. On demand are realized the graphics in 3D and 2D, which to allow finding, according to certain rules, the optimal values of the process and it obtain the calculated value of the output variable. With these technological parameters, in natural values, regulate the real process and it obtained the measured value of the output variable. The measured value obtained is compared with the value calculated and if the difference between these is acceptable, it considered that the analyzed textile process is optimized. If this difference is considered unacceptable, it resumes the OPTEX application with other input values. After completing the entire program data can be saved as independent files or can list printed in alphanumeric reports (text) or graphics. The "Optex" is easy to operate, requires a little time to perform processing of experimental results and has the advantage of being based on the algorithm used to solve a mathematical model manually. The application performed can be a useful tool in empirical studies on optimization of technological processes.*

Key words: *technological parameters, textile process, regression coefficients, software, mathematical modelling.*

1. INTRODUCTION

Textile technological processes depend on a multitude of technological parameters. The management of such process that gives the best results is a laborious operation. Choosing the group of technological parameters which to ensure high yields and obtain proper quality cannot be achieved empirically, based only on personal experience. It requires the use of scientific methods to ensure the selection of technological parameters to achieve the objective. Making research using mathematical methods planning and analysis of experiment eliminates the passive methods of research and increase scientific activities efficiency. Used mathematical methods for planning the experiment provide increased manoeuvre opportunities for researcher, facilitates problem formulation, experimental results have a clear and convincing nature and permit a rapid interpretation of the results generated by the mathematical model. Interpretation of the mathematical model to optimize the process require the experience of researcher, because verification of the veracity model it does by adjusting the actual process parameter values provided by basic theoretical elements.

This paper presents a statistical processing program of the experimental data by a program a second degree central composite rotatable in order to obtain a mathematical model and the graphic representation thereof. [4]

2. GENERAL INFORMATION

Using mathematical methods of planning the experiment provides increased opportunities for maneuver researcher facilitates problem formulation, experimental results gives a clear and compelling character and rapid interpretation of results.

Active method of developing mathematical and statistical models involves obtaining experimental data after performing experiments directed.

To determine the functional relationship runs a number of experiences ordered in a certain way, and all these experiences is an experimental program (equation 1).

$$Y=f(x_1, x_2, \ldots x_k) \quad \textbf{(1)}$$

For each independent variable (technological parameter of the process), in the considered experimental region, it sets a basic level (z0I) and a variation step / day. And it calculates specific values of experimental program. The addition the variation step to base level it obtain the upper level and the diminish of base level with variation step it obtain lower level value of technological parameter. The transition from the natural values of the independent variables in coded values is performed by transforming the variable according to the relation 2.

$$x_i = \frac{z_i - z_{0i}}{\Delta z_i} \quad \textbf{(2)}$$

The coded value Xi of the parameter; Day - the natural value of the parameter;
z_0 - the natural value of the parameter in the central region of experiment
z_i - the natural value of the step of variation for the parameter

With the encoded values of parameters it complement experimental matrix, the number of experiments in the array must exceed the number coefficients of the mathematical model to be determined. For example, the experimental matrix for two variables is the form [1, 2, 3,6].

Table 1: The experimental matrix for the two independent variables

No. Crt.	Independent variables				Dependent variables
	X_1		X_2		Mesured value
	cod	real	cod	real	$Y_{mesured}$
1	-1		-1		
2	+1		-1		
3	-1		+1		
4	+1		+1		
5	-1,414		0		
6	+1,414		0		
7	0		-1,414		
8	0		+1,414		
9	0		0		
10	0		0		
11	0		0		
12	0		0		
13	0		0		

The coefficients of equation 3, is calculated by the method of least squares.

$$y = b_0 + \sum_{1}^{k} b_i x_i + \sum_{\substack{1 \\ i \neq j \\ j=i+1}}^{k} b_{ij} x_i x_j + \sum_{1}^{k} b_{ii} x_i^2 \quad \textbf{(3)}$$

The coefficient values are tabulated according to the literature [1-4].
To verify the significance of the model coefficients b_0, b_i b_{ii}, b_{ij} using Student test [1-4]
The calculating of confidence interval coefficients is done with equation 4.

$$|\Delta b_i| = t_{\alpha;n} s_{bi} \quad \textbf{(4)}$$

Where: $t_{\alpha,n}$ - Student criterion for materiality α and n number degrees of freedom;
S_{bi} - standard deviation of the regression coefficient.

The significance of regression coefficients check if the absolute value of the coefficients *bi* to be greater from confidence interval (equation 5).

$$|b_i| \geq |\Delta b_i| \quad \textbf{(5)}$$

If the above relation is not satisfied, the calculated regression coefficient is insignificant, that coefficient is removed from the model. The next step is the verification of the model adequacy. The objective of this verification is to determine the ability of the model to represent, with the probability chosen, modelled process and if yes, it will be used for process optimization study analyzed. Hypothesis about the adequacy of the model is checked using the test Fischer, whose calculated value is determined by the relation 6.

$$F_C = s^2_{conc} / s^2_0 \quad \textbf{(6)}$$

Where: S^2_{conc} – according dispersion; s^2_0 - central dispersion.

The mathematical model is appropriate when the relation 7 is satisfied:

$$F_C < F_{\alpha, \mu 1, \mu 2} \quad \textbf{(7)}$$

Where: α is level of significance. μ_1, μ_2 - number of freedom degrees of the dispersions.

3. DESCRIPTION THE SOFTWARE APPLICATION

The software application "Optex" is made in Delphi, version 3.0. Basic software required for running the program is Windows. Minimum space allocated to the program is 518KB.

The transition from one stage to another program is done with the mouse; the data are entered in the respective boxes. After completing the entire program data can be saved as independent files or can list printed in alphanumeric reports (text) or graphics.

The program is easy to operate, requires a little time to perform processing of experimental results and has the advantage of being based on the algorithm used to solve a mathematical model manually.

4. USING MANUAL WITH EXEMPLES

The program starts by loading from the CD or by icon's selection. Running the program beginning with opening the window conversational "initial data" (figure 1) which selects the number of independent variables in the X box, and is confirmed by pressing the button "Select X". The "Reset X" isused to reset the initial data, where appropriate. After confirmation of choice of the number of independent variables X, are introduce the names and values of the technological parameters , independent variables (the base value and the variation step), and after the experimental matrix is filled in with experimental values obtained $y_{mes.}$ in each box of the array. Validation of the values $y_{mes.}$ is made by pressing "Enter".

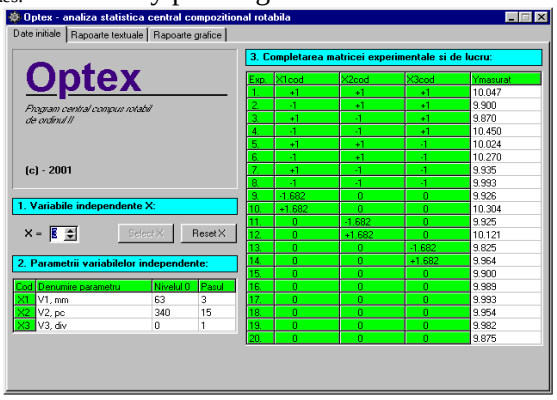


Fig. 1: *The window conversational "initial data"*

Proceed to next step for the calculations of the coefficients of the mathematical model by opening the table "textual reports," which has three options. The option „technological parameters-independent variables" (figure 2) shows the table with coded values and natural values of the independent variables-technological parameters for the five levels of the experimental matrix.

The table "coefficients of the regression, the adequacy of model" (figure 3) shows the general formula for the model for the selected number of independent variables as well as numerical values of the regression coefficients, the verification of their significance and verification of adequacy of the mathematical model.

The table „Experimental and work Matrix" (figure 4) shows the measured and calculated values of the dependent variable Y and the percentage deviations between these.

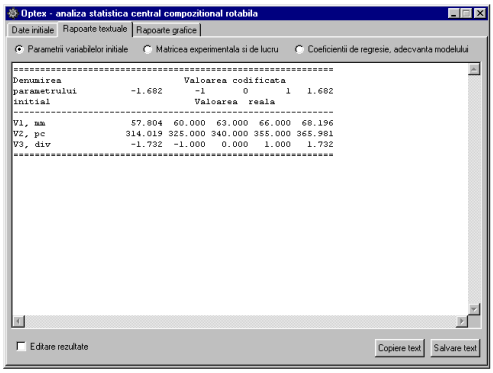


Fig. 2: *The option „technological parameters-independent variables"*

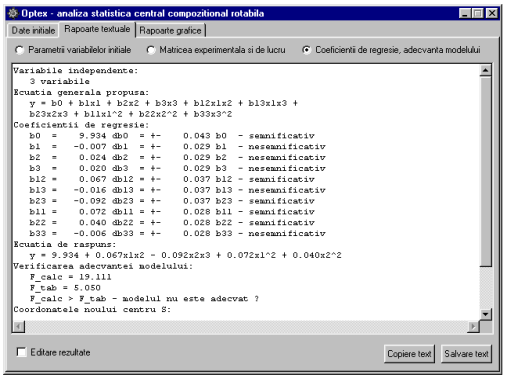


Fig. 3: *The values of regression coefficients, their significance and adequacy of the model*

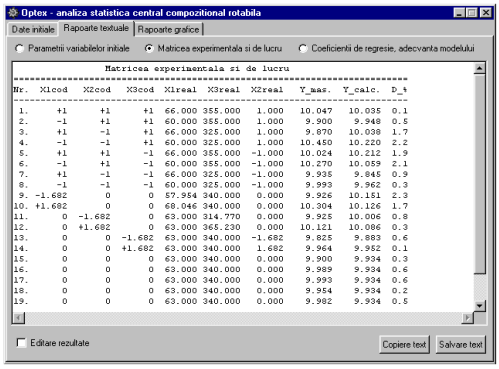


Fig. 4: *Experimental and work matrix*

It offers a choice of an editing mode (box "Edit Results"), copy the text or save the text (button "Copy Text" or "Save text"). Open the window "Graphical reports" has the effect of generating a response surface 2D and 3D graphic (figure 5).

The box from base from Figure 5 "Changing significance of regression coefficients" gives the user the opportunity to decide on changing significance of one or more regression coefficients. Box "Cancelling independent variables" provides the ability to generate response surfaces 3D and 2D for any combination of two independent variables by cancelling other independent variables (the cancellation of coded value is equivalent with an optimal natural value). The buttons "Copy

3D", "Save 3D", "Copy 2D", "Save 2D", have the same effect like from last step and the "Refresh "button allows returns to previous version for changing the significance of regression coefficients.

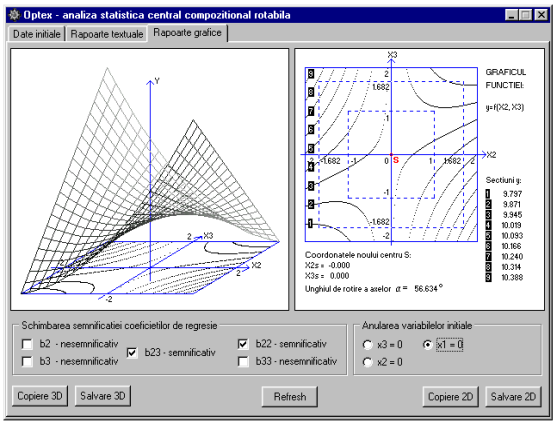


Figure 5: *The graphics 3D and 2D*

5. CONCLUSIONS

This paper presents a software application OPTEX - a statistical processing program of the experimental data by a program a second degree central composite rotatable in order to obtain a mathematical model and the graphic representation thereof. OPTEX program allows mathematical modelling of a technological process, highlighting trough the values and signs of numerical coefficients, the influence of technological parameters as independent variables on the dependent variable. Also, the program OPTEX allows optimization of the technological modelled process, by analyzing regression equation and by analyzing 2D and 3D which it generates upon request [4].

The program allows mathematical modelling of the technological process in any field. The application allows students in knowledge modelling process. Optimal nature of the dependent variable is obtined by comparing the calculated and measured values, obtained after adjusting the values of the new parameters of technological process. [5,6].

REFERENCES

[1] R. Mihail *"Introducere în strategia experimentală cu aplicaţii în industria chimică"*, Ed. Ştiinţifică, Bucureşti, 1976.

[2] D. Taloi *"Optimizarea proceselor tehnologice",* Ed. Academiei Române, Bucureşti, 1987.

[3] M. Ciocoiu *"Bazele statistico–matematice ale analizei si controlului calitatii in industria textila"*, Ed Performantica, Iasi, 2002, ISBN 973-8075-31.

[4] M. Irovan *"Aspecte teoretice si experimentale privind optimizarea proceselor de proiectare constructiva a produselor de imbracaminte exterioara pentru barbati",* Teza de doctorat, Iasi, 2002.

[5] M. Irovan, M. Ciocoiu *"Optimizarea parametrilor constructivi ai produselor de îmbrăcăminte."* Revista „Meridian ingineresc", Chişinău: Editura U.T.M., nr. 4/2004. pag. 78-81.

[6] M. Ciocoiu, *Optimizarea Proceselor Tehnologice Textile* / Mihai Ciocoiu, Iaşi: Performantica, 2002. ISBN 973-8075-30-0.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

100% BIO-BASED MICROENCAPSULATED PHASE CHANGE MATERIALS AS REGULATOR OF TEMPERATURE OF TEXTILE FABRIC

LOPEZ HERNANDEZ Oscar Erick[1, 2], HERCZYŃSKA Lucyna[1,2], BONET-ARACIL Marilés[2], BOU-BELDA Eva[2], GISBERT-PAYÁ Jaime[2]

[1] Lodz University of Technology, 116 Żeromskiego, 90-924 Lodz, Poland

[2] Universitat Politècnica de València, Departamento de Ingeniería Textil y Papelera, Pl. Ferrándiz y Carbonell s/n, 03801, Alcoy, Spain

Corresponding author: BONET-ARACIL Marilés[2], E-mail: maboar@txp.upv.es

Abstract: *Phase change materials (PCM) are very useful in many fields due to their capacity to absorbe and release heat energy when it is necessary. In this paper it was managed to microencapsulate 100% biodegradable PCMs to apply them into textile fiber in order to regulate its temperature. The microencapsulation method used in the present work was solvent evaporation with oil-in-water emulsification. Scanning Electron Microscope (SEM) was conducted to confirm the successful microencapsulation. Differential Scanning Calorimeter (DSC) was used to evaluate thermal properties of the core material and also efficience of the microencapsulation. Coconut oil and bee wax were used as PCM due to their melting point (Coconut oil - 23°C, Beeswax – 60°C) and, Polylactide (PLA) and Ethyl cellulose (EC) as shell materials because of their biodegradable nature. The microPCMs were applied onto the non-woven PLA with the help of a binder which in this case was calcium alginate and chitosan and then it was confirmed by SEM the microcapsules were inside the fabric and stick them to it. The thermal regulating properties of modified textiles were investigated by an IR camera. The results obtained from thermal analysis of samples showed that the temperature of the unmodified sample decreases faster than the modified sample.*

Key words: *Coconut oil, bee wax, polylatide, ethyl cellulose, calcium alginate, chitosan.*

1. INTRODUCTION

Phase Change Materials (PCMs) are substances that can absorb and release large quantity of latent heat energy during the change of their phase. This phase change depends on the specific melting point of the PCM and with it calculates the enthalpy of the reaction. Phase change materials (PCM) can be employed in many fields because of their capacity to absorb and release energy when it is necessary.

There are many types of organic PCM with phase change temperatures from -5 ° C to 190 ° C. [1-5] Speaking of thermal comfort applications in textiles or building, PCM's and their mixtures are used with phase change temperatures between 18 ° and 65 ° C.

1.1. Solvent Evaporation

In this microencapsulation technique, the polymer must be dissolved in a volatile solvent, and mixed in a water-based emulsifying solution, in which the solvent must be evaporated, releasing

the polymer that encloses the core material also dissolved in the solvent. This technique is widely used in the pharmaceutical industries. Initially the coating solution is prepared by dissolving the coating polymer in a volatile solvent that is immiscible in the emulsifier solution. After that depending on the nature of the core material (hydrophobicity or hydrophilicity) it is dissolved or dispersed in the polymeric coating solution. The mixture is added to the emulsifying solution with continuous stirring until the solvent is distributed in the aqueous phase and evaporated. At this point the material coat contracts around the core material and results in hardened microspheres [6].

1.2. Textile and clothing applications of PCMs.

Textile products and clothing have been fundamental materials for the human being to feel comfortable and protected against certain external factors and thus ensure that the physical conditions of our body are adequate for survival. This protection can comprise a series of functions, maintaining the appropriate environment for the body [7-13]. One of the main functions of clothing is to protect the body from the climate by creating a microclimate-stable next to the skin to support the system of thermal regularity of the body for which the textile fibers must have certain properties.

1.3. Incorporation of microencapsulated PCMs to fibers, fabrics and foams.

The application of PCM in textiles brings many advantages for example: they are very easy to apply to textiles, fabrics, nonwovens and fibers, they usually do not affect the properties that the textile already has, they have a shelflife on a garment that permits normal fabric-care processes, they promote mixing of core materials, they reduce the reactivity of the PCMs with the external environment, they decrease the evaporation of the core material to the outside environment, they increase the area of heat transfer and they provide a constant volume in the core material [8,14-15]. The composition of the material shell and the amount of microcapsules added to the structure are the main factors that provide a suitable management in the textile product. When a sufficient amount of microPCM is added to a textile structure as a suitable component for coating of fabric, fibers, yarns and breathable foams a suitable thermal management in the textile product, which satisfies the end-use needs for which it was created. These will continue to function as long as the coating or the fibers remain intact otherwise the properties provided will be lost [16-17].

2. EXPERIMENTAL.

In the present paper it is shown the procedure to microencapsulate organic phase change material (bee wax and coconut oil) by interphase precipitation during evaporation of the solvent from water/oil emulsion. 100% biodegradable polymer materials were used as shell (Poly(lactic acid) (PLA) and Ethyl cellulose (EC)).

2.1 Materials.

- Coconut Oil as phase change material - commercial product.
- Beeswax as phase change material - commercial product.
- Different sort of Poly(lactic acid) (PLA) as shell material – a commercial product of NatureWorks®LLC
  - PLA 4060D - a amorphous resin
  - PLA 6201D - a thermoplastic fiber-grade resin
  - PLA 6400D - thermoplastic fiber-grade resin
- Ethyl cellulose (EC) as shell material - a commercial product manufactured by Aldrich (4cP viscosity measured for 5% toluene/ethanol 80:20 solution).

- Dichloromethane, chloroform, ethyl acetate were used as organic solvent - a commercial product manufactured by Chempur.
- Poly(vinyl alcohol) (PVA) (Mw = 1000, manufactured by Aldrich) as a surfactant/emulsifier.
- For the coating of the PCM microcapsules on textile a coating binder was used as follows:
  - Sodium alginate (ALDRICH product of 15-20 cP viscosity, (1% solution in H_2O, temperature 25°C)) at a 1,5% w/w. concentration of in aqueous solution, and 10% w/w. calcium chloride dihydrate (Chempur) solution – as a coagulant.
  - Chitosan (ALDRICH product of 200-800 cP viscosity, (1 wt.% in 1% acetic acid, 25°C) at a 1% w/w concentration of in 1% acetic acid solution.
- Polylactide nonwoven (a commercial product manufactured by FET Taiwan, SLN-2539W5, 1,5 den/38 mm FB) was applied for the modification with PCM microcapsules.

2.2. Methods and results

Microcapsules preparation.

Microcapsules with polylactide or ethyl cellulose shell were obtained by solvent diffusion from the emulsion. The oil-in-water emulsion was obtained by homogenization of the organic phase (polylactide or ethyl cellulose and coconut oil or bee wax in organic solvent) in the aqueous phase containing a surfactant/emulsifier – 1% solution of poly(vinyl alcohol). In this technique, a poly(vinyl alcohol)(PVA) emulsifier is used to reduce the interfacial tension between the dispersed droplets and the continuation phase, in addition to protecting the droplets from aggregation.

The microcapsules were created after complete removal of the solvent from the droplets by evaporation during the mixing process. The manufactured microcapsules were washed, decanted and dried. Among the effective parameters affecting the microcapsule preparation process can be mentioned: the type and amount of polymer used as the shell layer, the type and amount of core material, the rate of homogenization or the type of solvent used.

Scanning Electron Microscopy (SEM).

The surface structure of the obtained microcapsules was analyzed using microphotography obtained by means of the High-resolution electron microscope Nova Nanosem 230 and Scanning electron microscope JSM-5200LV (JEOL). The observations were carried out under high conditions at 10 kV and different magnifications.

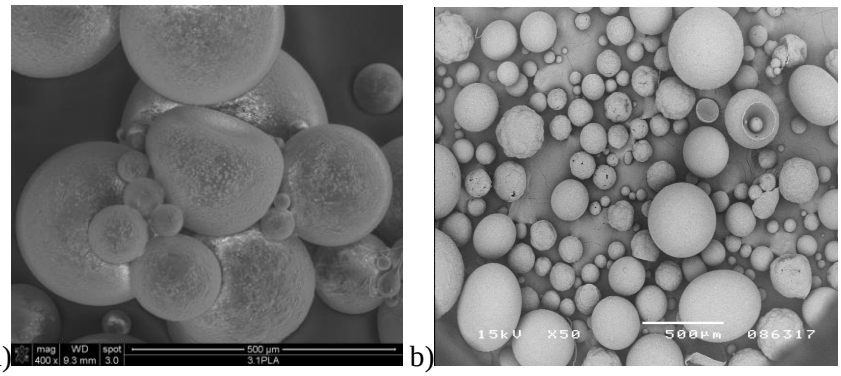


Fig. 1: *SEM images of: (a) sample COPLA3 made with PLA 4060D and (b) sample COPLA14 made with PLA 6201D.*

This technique it was also used to make the measurements of the microcapsules diameter.

Differential Scanning Calorimeter (DSC).

DSC measurements were done on a differential calorimetry of TA Instruments Thermal Analysis -- DSC Standard Cell RC equipped with a refrigerated cooling system. DSC analyses were conducted under a nitrogen atmosphere and the temperature interval cycle was set to -40 - 40°C (Coconut Oil) or 0 – 80oC (Bee wax) at 10°C/min. The tests were made in order to identify the thermal capacity and phase change enthalpy values. The latent heat capacity of the Bio-based PCM microcapsules was determined by calculating of the area under the peaks that represent the solid–solid and solid–liquid phase transitions. Moreover DSC gave the melting point of the core materials thereby it could know the temperature which they would start to absorb or release heat energy depending on the cooling or heating process.

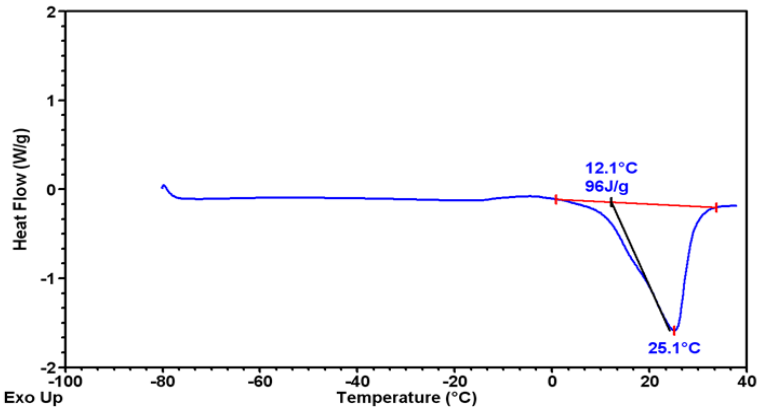


***Fig. 2**: DSC thermograms of pure coconut oil: heating cycle.*

Infrared thermography.

Infrared thermography was used to investigate the thermal changes in the fabric, i.e. the temperature distribution but also the thermoregulation effect. Thermo-graphic camera is used to measure the amount of heat energy that some material releases and the most important thing is how it decreases or increases the temperature of that material after time. In addition, this technique provides visual information of the temperature changes that are occurring in the material that has been exposed to temperature, either low or high.

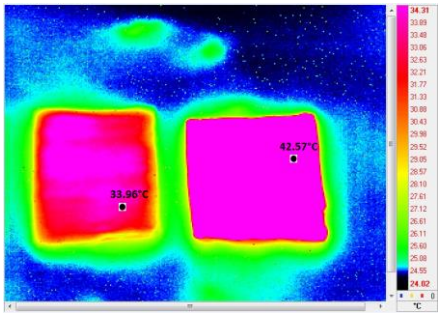


***Fig. 2:** IR images of non-woven PLA unmodified (sample on the left) and modified with COEC3 (sample on the right) at 0 sec.*

3. CONCLUSIONS

The important contribution in this work is the creation of a new technology of textile PCM application being environmental friendly with 100% biodegradable materials, useful and also inexpensive. Coconut oil and bee wax are candidates for core as temperature regulator due to their capability to absorb and release large amount of heat energy by changing their phase. It is possible to microencapsulate these two organic PCMs in polylactide (PLA) and ethyl cellulose (EC) as well. PLA as shell material is the best option due to this polymer is enough resistance to the normal situations woven or non-woven textile materials are exposed. Ethyl Cellulose (EC) is also a good option due to its biodegradable properties. The microcapsules were obtained as a result of interphase precipitation during evaporation of the solvent from water/oil emulsion.

The method used to obtain microcapsules allowed to obtain microcapsules with an average diameter of 26 μm. This indicates that the microcapsules are tiny and easy to coat onto the fabric surface.

The thermal regulating properties of modified textiles were investigated. The results obtained showed that the temperature of the unmodified sample decreases faster than the modified sample, which means that the modified sample can absorb more thermal energy and stay in it for a longer time due to the microencapsulated phase change material that is inside. Modified nonwovens with microcapsules containing coconut oil or bee wax provide cooling effect, which confirms the effectiveness of the modification.

REFERENCES

[1] J.K. Choi, J.G. Lee, J.H. Kim, H.S. Yang, Preparation of microcapsules containing phase change materials as heat transfer media by in-situ polymerization, J. Ind. Eng. Chem. 7 (2001) 358–362.

[2] C. Alkan, Enthalpy of melting and solidification of sulfonated paraffins as phase change materials for thermal energy storage, Thermochim. Acta 451 (2006) 126–130.

[3] B. Zalba, J. MaMarin, L.F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, Appl. Therm. Eng. 23 (2003) 251–283.

[4] V.V. Tyagi, D. Buddhin, PCM thermal storage in buildings: a state of art, Renew. Sust. Energ. Rev. 11 (2007) 1146–1166.

[5] A. Agbossou, Q. Zhang, G. Sebald, D. Guyomar, Solar micro-energy harvesting based on thermoelectric and latent heat effects. Part I: theoretical analysis, Sens. Actuator A: Phys. 163 (2010) 277–283.

[6] M. Michalak, M. Felczak, B. Wi¸ecek, A new method of evaluation of thermal parameters for textile materials, in: 9th International Conference on Quantitative InfraRed Thermography, Krakow, Poland, 2–5, 2008.

[7] B. Boh, E. Knez, M. Staresinic, Microencapsulation of higher hydrocarbon phase change materials by in-situ polymerization, J. Microencapsul. 22 (7) (2005) 715–735.

[8] X.X. Zhang, Heat-storage and thermo-regulated textiles and clothing, in: T. Xiaoming (Ed.), Smart Fibres Fabrics and Clothing, Woodhead Publishing and CRC Press LLC, England, 2001, ISBN 1-85573-546-6, pp. 34–79.

[9] D.P. Colvin, Y.G. Bryant, Protective clothing containing encapsulated phase change materials, ASME: Adv. Heat Mass Transf. ASME-IMECE 362 (40) (1998) 123–132.

[10] Y.G. Bryant, D.P. Colvin, J. Driscoll, J. Mulligan, Thermal insulating coating employing microencapsulated phase change material and method, PCT patent WO9941067A1, Triangle Research and Development Corporation, 1999.

[11] O. Pamuk, Clothing comfort properties in textile industry, E J. New World Sci. Acad. 3 (1) (2008), Article Number: A0051.

[12] Y.J. Ren, J.E. Ruckman, Condensation in three-layer waterproof breathable fabrics for clothing, Int. J. Clothing Sci. Tech. 16 (3) (2004) 335–347.

[13] B. Pause, Development of heat and cold insulating membrane structures with phase change material, J. Coated Fabric 25 (1995) 59–68.

[14] M.M. Farid, A.M. Khudhair, S.A.K. Razack, S. Al-Hallaj, A review on phase change energy storage: materials and applications, Energ. Convers. Manage. 45 (2004) 1597–1615.

[15] J.L. Zuckerman, R.J. Pushaw, B.T. Perry, D.M. Wyner, Fabric coating containing energy absorbing phase change material and method of manufacturing, US Patent 6,503,976 (2003), available from

[16] H. Kumano, A. Saito, S. Okawa, S. Takeda, A. Okuda, Study of direct contact melting with hydrocarbon mixtures as the PCM, Int. J. Heat Mass Transf. 48 (2005) 3212–3220.

[17] M. Jiang, X. Song, G. Ye, J. Xu, Preparation of PVA/paraffin thermal regulating fiber by in-situ microencapsulation, Compos. Sci. Technol. 68 (10–11) (2008) 2231–2237.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

IMPROVEMENT OF THE ERGONOMIC FUNCTION – AN ESSENTIAL CONDITION FOR ENSURING KNITTED PRODUCTS QUALITY

LUTIC Liliana

"Gh. Asachi" University, Faculty of Textile Leather and Industrial Management, Knitting and Ready – Made Clothing Department, 29 Dimitrie Mangeron Street, 700050, Iași, România

Corresponding author: Lutic Liliana, E-mail: llutic@tex.tuiasi.ro

Abstract: *The evaluation products quality in general and particularly in knitted fabrics starts with determining their most important quality characteristics as an initial step in the multicriterial analysis used to establish the optimum ratio between the requirements of the users and the product's quality.*
The behaviour of the knitted products during use is essential for the beneficiaries, the ergonomic-constructive characteristics correlated with the comfort characteristics being used in the product quality evaluation. The quality evaluation implies establishing the representative characteristics as well as applying the standardized testing methods, in order to choose the optimum knitted variants for the required destination.
Extensibility is an essential quality characteristic for form – fitting knitted products or areas of the product, that during dressing – undressing or wearing process, must modify in a significant and positive way their initial dimensions. For these reasons it can be affirmed that the ergonomic function of a knitted product is determined greatly by extensibility. Measuring extensibility on two stress directions is a compulsory test effectuated in order to properly design knitted products. For this purpose, in knitted products, the minimal and maximal extensibility areas are established, for a precise selection of knitted structure, structural parameters as well as the position of the product elements.
The paper encompasses an experimental study on the comparative evaluation of the extensibility of eight knit variants used in the production of outer garments in order to assess their ergonomic function and implicitly the ability to guide the quality of the knitted products during their design.

Key words: *product, knitted, evaluation, quality, extensibility, ergonomics*

1. INTRODUCTION

One of the most important functions of a garment product is the constructive – ergonomic one, which refers to:

- the ability of the product to conform to the shape and dimensions of the human body (regardless of the state - static or dynamic in which it is at a certain moment);
- providing easy dressing - undressing of the product;
- the ability of the product to allow freedom of body movement.

Extensibility is an essential quality characteristic for form-fitting knitted products or areas of the product (collars, accents, cuffs, welts), that during dressing-undressing or wearing process, must modify in a significant and positive way their initial dimensions [1, 2, 5]. For these reasons it can be affirmed that the ergonomic function of a knitted product is determined greatly by extensibility.

2. GENERAL CONSIDERATIONS

Both during the technological processing and during the wearing and household maintenance, textile products are subjected to a set of stresses, of which the non-destructive ones (where the driving force is less than the breaking load of the P < PR specimen) highlight fatigue resistance of the product.

Of the most common non-destructive stresses during use, unidirectional or multidirectional stretching (static, dynamic, or cyclical) **highlights the extensibility and elasticity of textile products**.

The domain of unidirectional stretching stress is divided into:

- the field of elastic stresses (which cause reversible deformations);
- field of plastic or retentive stresses (which produce irreversible deformations); in turn, the field of plastic deformations is divided into non-destructive plastic deformations and destructive deformations completed by breaking the material.

In figure 1 the force – elongation diagram is presented in which three domains are marked:

- elastic elongation domain that reveals the elasticity ε_{el} (point A abscissa is the limit of the elastic domain);
- extensibility domain ε_{ex} (between point A abscissa and point B abscissa);
- plastic elongation domain ε_{p} (after point B abscissa).

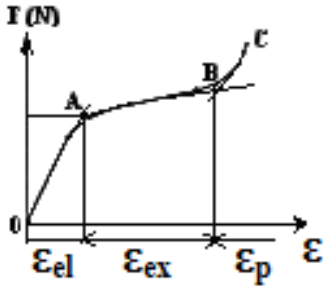


Fig. 1: *Force – elongation diagram*

Knitted fabrics, in comparison to other textile surfaces (woven or unwoven materials) have a greater capacity to elongate on the direction of a stretch strain, as a result of the migration of the yarn in the stitch.

Also knows as structural deformity, **extensibility** is the capacity of a knitted material to elongate under the action of a static strain, whose intensity is at the limit between the non-destructive plastic strain domain and the destructive one [1].

The extensibility of a knitted fabric or product is determined by:

- yarn characteristics (nature, extensibility grade, surface aspect, bending rigidity, yarn – yarn friction coefficient);
- knitted characteristics (structure, count, compactness coefficient);
- parameters of the finishing process applied to the knitted (temperature, strain).

By contrast to extensibility, elasticity is the capacity of the material (especially knitted) to store up reversible energy during static stretching loads and to revert to its initial dimension after ceasing the elastic stretching loads. If the knitted fabric returns completely to its original dimensions, the deformation is elastic. In the case of a partial recovery, it means that the stretching force exceeded the elastic domain – is the case of extensibility.

The extensibility of a knitted must be analyzed in relation with its elasticity.

By combining the extensibility and elasticity values, we get four possible variants of knitted fabrics:

- knitted fabrics with high values for extensibility and elasticity (recommended for collars, fittings at the base of neck, hose gusset, fitting bands, form-fitting products);
- knitted fabrics with high extensibility and low elasticity (that deform under stretch strains and have a low quality level);
- knitted fabrics with low values of both elasticity and extensibility (compact structures made out of very low elasticity yarns); recommended for products that keep their shape and dimensions during wearing.
- knitted fabrics with low extensibility but high enough elasticity (compact structures that present a low elongation on the strain solicitation and return to their initial shape and dimensions because of the high elasticity yarns [1, 2, 4].

In the design of a knitted product, the extensibility values on different directions determine the choice of structure and structural parameters, the shape, dimensions and position of the reference components of the knitted product, the type and parameters for the applied seams, as well as the finishing operations parameters.

3. EXPERIMENTAL METHODS OF EVALUATING THE EXTENSIBILITY

For studying the fabric behaviour under stretching, with a force less than the breaking load, three methods may be used with specific equipment:

- standardized method based on textile relaxometer;
- dynamometric method (on textile dynamometer);
- the method based on the use of Fryma extensometer.

3.1 Standardized method

This method involves straining the test sample, with standard dimensions, on a textile relaxometer and calculating the maximum deformation εt1, the elastic deformation ε / and the plastic deformation ε // (with formulas 1, 2, 3):

Relative elastic elongation $$\varepsilon^{/} = \frac{l_t - l_r}{l_0} \cdot 100 = \frac{\Delta l^{/}}{l_0} \cdot 100 \ [\%] \quad \textbf{(1)}$$

Relative retentive elongation $$\varepsilon^{//} = \frac{l_r - l_0}{l_0} \cdot 100 = \frac{\Delta l^{//}}{l_0} \cdot 100 \ [\%] \quad \textbf{(2)}$$

Relative total elongation $$\varepsilon_{t1} = \frac{l_t - l_0}{l_0} \cdot 100 = \frac{\Delta l_{t1}}{l_0} \cdot 100 \ [\%] \quad \textbf{(3)}$$

where: 1_0 - represents the initial length of the specimen;

l_t - the final length of the specimen under the action of the deformation force;

l_r - the length of the specimen after removal of the force.

3.2 Dynamometric method

The method implies straining a test sample with standard dimensions on a dynamometer that has the capacity to record an effort - elongation diagram. By analyzing this diagram (figure 1) we can determine the point (B) that divides the curb into 2 zones: low rigidity zone (0 – B) – coincides with the extensibility domain; high rigidity zone (B – C) – coincides with the domain in which stretches are destructive.

3.3 Method based on the use of Fryma extensometer

This method is used to determine the extensibility of knitted materials under the action of a constant stretching force. The purpose of the test is to establish the degree of stretching and rebound of a material with the precision required by British Standard BS 4292/1968 [3].

The device allows measuring the extensibility of knitted with a maximum value of 300%, or of wefts with a maximum elongation of 50%.

The Fryma extensometer scheme is shown in Figure 2.

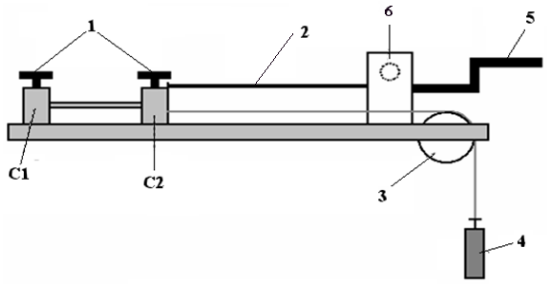


Fig. 2 *Construction of Fryma extensometer*
C1 – fixed clamp; C2 – moving clamp; 1 – tee screws; 2 – screw shaft; 3 – sustain wheel of the weighted cable 4; 5– winding handle; 6 – quick return button

4. EXPERIMENTAL DETERMINATIONS OF EXTENSIBILITY

In this paper were taken into study eight variations of knitted structures, of different counts, made out of 100% cotton yarns, with 19 tex linear count, intended for exterior clothing products. The extensibility testing was done on two directions (stitch rows and stitch wells respectively), with the use of the Fryma extensometer.

The samples with standard dimensions (75x85 mm), cut on the two directions were acclimated and put under a 3 daN force stretch load. The determinations were executed on a 5 samples specimen (on each direction), for each structure analyzed, after which the medium values of extensibility were calculated, as read on the machines graded scale.

In table one are presented and characterised the adopted structure variants.

Table 1: *Characterization of knitted structures variants*

Variant number	Analyzed structure	Adapted raw material	Medium value of extensibility [%]	
			On the direction of stitch wells	On the direction of stitch rows
V1	**Jersey**	**100% Cotton Ttex = 19**	27	98
V2	**Jersey with miss stitches**		24	67
V3	**Plain pique**		25	117
V4	**Rib 1:1**		28	240
V5	**Rib 2:2**		34	262
V6	**Rib 1:1 with miss stitches**		20	190
V7	**Rib 2:2 with tuck stitches**		29	282
V8	**Interlock**		14	163

The comparative analysis of extensibility in two directions for the analyzed and tested structures is illustrated in Figures 4, 5, 6, 7, 8.

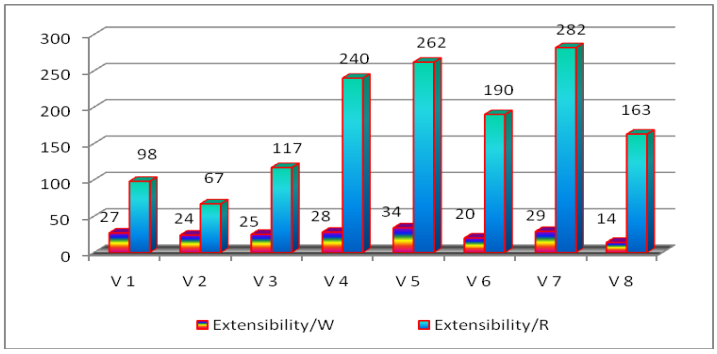


***Fig. 4**: Comparative variation of extensibility for the eight knitted variants on the directions of stitch wells and stitch rows.*

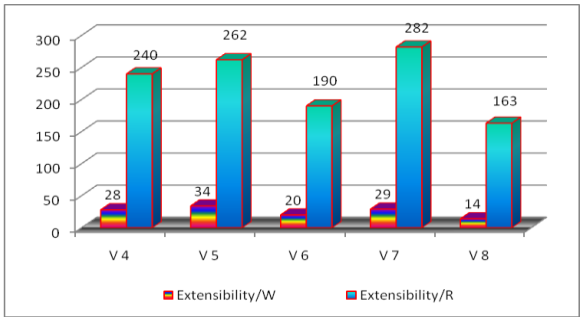


***Fig. 5**: Comparative variation of extensibility for the knitted variants rib and interlock*

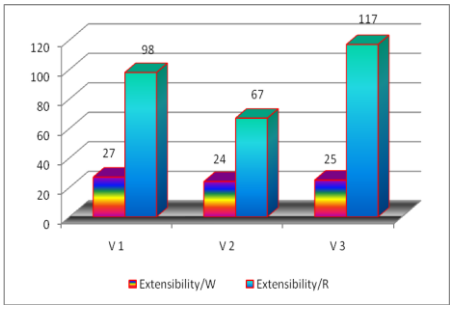


***Fig. 6**: Comparative variation of extensibility for the knitted variants type jersey.*

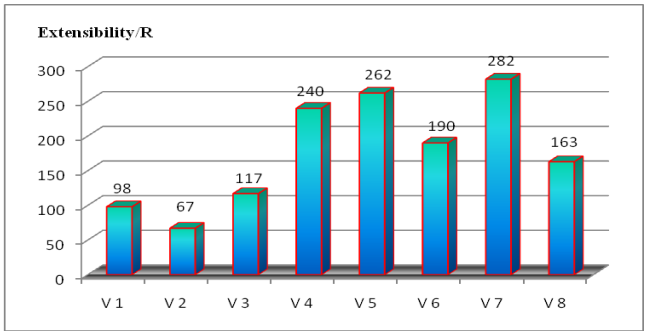


***Fig. 7**: The variation of extensibility on the direction of stitch rows in the eight structure variants*

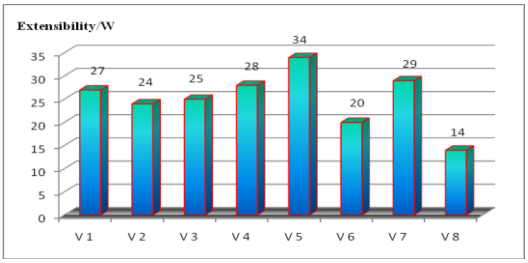


***Fig. 8**: The variation of extensibility on the direction of stitch wells in the eight structure variants*

Results interpretation

Based on the comparative analysis of extensibility for all the knitted variants analyzed, the following aspects were observed:

- significant differences occur between the extensibility values registered in the two directions;

- transversal extensibility (in the direction of the stitch rows) has net values higher than the longitudinal extensibility (in the direction of stitch wells) (Figure 4);
- due to the formation of the rib type knitted (V4, V5, V6, V7) and the closeness tendency of stitch wells with different aspects, their transversal extensibility is much higher (varies between 190% and 282%), compared to the similar extensibility recorded on jersey type knitted (V1, V2, V3), where the values vary between 67% and 117% – Figures 5, 6;
- in both jersey and rib type, the presence of miss stitches in the structure (V2, V6) gives stability to the structure and thus reduces the extensibility (Figures 5, 6);
- the lowest values of longitudinal extensibility are for: V8 variant (interlock - 14% due to compactness and distinct stability), variant V2 (jersey with miss stitches) and variant V6 (rib 1:1 with miss stitches);
- on all jersey and rib variants the presence of tuck stitches in the structure (V3, V7) determines an increase of transversal extensibility and decrease of longitudinal extensibility; this is explained by the greater mobility of the yarn withing tuck stitches (figures 5, 6);
- among the jersey variant, the highest value of the transversal extensibility was recorded in V3 variant (jersey with tuck stitches);
- among the rib variants, the highest value of the transversal extensibility was recorded in variant V7 (rib 2:2 with tuck stitches).

5. CONCLUSIONS

Measuring extensibility on two stress directions is a compulsory test effectuated in order to properly design knitted products. For this purpose, in knitted products, the minimal and maximal extensibility areas are established, for a precise selection of knitted structure, structural parameters as well as the position of the product elements. Only the optimal choice of structure and structural parameters for the same variant of yarn concur greatly to a quality improvement of the knitted products. For the structures analyzed in this paper it can be concluded that:

- the variant with the highest extensibility on the stitch well direction (34%) is rib 2:2; and the variant with minimal extensibility (14%) is interlock;
- maximal extensibility on the stitch row direction (282%) corresponds to V7 variant (rib 2:2 with tuck stitches, and minimal extensibility (67%) is valid for the V2 variant (jersey with miss stitches).

Only an exact knowledge of extensibility allows judicious choice of optimal knit variants, depending on the intended use of the product and in strict correspondence with the requirements of the beneficiaries.

REFERENCES

[1] L. Lutic, "*Metrologie aplicată în Textile - Pielărie*", Ed. Performantica, Iași, 2016.

[2] M. Crețu, "*Proiectarea și tehnologia confecțiilor din tricoturi*", Ed. Gh. Asachi, Iasi, 2000.

[3] ***, "*Instruction manual for the M031 Fryma Fabric Extensiometer*", BS 4294/1968.

[4] E. Moisescu, "*Asigurarea calității*", Ed. Performantica, Iași, 2007

[5] E. Moisescu, L. Lutic, "*Metrologie textila, Tricotaje – Confecţii*", Ed. Performantica, Iași, 2008.

[6] L. Lutic, "*Assessing the Quality of integrated Knitted fabric used for upholstery*", International Symposium in Knitting Apparel – ISKA 2013, Iasi 21-22 June 2013.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

3D PRINTING OF PLA ONTO TEXTILE FABRICS

MPOFU Nonsikelelo Sheron[1], MWASIAGI Josphat Igadwa[2], NKIWANE Londiwe[3], NJUGUNA David[4]

[1, 2,4] Moi University, School of Engineering, Department of Manufacturing, Industrial and Textile Engineering, Po Box 3900-30100, Eldoret, KENYA

[3]National University of Science and Technology, Faculty of Industrial Technology, Department of Fibre, Polymer and Materials Engineering, Po Box Box AC939, Bulawayo, ZIMBABWE

Corresponding author: Mwasiagi, Josphat Igadwa, E-mail: igadwa@gmail.com

Abstract: *3D printing is an additive manufacturing technique that produces three dimensional objects through a layering process. Due to its ability to print complex structures, 3D printing has been applied in many disciplines including textiles. Different textiles structures have been printed using 3D printing techniques. 3D printed polymers have also been combined with textile structures to create composites and also enhance mechanical properties. The challenge with those composites has been the adherence of the 3D printed polymer to the textile substrate. Research has been done to improve the adhesion properties by varying 3D printed polymers, modifying fabric properties and also varying the fabric to polymer combinations. In this study a Polylactic Acid (PLA) model was printed on 8 fabric samples that differed in fabric weight, warp density, weft density, warp linear density and weft linear density. The samples were printed using the Athena 3D printer that uses the Fused Deposition Modelling (FDM) technique. The adhesion strength of the polymer to the fabric was then tested according to DIN53530 standard. The results were analysed based on the different elements of the fabric structure. Results showed that while some elements had a great effect on adhesion, others showed no direct effect on adhesion force.*

Key words: *3D Printing, Adhesion, Polylactic Acid (PLA), FDM process, textile fabric*

1. INTRODUCTION

3D printing technique is an additive production method that prints 3-dimensional products. The technique has been applied in many disciplines because of its flexibility and the possibility to print complex designs. 3D printing has been used in textiles to produce knit-like structures, woven structures, lace structures and multi-material products [1][2][3]. 3D printed polymers have also been combined with textile fibres, yarns and fabrics to create composites and also to enhance mechanical properties [4][5][6][7][8]. Although this has increased possibilities for new applications of textiles, there have been challenges in the adherence of the 3D printed polymer to the textile substrate. Adhesion is an important factor as it affects the end uses, durability and the quality of the product. There are different mechanisms for polymer to substrate adhesion, that is, molecular bonding, mechanical interlocking and thermodynamic adhesion [9]. To be able to achieve the best adhesion it is important to modify the parameters and factors that affect the adhesion mechanisms. Brinks et al [10] highlighted the importance of the polymer penetrating into the fabric for better adhesion and

they reported that adhesion can be controlled by varying several factors which include polymer viscosity and pressure [10]. Other researchers [11][12] [4][13] have varied fabric and polymer combinations and also experimented with some pretreatments methods such as washing and plasma treatments of the fabric substrates. The structure of the fabric can affect the mechanical interlocking of the polymer to the fabric and hence affect the adhesion. Researchers have hypothesized that mechanical interlocking results in higher adhesion strength and that roughening of the surface provides higher adhesion [9]. Recent studies have shown that the weave pattern and weft density influence adhesion of the polymer to the textile substrate [14]. This study aimed at keeping the printing polymer constant while varying the fabric structures to be able to study the structural properties of fabric that affect adhesion.

***Fig. 1**: Fabric Samples for Adhesion Tests*

The samples differed in weave pattern, weight (grams per square meter), warp density (ends per inch) and weft density (picks per inch), warp count and weft count as shown in Table 1.

***Table 1**: Fabric sample properties*

Sample Number	Fabric Weight (Gsm)	Warp Density (Ends/inch)	Weft Density (Picks/inch)	Warp Count (Tex)	Weft Count (Tex)
1	210	52	46	17	73
2	218	282	81	10	50
3	228	69	28	19	59
4	126	68	48	26	31
5	146	68	60	28	32
6	247	75	54	20	72
7	138	64	50	30	33
8	129	25	22	71	76

The 3D printing was performed using the low-cost Athena Fused deposition modelling 3D printer with a 0.4mm nozzle. A rectangle was created using the Solid Works software and converted to a standard tessellation language (stl) file for slicing using the Cura Software. The Cura software sliced the model into the different layers for printing and converted it into a G-Code. The dimensions of the printed rectangles were 150mm x 25mm. The thickness of the rectangles was 0.4mm. Printing was done at an extrusion temperature of 200°C, a printing speed of 50mm/s, a fill density of 65% and a layer height of 0.15mm. Adhesion tests were then carried out on the fabric according to standard DIN 53530 using a Universal Tensile Tester.

3. RESULTS AND DISCUSSION

The variation of the adhesion force of the printed PLA polymer on the selected fabric samples with changes of fabric weight (grams per square meter) is given in fig. 2. The different fabric samples showed different adhesion strengths as shown in the fig. 2. The fabric weight is directly proportional to the warp and weft linear density and the ends/inch and weft per inch. Therefore the results of the aforementioned factors discussed in the following sections may shed some light as to how fabric construction factors affect adhesion force.

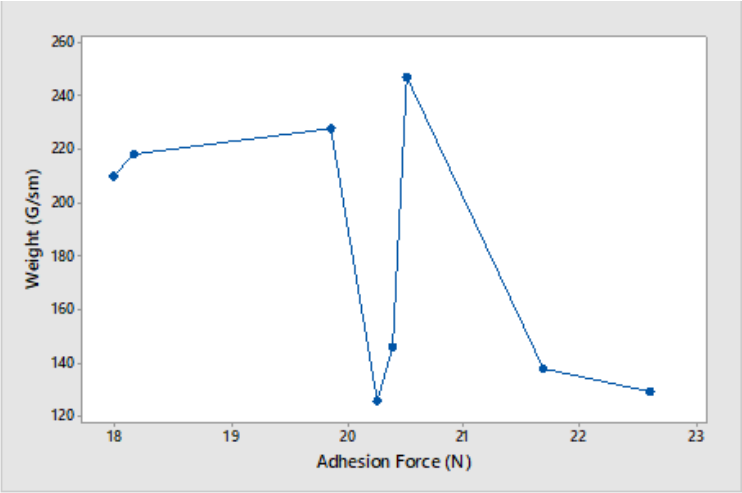


Fig. 2: *Dependence of adhesion on fabric weight*

Fig. 3 shows the relationship between polymer adhesion force and warp density. While the relationship is not direct, there is however a general tendency for the adhesion force to increases the warp density decreases. This can be explained by the fact that as the warp yarns become more densely packed it becomes difficult for the polymer to surround the individual yarns. This leads to less area available for the polymer to hold on to the fabric hence reducing the adhesion force.

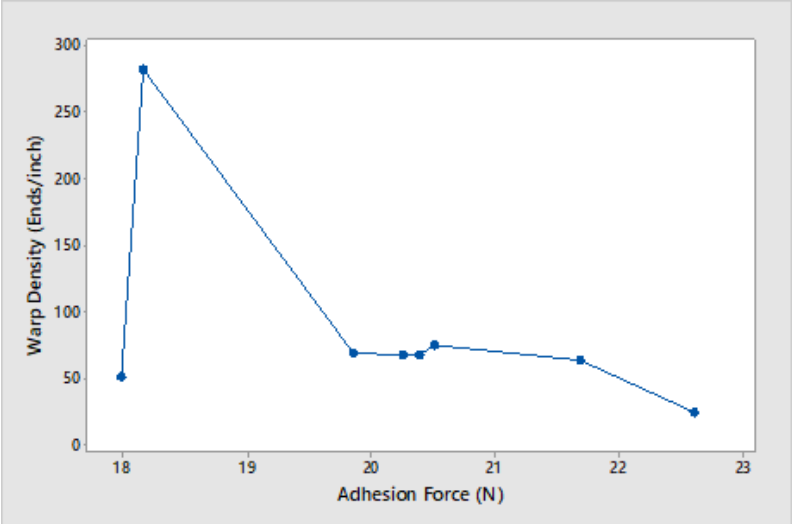


Fig. 3: *Dependence of adhesion on warp density*

The relationship between polymer adhesion force and weft density is shown in Fig. 4, which also shows a general decrease in adhesion force with an increase in weft density. This may be due to the same reasons as discussed for the warp density.

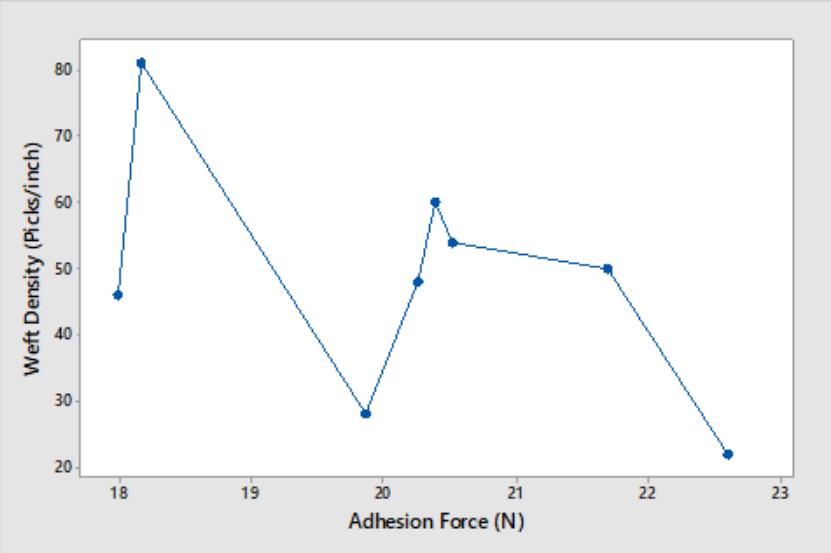


Fig. 3*: Dependence of adhesion on weft density*

In Fig. 5 the relationship between the warp linear density and the polymer adhesion force onto the fabric samples is given, which indicates that linear density is directly proportional to adhesion force. While it may appear that an increase of the linear density provides more area for the polymer to hold onto the fabric, the results of the relationship between the adhesion force and the weft linear density, as shown in Fig. 6, tends to suggest otherwise.

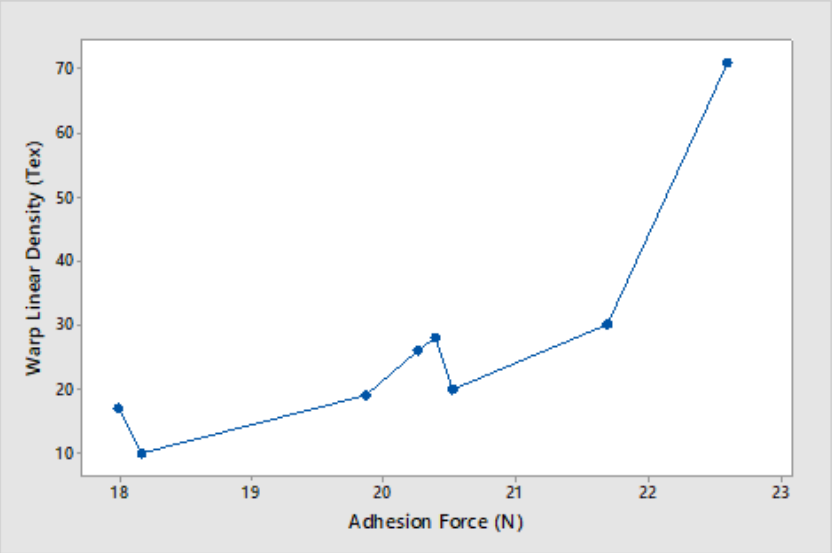


***Fig. 4**: Dependence of adhesion on warp linear density*

As exhibited in Fig. 6, the adhesion force did not indicate an easily discernable relationship between the polymer adhesion force and weft density. This calls for more research, especially when there seems to be a direct relationship between the polymer adhesion force and the warp linear density (seen fig. 5).

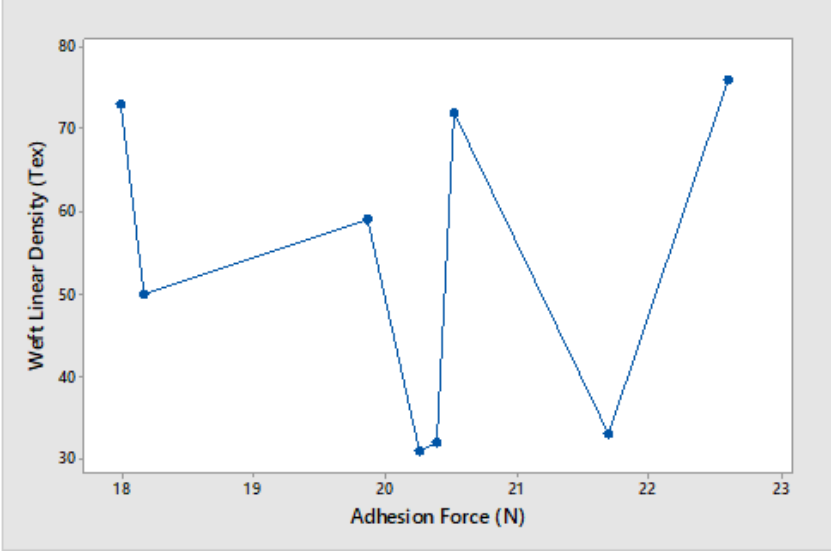


***Fig. 5**: Dependence of adhesion on weft linear density*

4. CONCLUSIONS

The aim of this paper was to determine the effect of selected fabric properties on then polymer adhesion onto the fabric. PLA was printed on a variety of fabric samples that differed in weight, warp and weft density as well warp and weft linear density. The samples were tested for adhesion force and the results showed that while warp density, weft density and warp linear density

showed an effect on adhesion; fabric weight and weft linear density had no direct effect on adhesion. These tests gave us preliminary results on the adhesion of polymers to fabrics. Future tests can focus on studying the effects of weave pattern and fibre content on adhesion properties.

REFERENCES

[1] Melnikova, R., Ehrmann, A., & Finsterbusch, K. (2014). 3D printing of textile-based structures by Fused Deposition Modelling (FDM) with different polymer materials. *2014 IOP Conf. Ser.: Mater. Sci. Eng. 62*, pp. 1-6. IOP Publishing.

[2] Beecroft, M. (2016). 3D Printing of weft knitted textile-based structures by selective laser sintering of nylon powder. *IOP Conf. Series.: Materials Science and Engineering. 137*, p. 012017. IOP Publishing.

[3] Partsch, L., Vassiliadis, S., and Papageorgas, P., "3D printed textile fabric structures," *5th International Instabul Textile Congress*, Instabul, Turkey, 2015

[4] Pei, E., Shen, J., Watling, J. (2015). Direct 3D printing of polymers onto textiles: experimental studies and applications. *Rapid Prototyping Journal*, 21, pp. 556-571

[5] Mahajan, C., & Cormier, D. (2015). 3D Printing of Carbon Fibre Composites with Preferentially Aligned Fibres. *Proceedings of the 2015 Industrial and Systems Engineering Research Conference*, 1-10.

[6] Döpke, C., Grimmelsmann, N., Ehrmann, A. (2016b). 3D printing on knitted fabrics. *Proceedings of 48th IFKT Congress*, Mönchengladbach, June 8-11, 2016.

[7] Grimmelsmann, N., Meissner, H., & Ehrmann, A. (2016). 3D printed auxetic forms on knitted fabrics for adjustable permeability and mechanical properties. *IOP Conf Series: Materials Science and Engineering. 137*, p. 012011. Hangzhou: IOP Publishing.

[8] Martens, Y., Ehrmann, A., (2017). Composites of 3D-printed polymers and textile fabrics. *Elsvier Materials Today: Proceedings*

[9] Awaja, F., Gilbert, M., Kelly, G., Fox, B., Pigram, P.J. (2009) Adhesion of polymers, *Progress in Polymer Science*. 34, pp. 948-968

[10] Brinks, G. J., Warmoeskerken, M. M. C., Akkerman, R., Zweers, W. (2013). The Added Value of 3D Polymer Deposition on Textiles. *Proc. of 13th AUTEX World Text. Conf.*, Dresden / Germany, 1-6.

[11] Sanatgar, R. H., Campagne, C., Nierstraz, V. (2017). Investigation of the adhesion properties of direct 3D printing of polymers and nanocomposites on textiles: Effect of FDM printing process parameters. *Applied Surface Science*, 403, 551-563.

[12] Spahiu, T., Grimmelsmann, N., Ehrmann, A., Piperi, E., Shehi, E. Effect of 3D printing on textile fabric. *1st International Conference "Engineering and Entrepreneurship" Proceedings*, Albania

[13] Korger, M., Bergschneider, J., Lutz, M., Mahltig, B., Finsterbusch, K., Rabe, M. (2016). Possible Applications of 3D Printing Technology on Textile Substrates. *IOP Conf. Series: Materials Science and Engineering*, 141, 012011.

[14] Malengier, B., Hertleer, C., Cardon, L., & Van Langenhove, L. (2017). 3D Printing on Textiles: Testing of adhesion. *ITMC2017 - International Conference on Intelligent Textiles and Mass Customisation*, Gent (pp. 1-17). Gent

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

METHODS FOR OBTAINING THE EFFECT OF LONGITUDINAL STRIPES IN FABRIC

OANA Ioan Pavel[1], OANA Dorina [2]

[1, 2] University of Oradea, Faculty of Energy Engineering and Industrial Management, Department of Engineering and Industrial Management in Textiles and Leatherwork, Postal address, **410058str. B.** Ştefănescu Delavrancea, no. 4, Oradea, Bihor, România, E-Mail: oanaioanpavel@yahoo.com

Corresponding author: Oana, Ioan Pavel, E-mail: oanaioanpavel@yahoo.com

Abstract: *The fabrics with longitudinal stripes have become more common both by their structure and diversity of appearance, and also the products made of them, this being the reason they occupy an important place in fabrics production. Associating links with equal or different average float produces a profound change in the internal fabric structure, giving it a permanent and stable character in stripe appearance. The stripe effect obtained by weaving technology provides stripping stability to the stripes, both in the humid-thermal finishing processes and in the current maintenance, in the wearing process (repeated washings).*
Also due to their structure, striped fabrics obtained by weaving technology can not be replaced by other fabrics whose stripes are obtained by other methods and technologies.
This is the reason why, in most cases, striped fabrics obtained by weaving technology are preferred, and not striped fabrics obtained by other processes, such as printing. From the point of view of the structure, the particularities of striped fabrics obtained by the weaving technology, consist in the way the basic parameters - the connection, the density and the fineness of the yarns, as well as the auxiliary parameters - the curling degree, the dimensional change of the threads by integrating it into the fabric, influence their internal structure.
The relationship of the longitudinal strip line depends on the fundamental diagonal link ratio, if it is the even or odd number, and the number of ***(Xi)*** *lines in the stripe with weft and warp effect.*

Key words: *texture ratio , warp, weft, yarns, weave, fineness of yarns.*

1. INTRODUCTION

The stripe effect obtained by weaving technology provides stripping stability to the stripes, both in the humid-thermal finishing processes and in the current maintenance, in the wearing process (repeated washings). The fabrics with longitudinal stripes have become more common both by their structure and diversity of appearance, and also the products made of them, this being the reason they occupy an important place in fabrics production. Associating textures with equal or different average float produces a profound change in the internal fabric structure, giving it a permanent and stable character in stripe appearance. [1]

Also due to their structure, striped fabrics obtained by weaving technology can not be replaced by other fabrics whose stripes are obtained by other methods and technologies.

This is the reason why, in most cases, striped fabrics obtained by weaving technology are preferred, and not striped fabrics obtained by other processes, such as printing. From the point of

view of the structure, the particularities of striped fabrics obtained by the weaving technology, consist in the way the basic parameters - the texture, the density and the fineness of the yarns, as well as the auxiliary parameters - the curling degree, the dimensional change of the threads by integrating it into the fabric, influence their internal structure.

Only methods of obtaining longitudinally striped fabrics from single-woven fabrics, consisting of a warp yarn and a weft yarn system, will be disclosed. [2]

2. GENERAL INFORMATION

2.1 Longitudinal stripes obtained with ground textures

One of the characteristics of the ground textures is that within the texture ratio all yarns contain a single pair of texture segments, one of which has unitary value. [3]

The effect of stripes can be obtained only with ground texture with the opposite effect of the two yarn systems, warp and weft within the texture ratio.

The degree of issuance of the two yarn systems on the surface of the fabric must be done so that one side of the fabric must be the negative of the other.

The cloth is the only one that gives the fabric identical sides and can not be used alone to obtain the striped effect.

The other ground diagonal textures in which the texture ratio of $R \geq 3$ or regular atlas to which the ratio of the texture is $R \geq 5$, the difference between the front and back of the fabric is obviously different. The contrast between the two sides of the fabric increases as the texture ratio increases, due to the different issuance degree of the effect of the two yarn systems on the two sides of the fabric.

For any ground texture, due to the fact that the ratio in warp Ru is equal to the weft ratio Rb, ie Ru = Rb = R, the number of binding points within a texture ratio is R2. In the case of a fabric with a ground texture with ratio R and a dominant weft, the number of warp binding points will be R, and those with the weft effect R2 - R or R (R - 1). [4]

The difference between the front and the back of the fabric regarding the effects of the system is:

$$c = \frac{R^2 - R}{R} = R - 1 \quad \textbf{(1)}$$

where:

- c is a coefficient that shows how many times the number of binding points of a system is greater than the other system on the same side of the fabric.

For the cloth where R = 2, c = 1, the number of binding points on both sides of the fabric is equal for the two yarn systems, the fabric has identical fronts.

For the texture with R = 3, c = 2, the number of binding points of a system (weft) is twice as big as the other (warp). [5]

The ground texture with an $R \geq 3$ ratio shows differences between the two sides of the fabric, front and back, by the issuance of a dominant system.

The higher the ratio of the texture R, the more the number of binding points in a system increases to the detriment of the number of binding points of the opposite system. The contrast between the two sides of the fabric is more and more obvious due to the system of yarns with dominant points. The stripes effect with ground texture is based precisely on the number of points of a yarn system, dominant on one side or another of the fabric.

The analysis of the two sides highlights the fact that they represent the negative and the positive effect of the dominant system.

Obtaining the effect of longitudinal stripes on fabrics with ground textures is based precisely on the contrast between the dominating system on one side and on the other of the fabric

2.2. Textures with longitudinal stripes obtained from the ground diagonal texture

The ground diagonal texture is characterized by the size of the Ru = Rb = R≥3 ratio and the displacement of the binding points S ± 1. [6]

Due to the size of the R-ratio, variants with a great diversity of aspect can be obtained, whereby if the shift sign ± of displacement is added to obtain the change in the direction of the diagonal lines on which the bonding points are located, then it can be stated that the diagonal textures is situated first, with regard to the possibilities of diversifying the aspect of fabrics. [7]

Due to the difference between the dominant yarn system on the two sides of the fabric, **the negative bias method is used to obtain the stripe effect**.

The negative bias method contains the following sequences:

- **Establish the ratio R of ground diagonal texture.** The ratio of the texture is established so that the positional stability of the yarns ensures a good behavior of the fabric in the wearing process. To do this, big flotation will be avoided. They depend on the fineness and density of the yarns. Flotation can grow together with the density until there is no possibility to easily snag the fabric.
- **Establish the number of stripes .** It is recommended that the number of yarns in a strip be equal to the ratio of R or a multiple of R:

$$Nu=X\text{-}R, \qquad X \in N^* \qquad \textbf{(2)}$$

The yarns of a stripe have to be put end to end in a whole number of blade of shears. It follows that the boundary yarns between two consecutive strips with contrasting textures are separated by blade.

The number of stripe yarns can be equal or different, obtaining fabrics with equal or non-uniform stripes. **Negative bias can also be done by changing the direction of the diagonal lines or maintaining it.** [8]

Bindings with equal longitudinal stripes

To obtain e**qual longitudinal stripes by the negative bias method,** it is necessary to establish: **the ratio R of ground diagonal texture, the number of yarns in a strip and the direction of the diagonal lines after the negative bias.** [9]

The R ratio of the ground diagonal texture is chosen so that the texture segments (flotation) have values that eliminate or improve the possibility of snagging in the wearing process.

The higher the density of the yarns, the higher the R ratio texture can be adopted, which implicitly has larger flotation of the yarns.

The number of stripes is chosen depending on the width of the stripes, the yarn density and the ratio R of the ground texture. [10]

Passing in the reed will be done so that boundary yarns of two consecutive stripes that bind in opposition are separated by a blade.

a. Textures with equal longitudinal stripes with changing the direction of the diagonal line. In figure 1 is represented the programming scheme for an equal longitudinal stripe fabric obtained by negating a ground diagonal texture with an odd ratio

$D\frac{1}{4}$, *R=5* with a number of yarns on stripes *Nu = 2R = 2 • 5 = 10 yarns.*

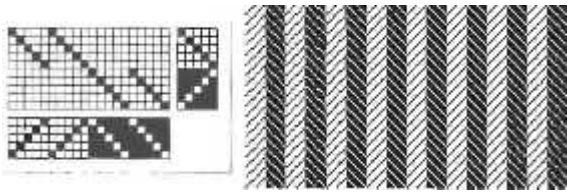


***Fig. 1**. Representing the programming scheme that includes: texture drawing, drawing in the leaves, and the drawing file*

The diagonal lines on consecutive stripe with effect in opposition, weft-warp (B-U), are opposite to right-left (Z-S).

The stripe effect is well highlighted and is maintained over time by the fact that the yarns adjacent to the consecutive stripes bind in opposition so that their positional stability is assured. In figure 1 is shown the programming scheme which contains: the texture drawing, the drawing in the leaves and the drawing file (the card). Each diagram is accompanied by a drawing in which the stripes are shown by simulation.

The texture ratio of the longitudinal strip line with the change of diagonal line is:

$$Ru_1=\Sigma Nu_i \quad where\ Nu_i=R\cdot\Sigma\ X_i - Rbl=R \qquad \textbf{(3)}$$

where:

Ru_1, Rb_1 is the ratio in warp and weft respectively of the texture with longitudinal stripes;

Nu_i – number of yarns in a pair of consecutive stripes with weft-warp effect (B-U);

Xi – number of ratio from the ground texture contained in a pair of consecutive stripes with weft and warp effect.

Example of calculus:

- for texture in figure 1

Number of yarns from the pair of stripes: $Nu_i=R\cdot\Sigma\ X_i=5(2+2)=20yarns$

Texture ratio with longitudinal stripes: $Ru_1 = Nu_i = 20\ yarns$

$Rb_1 = R = 5\ yarns$

α. **Textures with equal longitudinal stripes while maintaining the sense of the line diagonally.**

The negative bias in the consecutive stripes are made in such a way that bordering yarns of consecutive stripes with the opposite effect to bind in opposition. This makes the ratio of the texture with longitudinal stripes to be dependent on the ratio of the ground texture and the number of stripe yarns.

There are two cases:

Case 1. Ground diagonal texture with even ratio

In figure 2 is represented the programming scheme for a fabric with equal longitudinal stripes longitudinal stripes equal to maintaining the diagonal line, obtained by negating a ground diagonal texture $D\ \frac{1}{5}$, *R=6, Nu=2R=2-6=12 yarns.*

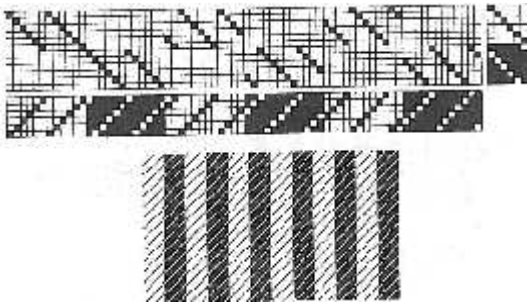


Fig. 2. *Programming scheme for a fabric with equal longitudinal stripes while maintaining the direction of the diagonal line*

The ratio of the texture with longitudinal stripes for the case where the ratio of the ground texture is even is calculated by the following algorithm:

$$Ru_1 = \frac{R}{2} \sum Nu_1 \text{ where } Nu_i = R \cdot \Sigma X_i - Rb_1 = R \quad \textbf{(4)}$$

Example of calculus:

- for texture in figure 2

Number of yarns in the pairs of stripes: $Nu_1 = R \cdot \Sigma X_i = 6(2+2) = 24$ *yarns*

Texture ratio of longitudinal stripes :

$$Ru_1 = \frac{R}{2} Nu_1 = \frac{6}{2} 24 = 72 \text{ yarns}$$

$Rb_1 = R = 5$ *yarns*

Case 2. Ground diagonal texture with odd ratio

In figure 3 is presented the programming scheme for a fabric with equal longitudinal stripes, obtained by negating a texture $D\ \frac{1}{4}$, R=5, Nu=2R=2-5=10 yarns, while maintaining the sense of the diagonal line.

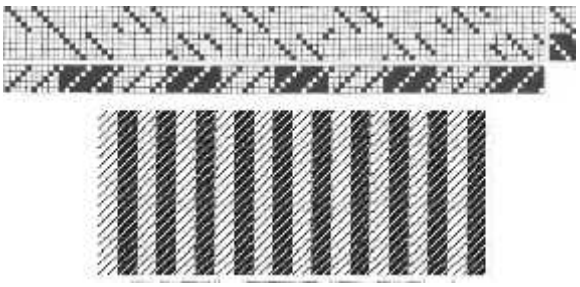


Fig.3 *Programming scheme for a fabric with equal longitudinal stripes, obtained by negating a texture*

The ratio of the texture with longitudinal stripes for the case where the ratio of the ground texture is odd is calculated like this:

$Ru_1=R\cdot Nu_i$ *where* $Nu_i=R\cdot\Sigma X_i$ $-Rb_1=R$ **(5)**

Example of calculus:
- for texture in figure 3:

Number of yarns in the pair of stripes: $Nu_i=R\cdot\Sigma X_i=5(2+2)=20$ *yarns*
Texture ratio with longitudinal stripes: $Ru_1=R\cdot Nu_i=5\cdot 20=100$ *yarns*
$Rb_1 = R = 5$ *yarns*

3.CONCLUSIONS

The texture ratio with longitudinal stripe line depends on the ground diagonal texture, if it is the even or odd number of ratio **(Xi)** in the stripe line with weft and warp effect.

The number of pairs of warp-weft stripes included in a texture ratio with equal longitudinal stripes, in the case of maintaining the diagonal line direction, is R/2 for even ratio and R ratio for the odd ratio of the ground texture. The reason is that, when negating the bordering yarns of consecutive stripes with the opposite effect must bind in opposition. This results in the ratio with longitudinal stripes to be terminated after R/2 pairs of stripes with weft-warp effect when the ground texture has an odd ratio, and after R striped pairs with a weft-warp effect when the fundamental bond has an odd ratio. Laying of yarns in the case of fabrics with longitudinal stripes obtained by negating a ground texture is done in two groups of loom blades each having an equal number of blades with R. It is recommended that the texture drawing of the longitudinal stripe obtained by the method of negating a ground texture begins with the weft effect stripe. The reasoning is that if the laying of yarns in the loom starts as normal with the first warp yarn in loom blade 1, etc., then the laying criterion will be applied implicitly according to the buckling yarns frequency in the joint formation for a weft ratio.

REFERENCES

[1] D.Chinciu, G.C.Chinciu, "*Proiectarea țesăturilor*", vol. 1, Ed. MEGA-Mix, Iaşi 2003.
[2] D.Chinciu, G.C.Chinciu, "*Proiectarea țesăturilor*", vol. 2, Ed. MEGA-Mix, Iaşi 2003.
[3] D.Chinciu, "*Geometria structurii țesăturilor.Aplicații*," Ed.BIT, Colecția CARTEX nr.3, Iaşi, 1996.
[4] D.Chinciu, "*Strucura și proiectarea țesăturilor, Partea I-a Legături pentru țesături simple. Vol II Desene de legătură*," Ed.Universității Tehnice "Gh. Asachi", Iași,1990.
[5] D.Chinciu, G.C.Chinciu, "*Strucura și proiectarea țesăturilor, Partea II-a Vol I, Proiectarea țesăturilor simple"*, Ed.Universității Tehnice "Gh. Asachi", Iași, 1990.
[6] D.Chinciu, G.C.Chinciu, "*Strucura și proiectarea țesăturilor, Partea II-a Vol II, Proiectarea țesăturilor simple"* Ed.Universității Tehnice "Gh. Asachi" Iași 1990.
[7] D.Chinciu., Teză de doctorat, Iaşi, 1977, Biblioteca Facultății de Textile-Pielărie, Iaşi
[8] D.Chinciu, D.Oana, "*Structura țesăturilor cu dungi longitudinale*", Ed. Universității din Oradea, 2005
[9] Marchis A, Macovei, M., Muresan, T., Ionescu, St., "*Structura si proiectarea tesaturilor*", Ed. Tehnica, Bucuresti, 1964
[10] Cioara , L.., "*Structura tesaturilor*", Ed. Performantica, Iasi, 2001

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

COMPARATIVE STUDY ON DIFFERENT TYPES OF KNIT PRODUCTS USING SYNTHETIC INDICATORS

PUSTIANU Monica[1], AIRINEI Erzsebet [1], POPA Alexandru[1]
BUCEVSCHI Adina[1]

[1]"Aurel Vlaicu" University of Arad, Engineering Faculty, 77 Revolutiei Bd., 310130 Arad, Romania

Corresponding author: Pustianu Monica, pustianumonica@yahoo.com

Abstract: T*he work's purpose is the comparison of four types of knitted fabric with the same structure, but with different values of the constructive characteristics.*
The synthetic indicators of constructive characteristicsforfour variants of knitted fabric made of 100% cotton for sportive ware for the hot season have been determined.
The synthetic indicators are indicators of subgroups and groups of characteristics and are obtained by getting through the following steps: -determination of the importance degree of the representative characteristic, - the adoption of an evaluation scale, - reporting to the same evaluation scale, - determined the value of the synthetic indicators of quality.
For the calculation of the importance coefficient of the charcteristics, the matrix method that involves the comparison of pairs of values and completing a squarematrices was used, with 1 when the characteristic C_i is more important than Cj and 0 if C_i is less important than Cj.
Scaling was used for this study, which is a method of reproducing the intensity of manifestation of a characteristic on a linear graded space (scale), which extends from the unfavorable limit of quality up to the most favourable. On this scale, characteristics may be ordered depending on their intensity.
By comparing the synthetic indicators obtained, we could evaluate the best variant in terms of the constructive solution adopted.

Key words: *knitted fabric, synthetic indicators, constructive characteristics, the degree of importance, scale*

1. INTRODUCTION

The quality indicators are numerical expressions of quality characteristics and they can be expressed in absolute , relative or average value.

The value of the indicator is obtained by statistical calculation resulting statistical indicators, which can be: synthetic, analytical, intergral indicators.

The synthetic indicators are indicators of subgroups and groups ofcharacteristics and are obtained by getting through the following steps: - determination of the importance degree of the representative characteristic, - the adoption of an evaluation scale, - reporting to the same evaluation scale, - determined the value of the syntheticindicators of quality.

2. RESULTS AND DISCUSSIONS

2.1 Determination of the degree of importance for the characteristic

The determination of a synthetic indicator is based on a series of quality characteristics, which do not have the same importance for the product's users and requiresthe ranking of characteristics through the coefficient of importance [1].

Calculation of the coefficient of importance of the characteristics can be done through the following methods: direct comparison method, the matrix method, the marking method. The calculated values directly influence the value of the synthetic indicator.[2,3,4]

For this study the following quality characteristics were adopted, depending on the item's destination:

- linear coverage coefficient - δ_L
- specific weight - M [g/m²]
- knit thickness - g [mm].[5,6,7]

Samples were taken from knitted fabric and the following ranges of the values of each characteristics have been optained and at the same time the preffered order of variation for this characteristics (ascending↑ or descending ↓) was established. The results are presented in table 1.

Table 1: *The variation ranges of adopted characteristics*

No.	Characteristic	Range of the values' variation	preffered order of variation
1.	Linear coverage coefficient – δ_L	20 -30	↑
2.	specific weight - M [g/m^2]	100 - 150	↓
3.	thickness - g [mm]	0,4 - 1	↓

Measurements were made on the four types of knitted fabric and we have obtained the following values of the characteristics, presented in table 2.

Table 2: *The characteristics'values adopted for each variant of knitted fabric*

No.	Characteristic	variant V1	variant V2	variant V3	variant V4
1.	linear coverage coefficient – δ_L	21,2	20,5	23,2	24
2.	specific weight - M [g/m^2]	120	110	115	140
3.	thickness - g [mm]	0,65	0,60	0,63	0,80

For the calculation of the importance coefficient of the charcteristics, the matrix method that involves the comparison of pairs of values and completing a square matrices was used, with 1 when the characteristic C_i is more important than Cj and 0 if C_i is less important than Cj.[1,3,4]

Three constructive characteristics were chosen, depending on the destination of the article and after the analysis of the characteristics, the order of importance was determined: The coverage factor-δ_L is the most important, followed by thickness-g and the last was the specific weight-M.

The square matrix built with the three characteristics is presented in table 3.

Table 3: *The square matrix*

Ci / Cj	C1 (δ_L)	C2(M)	C3(g)	$\sum_i n_{ij}$
C1 (δ_L)	1	0	0	1
C2(M)	1	1	1	3
C3(g)	1	0	1	2

$\sum_j n_{ij}$	3	1	2	$\sum_i \sum_j n_{ij} = 6$

The importance coefficient α_i is calculated with the relation [1]:

$$\alpha_i = \frac{\sum_i n_{ij}}{\sum_i \sum_j n_{ij}} \quad \textbf{(1)}$$

The values of the coefficientsof importance obtained are presented in table 4.

Table 4: *The calculated importance coefficients*

No.	The importance coefficient	Values
1.	α_1	0,5
2.	α_2	0,17
3.	α_3	0,33

From the analysis and comparison of the important coeficients, it appears that the most important characteristic is the liniar coverage coefficient δ_L, followed by thickness-g and then the specific weight-M.

2.2. Adopting of the evaluation scale for the quality characteristics

Some conventions were established, through whichdifferent ways of expression of the characteristics to be put in accordance with numeric values, on a 0-1, 0-10 or 0-100 scale

2.3. Reporting on the same scale

Reporting on the same scale of evaluation of all adopted characteristics imposes the knowledge of the specific ranges and the preffered sense of variation for each characteristic.

Scaling was used for this study, which is a method of reproducing the intensity of manifestation of a characteristic on a linear graded space (scale), which extends from the unfavorable limit of quality up to the most favourable. On this scale, characteristics may be ordered depending on their intensity.

Values have been reported on a scale from 0 to 10 and the following values presented in table 5 were obtained.

Table 5: *The n_j scores granted to the characteristics adopted on scale (0-10) for each variant of knitted fabric*

No.	Characteristic	Score n_j	variant V1	Variant V2	Variant V3	Variant V4
1.	linear coverage coefficient – δ_L	n_1	1,2	0,5	3,2	4
2.	specific weight - M [g/m^2]	n_2	6	8	7	2
3.	thickness - g [mm]	n_3	5,8	6,6	6,1	3,3

2.4. Calculation of the synthetic indicator of the constructive characteristics

Calculation of the synthetic indicator of the constructive characteristics is done with the relation [1]:

$$I_c = \frac{N_p}{N_{p\max}} \quad \textbf{(2)}$$

Where:

N_p- average score obtained for the adopted quality characteristics

N_{pmax}- the maximum score

$$N_p = \sum_i \alpha_i \cdot n_i \quad \textbf{(3)}$$

Where:

α_j- the values of the coefficients of importance for the characteristics

n_j- the awarded score for the adopted quality characteristics

For our case N_{pmax} =10, because we have adopted a scale of 0-10.

The average values of the scores obtained and the values of the calculated synthetic indicators are presented in table 6.

Table 6: *The average values of the scores obtained and the calculatedvalues of the synthetic indicators*

No.	Variant	Average score	Maximum score	Synthetic indicators I_c
1.	V1	3,53	10	I_{c1} = 0,353
2.	V2	3,78	10	I_{c2} = 0,378
3.	V3	4,8	10	I_{c3} = 0,48
4.	V4	3,42	10	I_{c4} = 0,342

3. CONCLUSIONS

• By comparing the synthetic indicator values obtained for the four knit variants results that the indicators Ic3 > Ic2 > Ic1 >Ic4

• Variant V3 better corresponds to its destination in terms of constructive solution adopted.

REFERENCES

[1] AGIR, "*The Textile Engineer's Manual*", vol.III, Ed.AGIR, Bucharest, 2004

[2] A. Florea, "*Product Quality Control*", Ed.Gh. Asachi, Iaşi, 2001

[3] L. Lutic, *Evaluation of the Yarn Quality Characteristics Through Synthetic Indicators*, Bulletin of the Polytechnic Institute, Iași, Tomul LVI (LX), Fasc. 2, 2010

[4] E. Moisescu, "*Technical Quality Control- Knit wear*", Ed.Gh. Asachi, Iaşi, 2000

[5] M. Macsim, R. Butnaru and M. Penciuc, *Influence of finishing treatments on the physical-mechanical characteristics of cotton knitted fabrics*, rev. Industria textilă, vol. 61, nr. 6, pp. 297-303, 2010

[6] M. Slah, H.T. Amine and S. Faouzi, *A new approach for predicting the knit global quality by using the desirability function and neural networks*, The Journal of the Textile Institute, volume 97, issue 1, pp. 17-23, 2006

[7] L. Lutic, *Quality evaluation of the knitted products using the G – F – ND method*, Annals of the University of Oradea, Fascicle of Textiles, Leatherwork, vol, XIII, NO. 12, pp. 92-98, 2012

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

APPLICATION OF PCM BINDED WITH RESINE ON A COMPOSITE MATERIAL MADE OF A POLYESTER NONWOVEN AND A JUTE FABRIC RESISTIVE LAYER

SEGURA-ALCARAZ Pilar, BONET-ARACIL Marilés [1], SEGURA-ALCARAZ Jorge [2], MONTAVA-SEGUÍ Ignacio [1]

[1] Universitat Politècnica de València, Departamento de Ingeniería Textil y Papelera, Plaza Ferrándiz y Carbonell s/n, 03801, Alcoi, Spain

[2] Universitat Politècnica de València, Departamento de Mecánica de los Medios Continuos y Teoría de Estructuras, Plaza Ferrándiz y Carbonell s/n, 03801, Alcoi, Spain

Corresponding author: BONET-ARACIL Marilés, E-mail: maboar@txp.upv.es

Abstract: *Noise is an important concern nowadays. Thermal regulation is also an interesting issue which can be partially solved or improved by textiles. Thermal and acoustic conditioning of rooms can be achieved bymeans of different materials. Fibrous textile materials can be used for both purposes. In this work, PCM micro-capsules are applied by flat printing method on a jute fabric which is used as a resistive layer of a fibrous composite. PCM thermal properties on fabrics have been widely reported. However, The variations on acoustic isolation have not been reported nowadays.The aim of this study is to determine whether there is any alteration due to the preence of PCM on a textile surfece. The sound absorption coefficient of the obtained samples is measured using a standing wave tube. Results show that the application of these micro-capsules boosts the sound absorption coefficient of the composite material, and that the temperature does not affect to this characteristic. In this work we domonstrate that PCM presence improves the acoustic response of the system and it is not anly due to the presence of a binder but also improves whan PCM have been applied. Apparantly there is no differennce on the behaviour depending on the temperature what evidences a change in the phase is not latering the acoustic response.*

Key words: *sound absorption, fibrous absorber, acoustic conditioning, thermal.*

1. INTRODUCTION

The interest on natural materials in building and decoration is increasing nowadays. Some vegetal fibres have been studied as fibrous sound absorbers [1,2] and specially jute [3,4]. Textile fibrous materials have been widely used for acoustic purposes, like sound absorbers [5].
Phase change materials (PCM) are used for thermal regulation. When temperature raises over their melting point, they absorb the latent heat and use it to melt, avoiding the temperature in the surrounding to increase. When temperature drops, they act reversely, solidifying and releasing the latent heat [6]. These materials are commonly used in building, but also as functional finishes for textiles [7] Microencapsulation is a method that keeps the PCM isolated from the surrounding materials, and avoids its leaking when the material is melted.

In this work a microencapsulated PCM is applied on a jute fabric by flat textile printing. The resultant fabric is added on a 15 mm polyester nonwoven and the sound absorption coefficient of the resultant composite is measured. Results show that the addition of PCM increases the sound absorption of the composite material, and that the phase change does not affect this absorption.

2. MATERIALS AND METHOD

2.1. Materials

The studied jute fabric characteristics are shown in table 1. The nonwoven employed is made of 100% polyester with 63 mm long, 12,33 dtex, circular cross section fibres, without crimp. The used binder is an acrylic/styrene copolymer, and the PCM micro-spheres were supplie from Color Center Spain. The printing paste composition appears in table 2:

Table 1. *Characteristics of jute fabric*

Material	**Weave**	**Warp Yarn Count (Threads/cm)**	**Filling Yarn Count (Threads/cm)**	**Areal Density (g/cm^2)**
Jute	Plain	6.2	5.2	30

Table 2. *Characteristics of printing paste*

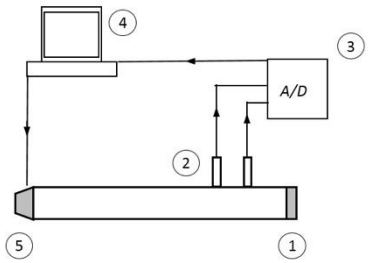
Material	Concentration (g/L)
Binder	15
PCM	50

2.2. Preparation of samples

Two samples are prepared by printing: one of them with all the elements of the printing paste except the PCM micro-capsules, and the other one with all the components. Three test specimens are cut from each sample. Only one specimen of nonwoven is used for all the tests.

2.3 Methods

Sound absorption coefficients of the different samples are measured without air gap at the back of the material. Tests are performed according to ISO Standard 10534-2: Acoustics. Determination of sound absorption coefficient and impedance in impedance tubes. Transfer function method. In this method, the sound wave strikes the material perpendicularly and the measured sound absorption coefficient is known as the normal incidence sound absorption coefficient. The impedance tube consists in is a narrow, rigid and airtight duct which meets certain characteristics described in the above standard. Measurements are performed between 400 and 4000 Hz. These frequencies are chosen due to the diameter of the available tube (around 40 mm).



1. Sample holder
2. Two microphones (microphones G.R.A.S. model 40AO)
3. Data acquisition system (NI-9233)
4. PC with data analysis tool
5. Sound source

Fig. 1. *Scheme of the apparatus employed to measure the sound absorption coefficient.*

To perform the test, the sample is placed at one end of the impedance tube (see point 1 in figure 1). The sample is fit snugly to the sample holder with no air gap. Plane waves are generated, in the tube by the sound source (see point 5 in figure 1). An interferential field decomposition is performed by measuring the sound pressure in two positions, using microphones hanged on the wall (see point 2 in figure 1). Using a Matlab function designed for this purpose, the transfer function of the complex acoustic signals at two microphones is determined.

3. RESULTS AND DISCUSSION

The areal density of the jute fabric before and after printing is shown in table 3.

Table 3. *Jute fabric areal density*

	Areal density (g/m^2)
Jute (untreated)	30,04
Jute + binder	33,94
Jute + binder + PCM	42,36

Sound absorption coefficient of the composite material is measured at a room temperature of 20º C. The combinations that form the composite material areshown in table 4. Results are shown in Fig. 2.

Table 4. *Measured combinations*

1	One layer of 15mm nonwoven and one layer of untreated jute fabric
2	One layer of 15mm nonwoven and one layer of jute fabric, printed only with binder
3	One layer of 15mm nonwoven and one layer of jute fabric, printed with PCM micro-capsules

The results are shown in Fig. 2.

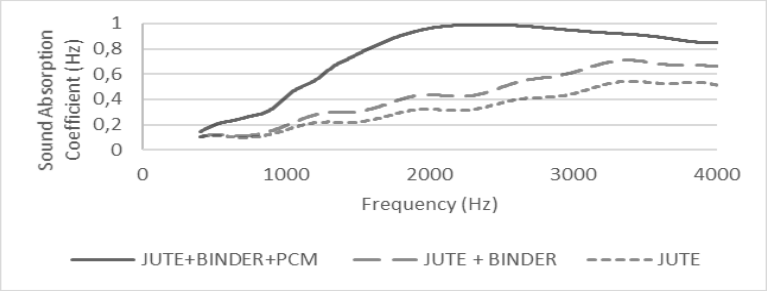


Fig. 2. *Sound absorption coefficient of a composite material made up of a layer of 15mm poliester nonwoven and a layer of untreated jute fabric upstream the sound source, jute printed with only the binder paste, and jute printed with paste containing PCM.*

Samples are heated up inside the sample holder using hot air, up to a temperature over 25ºC to achieve the phase change of the PCM. Then the sound absorption coefficient is measured. Results are shown in Fig. 3. What is clearly demonstrated is that microcpasules modify acoustic behavior. It is not only due to the areal density modification as when the binder is added the response is not as good as when microcapsules are included.

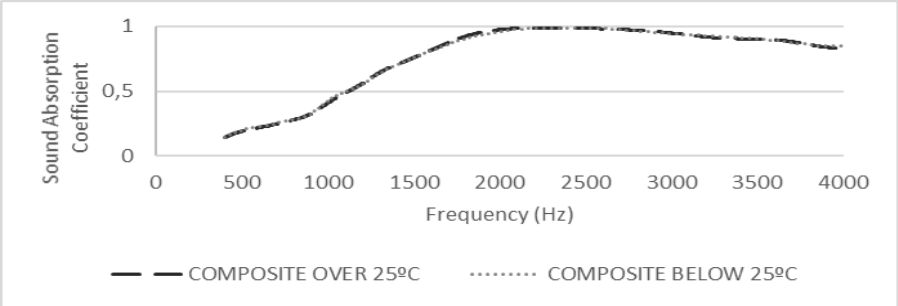


Fig. 3. *Sound absorption coefficient of a composite material made up of a layer of nonwoven and a layer of jute fabric printed with paste containing PCM at two temperatures, below and over the PCM melting point.*

Figure 3 demonstrates that temperature does not show any difference what can dbe understood as there is no modification due to the phase change inside the microcapsule.

4. CONCLUSIONS

The application of PCM microspheres on a jute fabric and nonwove composite improves its sound absorption coefficient in more tan 240% in frequencies from 1500 to 1600 Hz, reaching a maximum of 0,99 at about 2350 Hz. Vlues of sound absorption coefficient above 0,5 are found at frequencies over 1100 Hz The binder affects the absorption of the composite, improving the sound absorption coefficient about 38% between 2800 and 3000 Hz. Values above 0,5 are achieved for frequencies over 2500 Hz. The liquid or solid state of the interior of the micro-capsules does not show any difference in the sound absorption of the composite. In future trends we will study wheather this is similar with microcapsules containing different active core.

REFERENCES

[1] Arenas, J.P., and M.J. Crocker. 'Recent Trends in Porous Sound-Absorbing Materials'. *Sound and Vibration*, 2010, 12–17. http://www.sandv.com/downloads/1007croc.pdf.

[2] Berardi, Umberto, and Gino Iannace. 'Acoustic Characterization of Natural Fibers for Sound Absorption Applications'. *Building and Environment*, 2015. https://doi.org/10.1016/j.buildenv.2015.05.029.

[3] Fatima, S., and A. R. Mohanty. 'Acoustical and Fire-Retardant Properties of Jute Composite Materials'. *Applied Acoustics* 72, no. 2–3 (2011): 108–14. https://doi.org/10.1016/j.apacoust.2010.10.005.

[4] Mohanty, A.R., and S. Fatima. 'Jute as an Acoustical Material for Noise Control of a Domestic Dryer'. In *17th International Congress on Sound and Vibration 2010, ICSV 2010*, Vol. 5, 2010.

[5] Oldham, David J., Christopher A. Egan, and Richard D. Cookson. 'Sustainable Acoustic Absorbers from the Biomass'. *Applied Acoustics* 72, no. 6 (2011): 350–63. https://doi.org/10.1016/j.apacoust.2010.12.009.

[6] Onder, E., and N. Sarier. 'Thermal Regulation Finishes for Textiles'. In *Functional Finishes for Textiles: Improving Comfort, Performance and Protection*, 17–98, 2014. https://doi.org/10.1533/9780857098450.1.17.

[7] Zhou, D, C.y. Y Zhao, and Y Tian. 'Review on Thermal Energy Storag with Phase Change Materials (PCMs) in Building Applications'. *Applied Energy* 92, no. 92 (2012): 593–605. https://doi.org/10.1016/j.apenergy.2011.08.025.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EFFECT OF YARN STRUCTURE ON MECHANICAL PROPERTIES OF SINGLE JERSEY FABRICS

SUBRAMANIAN Kathirvelu

Kumaraguru College of Technology, Dept. of Textile Technology, India

Corresponding author: Kathirvelu Subramanian, E-mail: Kathirvelu.s.txt@kct.ac.in

Abstract: *Knitted fabrics are known to more complex and dimensionally sensitive structures than the woven fabrics. Variations in material, structural, mechanical processing and finishing parameters are bound to significantly influence the mechanical and comfort properties of knitted fabrics, as well as their qualities. It is obvious that the knitted fabric properties depend mainly on the constituent yarn properties and the knitting parameters. Yarns produced using various spinning technologies not only differ from one another in respect of their structures, but also in their bulk, mechanical and surface properties. The properties of the knitted fabrics produced from such yarns are bound to be influenced by their constituent yarn properties. This study was about the effect of yarn structure (ring/rotor) on some of the major mechanical properties of single jersey knitted fabrics.100% cotton carded ring and rotor yarns were spun using the same yarn parameters (count and twist) on ring spinning and rotor spinning machines using the same card sliver as the feed material. Two different single jersey fabrics were knitted using these two yarns separately using the same knitting machine and knitting parameters such as machine speed, loop length, gauge and machine diameter. These knitted fabrics were tested for their bursting strength, abrasion resistance and pilling resistance as per ASTM standards. From the results, it was found that fabric knitted using ring spun yarn was having better bursting strength and abrasion resistance than the knitted fabric knitted using rotor spun yarn.*

Key words: *ring yarn, rotor yarn, single jersey fabric, mechanical properties*.

1. INTRODUCTION

Knitted fabrics are popular for their shape fitting properties, softer handle, bulkiness and extensibility. Knitted fabrics have been extensively used in readymade apparel owing to their excellent mechanical and comfort properties [1]. Compared to woven structures, knit fabrics can more easily deform or stretch by compressing or elongating the individual stitches that from the fabric [2].Knitted fabrics are complex and dimensionally sensitive structures. Variations in material, structural, mechanical processing and finishing parameters significantly influence the mechanical and comfort properties of knitted fabrics, as well as their qualities. The knitted fabric properties depend mainly on the constituent yarn properties and the knitting parameters. Yarns produced using various spinning technologies not only differ from one another in respect of their structures, but also in their bulk, mechanical and surface properties. The properties of the knitted fabrics produced from such yarns found to be affected by yarn properties, as well as by their fabric construction parameters [3].

For knitted fabrics, the major mechanical properties are bursting strength, abrasion resistance and pilling resistance. The bursting strength of a knitted is very important because in a weft knitted structure, there is only one set of yarn. Multi- directional bursting strength testing is an alternative criterion to judge the fabric strength because the force is applied perpendicular direction to the plane of the fabric to rupture the yarn at a weak place [4]. A comparative study was carried out of open end spun yarn and ring spun yarn on single jersey weft knitted hosiery fabric using 20s nominal yarn count which was prepared from J34 cotton. All the fabric samples were produced in a circular knitting machine and concluded that the bursting strength of fabric samples in grey state is lower by 50% for fabric made from rotor spun yarn than for from ring spun yarn. [4].

The resistance of a fabric against the force of friction is known as the abrasion resistance. Abrasion is the physical destruction of fibers, yarns, and fabrics, resulting from the rubbing of a textile surface over another surface. Obviously from the consumer point of view, abrasion resistance is the most important mechanical characteristics of fabrics. Abrasion occurs during wearing, using, cleaning or washing process and this may distort the fabric, may cause fibers or yarns to be pulled out or remove fiber ends from the surface. Abrasion ultimately results in the loss of performance characteristics, such as strength, but it also affects the appearance of the fabric [5]. There are many factors, such as the yarn spinning system, fabric construction and finishing operation, which affect the abrasion resistance. Researchers did a comparative study on ring, rotor and vortex yarn knitted fabrics produced with 30/1 Ne yarns spun using three different spinning systems and the properties of yarns and knitted fabrics were studied and concluded that abrasion resistance of rotor spun yarn is better than ring spun yarn [6].

Pills are small knots or balls of mixture of large number of small fibers accumulated at the surface of the fabric and entangled by the mild frictional action during processing or wearing Pilling is a fabric defect observed as small fiber balls or a group consisting of intervened fibers that are attached to the fabric surface by one or more fibers**.** [6].There are many factors which affect the pilling resistances of knitted fabrics such as the yarn spinning system, fabric construction and finishing operation. A study of the dimensional, pilling and abrasion property of weft knitted fabric was conducted and the reported results showed that both structural differences of yarns and fiber types play a large role in determining the pilling property of knitted [7]. The yarns produced by the three spinning systems have major structural differences that are expected to impact pilling resistance. It was concluded that fabrics knitted from rotor spun yarns have a lower propensity to piling. The results showed that the ring spun fabric was slightly more pill- resistant than the rotor spun fabric [8].

Currently, there are many different methods of yarn manufacturing such as ring spinning, rotor spinning, air jet spinning ,break spinning, friction spinning etc. employed by the textile industry. Obviously, the type of yarn (ring spun, rotor spun, Dref spun, air jet spun) used for knitting (and hence, its properties) will be exerting considerable influence on the knitted fabric properties. For the purpose of our study, we have taken up two popular types of yarns namely the ring spun yarn and the rotor spun yarn as these two types of yarns are the most widely used among the different types of yarns spun in the textile industry. We have taken up weft knitting as it is the most popular method for producing knitted fabrics and the plain or single jersey as the weft knitted structure for our study as this is the simplest of all weft knitted constructions produced on machines employing only one set of needles.

2. MATERIALS AND METHODS

2.1 Material

100% cotton was used for this study as it is the dominant raw material in Ethiopia and the fiber properties of the same are tested using random sampling method and are listed below in Table 1. Both the ring-spun and rotor-spun yarns used for this study are produced from the same mixing only.

Table 1: *Fiber properties*

Staple length in	Short fiber content	Trash %	Micronaire
30.6	10.4	3.58	3.78

The yarn used for knitting the required fabric samples were 28's Ne single spun using 100% cotton using the ring spinning and rotor spinning machines of M/s. MAA Garments and Textiles, Mekele, Ethiopia at 16000 rpm and 120000 rpm respectively. Both the yarns were spun using the same sliver produced from the same mixing and were spun with same twist levels 1050 tpm. Both the fabric samples (knitted using ring spun yarn and rotor spun yarn separately) knitted for this study are produced in the said textile mill on a circular knitting machine as per the knitting machine parameters shown in Table 2 below**.**

Table 2: *Knitting Machine Parameters for knitted fabric sampling*

Speed (rpm)	Adjusted loop length(mm)	Number of needles	Gauge	Needle type	Number of feeders	Number of cam track	Machine diameter (inch)
20	3.21	2976	28	Latch	108	4	34

2.2. Method

This research is designed to study the effect of yarn structure on the mechanical properties of single jersey knitted fabric properties by producing and testing the knitted fabric samples obtained using two different types of yarns spun using the same mixing and yarn parameters on different spinning systems namely the ring spinning and rotor spinning. The fabric samples thus produced were tested for their mechanical properties as per ASTM standards [9-12] under the standard atmospheric conditions, at 21±1°C and 65±2% at EiTEX laboratory.

3. RESULTS AND DISCUSSIONS

3.1 Results

3.1.1 Bursting Strength

The bursting strength of the single jersey weft knitted fabrics tested with the Bursting Strength Tester as per ASTM in Test Methods D 3786 (option B) [10]. Full width fabric sample is used with laboratory sampling for acceptance method. The test results are shown in Table 3.

Table 3: *Bursting Strength Test Results (kg/cm^2)*

Yarn	Sample no										
	1	2	3	4	5	6	7	8	9	10	Mean
Ring	6.27	6.81	6.75	6.65	7.33	6.75	6.81	7.13	6.92	6.80	6.89
Rotor	4.63	4.74	5.18	5.13	4.70	4.92	5.02	4.74	4.59	4.69	4.69

3.1.2. Abrasion Resistance

The testing of abrasion resistance is done as per ASTM D 3886 by using the Martindale Abrasion Tester. The test option used was option 1 and the thickness test results are given below in Table 4.

Table 4: *Abrasion Resistance Test Results*

Sample Weight loss in %						
Yarn type	1	2	3	4	5	Mean
Ring spun	1.23	0.93	1.21	0.97	0.96	1.06
Rotor spun	3.11	3.28	3.98	3.86	3.65	3.576

3.1.2. Pilling Resistance

Martindale pilling tester was used to assess the pill formation on the fabrics. The determination of pilling resistance is done as per ASTM D 4970 standard for Abrasion resistance of Textile Materials [12]. These test results of pilling resistance tests are: Ring spun yarn fabric pilling grade is 2-3 and the rotor spun yarn fabric grade is 3-4.

3.2. Discussion

For the analysis of the test results, one way ANOVA in SPSS and Microsoft Excel are used.

3.2.1. Bursting Strength

The bursting strengths of single jersey weft knitted fabrics made out of ring and rotor spun yarns were studied and the results in Table 3 show that the bursting strength for single jersey fabric produced from ring spun yarn has an average of 6.82 kg/cm$^{2.}$ The single jersey fabric knitted with rotor spun yarn has an average of 4.83 kg/cm^2. As observed from the test results, bursting strength of single jersey knitted fabric knitted with ring spun is higher than that of single jersey knitted fabric knitted with rotor spun yarn. This is due to the fact the tensile strength of ring spun yarn is higher than that of the rotor spun yarn. The mean difference of 1.99 kg/cm2 is significantly different with (F = 319.064, Sig. = 0.000). It is confirmed with ANOVA analysis that p value is less than 0.05 at 95% confidence level, indicating significant differences in bursting strength of ring and rotor spun yarn fabrics. Knitted fabric from ring spun yarns has higher bursting strength than rotor spun yarn due to the fact that the work of rupture of rotor yarn (which is a product of strength and elongation) is lower than that of ring spun yarn.

3.2.2. Abrasion Resistance

The abrasion resistances of single jersey weft knitted fabrics made out of ring and rotor spun yarns were studied and Table 4shows that the single jersey fabric produced from ring spun yarn has the mean fabric Weight loss of 1.06% and the single jersey fabric produced from rotor spun yarn has an average of 3.576%. The ANOVA for the abrasion resistance shows that the mean difference between the two fabrics is highly significant (F=25.229, .001). It is confirmed with ANOVA analysis that p value is less than 0.05 at 95% confidence level, indicating significant differences in abrasion resistance of ring and rotor spun yarn. The fabrics knitted from rotor spun yarn have higher weight loss value than ring spun yarn. This may be because the wrapping fibers of the rotor spun yarns gradually break due to the abrasive forces, facilitating the removal of loose fibers from the yarn structure.

3.2.3. Piling property

The extent of pilling is assessed visually by comparison with the visual standards. Pilling characteristics of single jersey weft knitted fabrics made out of ring and rotor spun yarns were studied. Rotor spun yarn knitted fabric showed 3-4 scale pilling grade as compared to 2-3 of ring spun yarn knitted fabric. The piling grades of the samples show that the fabrics knitted from rotor spun yarns better than the single jersey fabric knitted from ring spun yarn. This maybe because of the fact that the ring spun yarns are more hairy than rotor spun yarns, which may allow easy exposure of the raised fiber ends to the abrading force.

4. CONCLUSIONS

The major mechanical properties such as bursting strength, abrasion resistance and pilling of single jersey knitted fabrics knitted with ring spun yarn and rotor spun yarn have been tested, studied analyzed and reported. From the results of this work, it was found that the type of yarn structure (ring/rotor) has a significant influence on the above said major mechanical properties. Single jersey fabric knitted using ring spun yarn was having better bursting strength and better abrasion resistance than single jersey knitted fabric knitted with rotor spun yarn. This can be attributed to the fact that the ring spun yarn is stronger than the rotor spun yarn. Therefore, this is in concurrence with the similar results obtained in the case of denim fabrics [13]. On the contrary, it can also be seen that the pilling resistance of single jersey knitted fabric knitted with rotor spun yarn is better than that of single jersey knitted fabric knitted with ring spun yarn. The improved pilling resistance of rotor spun yarn fabric could be due to the wrapper fibers, which have mobility on the yarn core and thus reduce the pilling tendency during normal use. It may be because of the fact that the wrapper fibers in the fabric are trapped and rotor yarns, by flattening, give a greater area of contact between the abradent and fabric, thus reducing pilling tendency.

ACKNOWLEDGEMENT

The authors sincerely acknowledge the management of EiTEX, Bahir Dar University, Ethiopia especially Mr. Addisu Ferede, Scientific Director, for his continuous encouragement, support, guidance and cooperation. The authors also thank the management of M/s.MAA Garments and Textile Factory, Ethiopia and their technical staff for their permission, support, help and cooperation.

REFERENCES

[1]. Rahman, S., & Smirithi, S. A. (2015). "*Investigation on the Changes of Areal Density of Knit Fabric with Stitch Length Variation on the Increment of Tuck Loop Percentages*". Journal of Polymer and Textile Engineering, *2*(3), 1-4. Retrieved from http://www.iosrjournals.org/iosr-jpte/papers/Vol2-issue3/A0230104.pdf

[2]. Akaydin, M., & Can, Y. (2010). "*Pilling Performance and Abrasion Characteristics of Selected Basic Weft Knitted Fabrics*". FIBRES & TEXTILES in Eastern Europe, 18(2), 51-54. Retrieved from http://www.fibtex.lodz.pl/2010/2/51.pdf

[3]. Kane, C., Patil, U., & Sudhakar, P. (2007). "*Studies on the Influence of Knit Structure and Stitch Length on Ring and Compact Yarn Single Jersey Fabric Properties*". Textile Research Journal, *77*(8), 572-582. doi:10.1177/0040517507078023

[4]. Mukherjee, S., & Chindalia, S. C. (1983). "*Comparative Performance of Open-end Spun Yarn and Ring-spun Yarn In Single Jersey Weft-knitted Hosiery Fabric"*. Indian Journal of Fibre &

Textile Research, 8(83), 121-124. Retrieved from http://nopr.niscair.res.in/bitstream/123456789/33086/1/IJFTR%208(4)%20121-124.pdf

[5]. Zdil, N., Zelik, G., & Spren, G. (2012). "*Analysis of Abrasion Characteristics in Textiles*". Abrasion Resistance of Materials. doi:10.5772/29784

[6]. Rameshkumar, C., Anandakumar, P., Senthilnathan, P., Jeevitha, R., & Anbumani, N. (2008). "*Comparative studies on ring rotor and vortex yarn knitted fabrics*". AUTEX Research Journal, *8*(4), 100-105. Retrieved from http://www.autexrj.com/cms/zalaczone_pliki/2-08-4.pdf

[7].Candan, C., & Önal, L. (2002). "*Dimensional, Pilling, and Abrasion Properties of Weft Knits Made from Open-End and Ring Spun Yarns*". Textile Research Journal, *72*(2), 164-169. doi:10.1177/004051750207200213

[8].Alston, P. V. (1992). "*Effect of Yarn Spinning System on Pill Resistance of Polyester/Cotton Knit Fabrics*". Textile Research Journal, *62*(2), 105-108. doi:10.1177/004051759206200208

[9]. Textile Standards. (n.d.). Retrieved from https://www.astm.org/Standards/textile-standards.html

[10]. ASTM D 3786, Standard Test Method for bursting strength testing

[11]. ASTM D 3886 Standard Test Method for Abrasion resistance testing

[12]. ASTM D 4970 Standard Test Method for Pilling resistance testing

[13]. Iqbal, S., & Kolhatkar, A. W. (2014). Denim fabrics: Ring vs rotor spun yarns. *The Indian Textile Journal*. Retrieved from http://www.indiantextilejournal.com/articles/FAdetails.asp?id=2467

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THERMOGRAPHIC ANALYSIS OF THE RICOMA 2 HEAD EMBROIDERY MACHINE

ŞUTEU Marius Darius[1], BABAN Calin Florin[2], BABAN Marius[2], PANCU Rareș Mihai[2], TOTH (Kiss) Edit[3]

[1]University of Oradea, Faculty of Energy Engineering and Industrial Management, Department Textiles, Leather and Industrial Management, 410058, Oradea, România, E-Mail: suteu_marius@yahoo.com

[2] University of Oradea, Faculty of Managerial and Technological Engineering, Department Industrial Engineering, 410087, Oradea, România, E-Mail: imt@uoradea.ro

[3] Doctoral School of Engineering Sciences, University of Oradea, România.

Corresponding author: Marius Darius, Șuteu, E-mail: suteu_marius@yahoo.com

Abstract: *The purpose of this paper is to quickly and accurately identify the points representing potential defects in 2 head embroidery machines by using infrared thermography. Thermography measurements were performed with the FLIR SC 640 thermal imaging camera, which is a portable thermographic scanning equipment. The Flir Reporter 9.1 software is used to create reports based on photos taken with the Flir Sc 640 thermal imaging camera. Measurements were taken on the Ricoma 2 head embroidery machine at different work patterns to track the way the needle temperature is transmitted on the fabric on which the embroidery patterns are made. The measurements were taken for several materials and the material chosen to be presented in the present paper is a synthetic and natural fiber compound, because of its large dimensional stability. In this paper the results of thermography measurements on the chosen material are presented at a minimum working regime of 300 sinkings/min, at the optimal working regime determined by the authors to be 790 sinkings/min and at the maximum working regime of 900 sinkings/min .*

Key words: *thermographic measurements, FLIR SC 640 thermal imager, needle, embroidered fabric.*

1. INTRODUCTION

In recent years, infrared thermography has shown applicability in more and more areas. A temperature-based image provided valuable information about the status of the analyzed item. Any failure of the equipment is preceded by an increase in temperature. Identifying the temperature that increases beyond normal operating limits allows the avoidance of malfunctions [1].

2. THE EXPERIMENTAL PART

Thermography measurements were made with the FLIR SC 640 [2], [3] thermographic camera on the RICOMA embroidery machine, which is a reliable industrial embroidery machine with two embroidery heads each with 12/15 colors. Ricoma machines incorporate state-of-the-art mechanical and electronic technology. It has its own operating system with an intuitive interface that allows the modification of the embroidery patterns on the spot and editing digits and letters directly

on the machine software without having to be previously edited and processed on a computer.

Thermo Camera FLIR SC 640 is a portable thermographic device for scanning, without cooling. It is equipped with the most powerful existing IR detector with a resolution of 640x480pixels, which shows thermal sensitivity (NETD) found only in cameras with cooling (<0.04 ° C).

The termographic camera FLIR SC 640 disposes of new functions such as:

-Possibility to overlay the thermal image into visible image (Picture-in-Picture)

-Possibility to combine the thermal image with visible image (Thermal Fusion)

Figure 1 depicts the component elements of Flir SC 640 thermo camera.

Fig. 1. *The component elements for Thermo Camera Flir SC640 [2,3,4]*

According to Figure 1, the thermo camera is equipped with a laser pointer, germanium lens, SD card, USB and Video connector [2,3,4]

The thermographic view of the objects are realized in 2 modes

-Through a tilt-able viewfinder

-Through a large color LCD

Advantages of testing with thermo camera Flir Sc 640 are as follows:

Allows scanning objects at a distance without contact, the testing is non-destructive against measured objects, provide predictive maintenance for equipments in the early stages to reduce costs. Flir Reporter 9.1 software is used to create reports in infrared based on pictures realized with thermo camera Flir SC 640.

With the Flir Reporter 9.1 software we have the posibility to:

- Detailed analysis of the infrared image
- Modify the: level, span, color palette
- Modify object parameters
- Add or delete the: spot, line, area, delta T
- Modify the properties of measurement units
- Add arrows to image

During the stitching (embroidery) process it is very important to know the influence of the

needle temperature on the material [5,6]. During the stitching (embroidery) process, the needle heats up, which result in stitching (embroidery) defects and implicitly decreases of the productivity[6].

Thermography measurements [7,8,9] were made on Ricoma 2 head embroidery machine (Figure 2). These measurements were taken on different materials and during different working regimes [10,11], from 300 sinkings/min until 900 sinkings/min, in order to track the way the needle temperature is transmitted to the material on which embroidery patterns are sewn. Measurements were taken on a 0,7 mm needle from Schmetz. The embroidery thread has a linear density of 135x2 dtex and is 100% polyester

In this paper we have chosen to present the results of thermography measurements on the chosen material at 300 sinkings/min, 790 sinkings/min and 900 sinkings/min. These working regimens were not chosen randomly. We chose to present measurements at a minimum working regime of 300 sinkings/min, a maximum working regime of 900 sinkings/min, and a 790 sinkings/min working regime that was determined by the authors to be an optimal working regime, established by the vibration measurement technique.

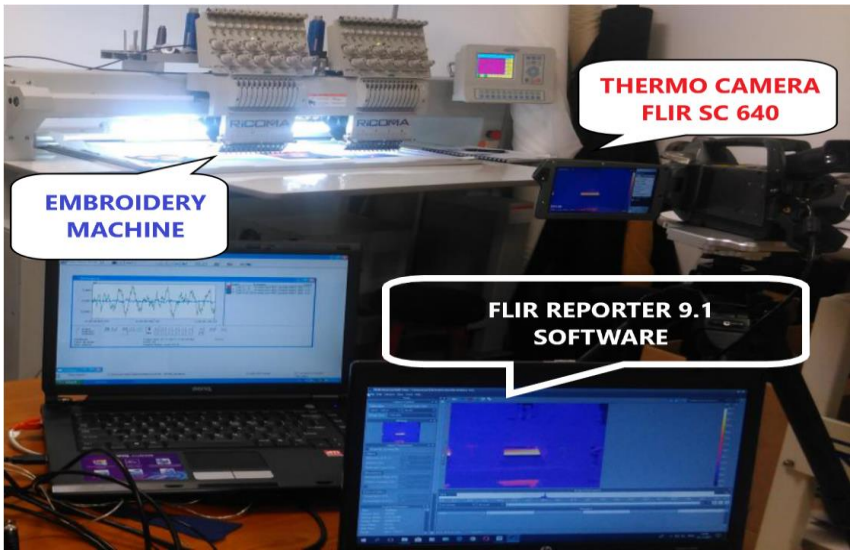
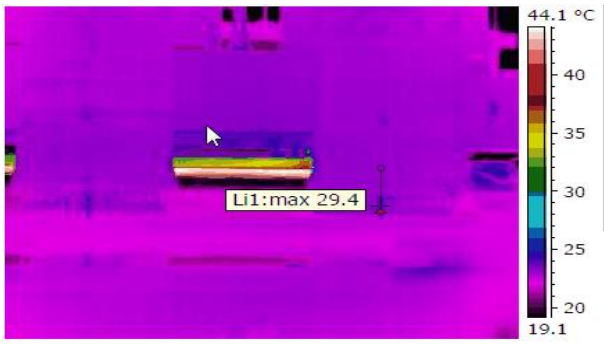


Fig. 2. *Thermography measurements on 2 head Ricoma embroidery machine*

For the first embroidery pattern, the thermography measurements were performed at a minimum working regime of 300 sinkings/min.



Date	24.11.2017
Image Time	11:06:32
Emissivity	0.95
Object Distance	1.0 m
Reflected Temperature	20.0 °C
Li1 Max. Temperature	29.4 °C
Li1 Min. Temperature	17.2 °C
Li1 Max - Min Temperature	12.1 °C
Li1 Emissivity	0.30
Li1 Object Distance	2.0 m
Li1 Reflected Temperature	25.0 °C

Fig. 3. *Image in the IR spectrum of the 2 head embroidery machine at 300 sinkings/min*

In (Figure 3) can be seen the graphic slider that is positioned on the needle and indicates a temperature of 29.4 ° C. The measurement distance was of 1m between the camara and the 2 head embroidery machine and the air temperature was 20 ° C. In (Figure 4), the needle temperature variations are displayed at 300 sinkings/min for the first embroidery pattern.

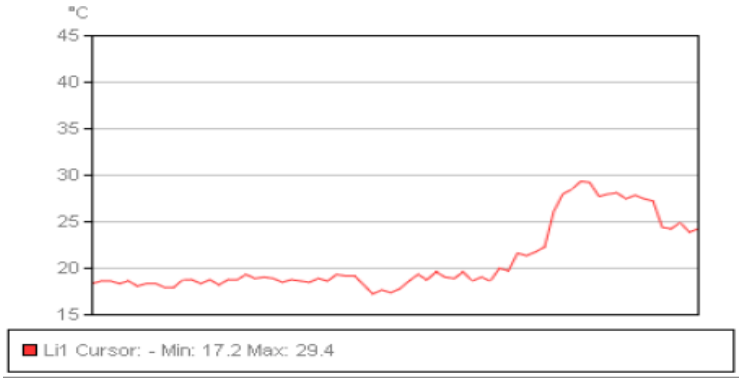


Fig. 4. *Variations of the needle temperature at 300 sinkings/min.*

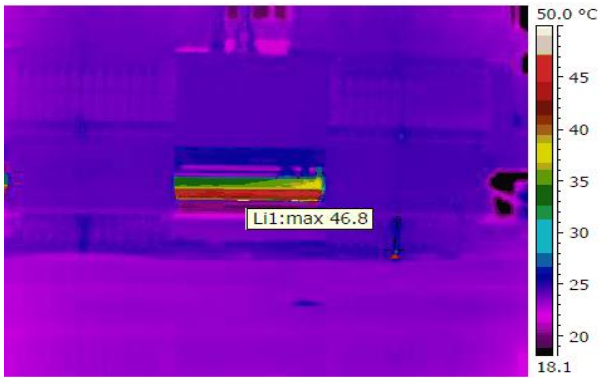


Fig. 5. *Image in the IR spectrum of the 2 head embroidery machine at 790 sinkings/min*

Date	24.11.2017
Image Time	11:37:44
Emissivity	0.95
Object Distance	1.0 m
Reflected Temperature	20.0 °C
Li1 Max. Temperature	46.8 °C
Li1 Min. Temperature	17.9 °C
Li1 Max - Min Temperature	28.9 °C
Li1 Emissivity	0.16
Li1 Object Distance	2.0 m
Li1 Reflected Temperature	25.0 °C

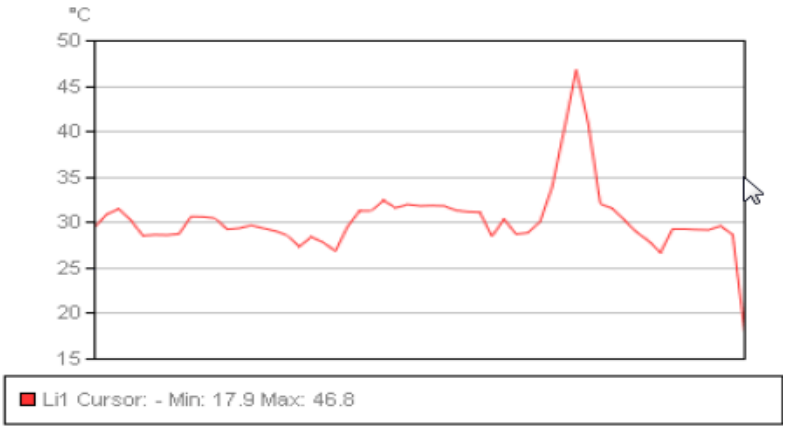


Fig. 6. *Variations of the needle temperature at 790 sinkings/min.*

In (Figure 5) can be seen the graphic slider on the needle indicating a temperature of 46.8 ° C. The measurement distance was of 1m between the camera and the 2 head embroidery machine

and the air temperature is of 20 ° C. In (Figure 6) are shown the needle temperature variations at 790 sinkings/min for the second embroidery pattern.

Date	24.11.2017
Image Time	11:40:01
Emissivity	0.95
Object Distance	1.0 m
Reflected Temperature	20.0 °C
Li1 Max. Temperature	60.3 °C
Li1 Min. Temperature	12.3 °C
Li1 Max - Min Temperature	48.0 °C
Li1 Emissivity	0.13
Li1 Object Distance	2.0 m
Li1 Reflected Temperature	25.0 °C

Fig. 7. *Image in the IR spectrum of the 2 head embroidery machine at 900 sinkings/min*

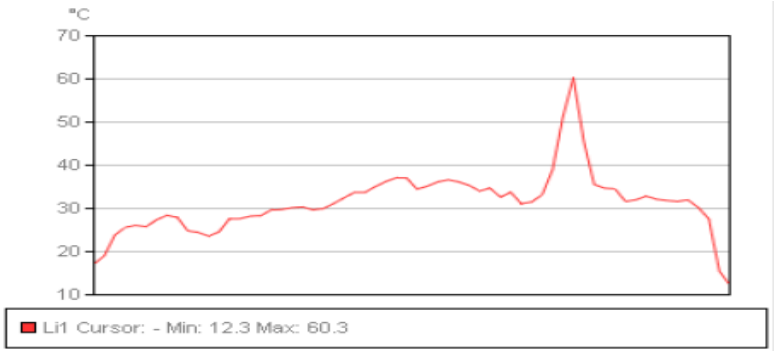


Fig. 8. *Variations of the needle temperature at 900sinkings/min.*

In Figure 7 can be seen the graphic slider on the needle indicating a temperature of 60,3 ° C. The measurement distance was of 1m between the camera and the 2 head embroidery machine and the air temperature was of 20 ° C. In (Figure 8) are shown the needle temperature variations at 900 sinkings/min for the third embroidery pattern.

3. INTERPRETATION OF RESULTS

Following the measurements of the RICOMA 2 head embroidery machine on the chosen material, at 300 sinkings/min the needle temperature was recorded as 29.4 ° C. At 790 sinkings/min, the needle temperature increases to 46.8 ° C and at 900 sinkings/min the temperature of the needle reaches a significant value of 60.3 ° C.

4. CONCLUSIONS

These measurements taken on the 2 head embroidery machine on the synthetic and natural fiber material lead to the conclusion that at the 300 sinkings/min working regime there are no high temperature increases of the sewing (embroidery) needle, even if the embroidery pattern is much more complex, which denotes an admissible needle behavior in relation to the embroidered material.

The authors have determined by means of the vibration measurement technique that the 790 sinkings/min working regime is an optimal working regime. At this 790 sinkings/min working

regime, the needle temperature is of 46.8 ° C. Although no major changes to the needle occur during this working regime, the needle temperature increases with the complexity of the embroidery pattern. At 900 sinkings/min, the needle temperature rises to a significant 60.3 ° C, which leads to the conclusion that as the working regime of the embroidery machine the temperature of the needle significantly increases and a degradation of the thread may occur.

ACKNOWLEDGEMENT

,,This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI - UEFISCDI, project number PN-III-P2-2.1-CI-2017-0107, within PNCDI III" Contract nr.88CI/2017.

REFERENCES

[1].*** http://www.electricalc.ro/servicii/termoviziune

[2]. Pancu Rareş, Bungău Constantin, Ganea Macedon, Thermographic diagnosis at machine tools, Neconventional Tehnologies Review, Revista de tehnologii neconventionale, Sibiu, nr.2/2013, ISSN 1454-3087, volume XVII, CNCSIS "Clasa B+ pp. 62-66, 2013.

[3]. Pancu Rareş, Moldovan Ovidiu, The importance of thermal vision tehniques in industrial applications. Case study, Neconventional Tehnologies Review, Revista de tehnologii neconventionale, nr.1/2014, ISSN ISSN 2359 – 8654, Volume XVIII, CNCSIS "Clasa B+, pp.34-38, 2014.

[4].***http://www.flir.com/uploadedFiles/Thermography/MMC/Brochures/T820147/T820147_APAC.pdf

[5] Oana, I.P., Oana, D., Doble, L., Analysis of the heating needle machine, in sewing process at high speeds, Annals of the University of Oradea, Fascicle of Textiles-Leatherwork, Oradea, vol XIV, nr. 2, 2013 pp. 71-75

[6]. Yukseloglu S. M., Çitoğlu F., Çetinkaya, B., A study on the needle heating in polyester blend upholstery fabrics, Revista Industria Textilă, vol 64, nr. 5, 2013, ISSN 1222–5347 (233–300), pp. 246-253

[7]. Șuteu, M., Indrie, L., Gherghel, S., Ganea, M.-" Using thermography to identify flaws in the Sunstar buttonhole sewing machine" Annals of the University of Oradea, Fascicle of Engineering and Industrial Management, ISSN 1843-813X, Oradea, Volume XIV, 2013, No. 1, pp. 89-94;.

[8]. Șuteu, M., Indrie, L., Gherghel, S., Timofte, A., - Identifying the points that represent potential defects in embroidery machines using infrared thermography – Revista Industria Textilă, ISSN 1222–5347, București, Vol. 66, 2015, No.1, pp. 39-42, revistă cotată ISI Thomson Rueter.

[9]. Șuteu, M., Indrie, L., Ganea, M. - Determination of optimum performance regime for SunStar buttonhole machine by vibrations measuring technique. Processing the data measured with Data Explorer Software, Annals of the University of Oradea, Fascicle of Textiles-Leatherwork, Oradea, vol XIII, nr. 1, 2012 pp. 146-157.

[10]. Baban,C.F., Baban,M., Suteu,M.D., (2016) - Using a fuzzy logic approach for the predictive maintenance of textile machines, Journal of Intelligent & Fuzzy Systems, 30(2), pp. 999-1006

[11]. Șuteu, M., Baidoc, M., Indrie, L., Ganea, M. - Determining the optimal operating mode for the embroidery machine by using the vibration measurement technique - Industria Textilă, ISSN 1222–5347, București, Vol. 65, 2014, No. 1, pp. 17-21, revistă cotată ISI Thomson Rueter;

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

AN ANALYSIS OF CONDUCTIVE FIBERS AS SMART TEXTILES

YUCE Ismail[1], YUKSELOGLU Muge[2], CANOGLU Suat[3]

[1] Trakya University, Edirne Technical Vocational High School, Textile, Clothing, Footwear and Leather Section, 22020, Edirne, Turkey, E-Mail: ismailyuce@trakya.edu.tr

[2] Marmara University, Faculty of Technology, Department of Textile Engineering, 34722, Istanbul, Turkey, E-Mail: myukseloglu@marmara.edu.tr

[3] Marmara University, Faculty of Technology, Department of Textile Engineering, 34722, Istanbul, Turkey, E-Mail: scanoglu@marmara.edu.tr

Corresponding author: YUCE, Ismail, E-mail: ismailyuce@trakya.edu.tr

Abstract: *This study aims to foreground the significance of conductive textiles as smart textiles for the clothing industry. As is known, smart textiles are materials and structures that sense and react to environmental changes. Conductive textiles have managed to become one of the fastest growing branches of smart textiles in that they have taken its place among the most leading products in recent years. As the literature review has shown, the significance of conductive textiles is mostly related to their wide range of usage areas such as medical, space, defense, industrial fields in which they create added value. Some of the studies have shown that electrical conductivity and static electricity are very important during the use and production of textiles. However, this study also wants to underline the probable disadvantages of static electricity for textiles products and/or their users. For this purpose, it has been explained that the generation of static charges or electrostatic behavior on the surface of textiles can lead to such disadvantages as electronical shocks of the consumer during product use or production process, breaking down of sensitive electronic devices, ignition in environments where flammable vapor and dust exists as well as rapid contamination of fabrics.*
In order to shed light on general features of conductive textiles, information regarding the basic principles of antistatic and conductive textiles, the methods of conductivity and their usage areas have been presented. To collect data, relevant literature has been reviewed by using qualitative research methods. After evaluating the collected data, it has been concluded that the fibers to which conductivity has been imparted are more suitable for the clothing industry.

Key words: *Smart, Static, Electricity, Conductivity, Fibers.*

1. INTRODUCTION

The real meaning of the word “electricity” comes from the word “amber” which means electrons in Greek. The materials are classified as conductive, semi-conductive and non-conductive (insulating) materials according to the state of electrical conduction. Electric history begins with the concept of electrostatic. Electrostatic can be defined as the electric charge of objects by friction. The earliest studies on electronics started with the static electronics studies of Milesian Thales during BC 600. Rubbing the amber against a wool baze, Thales observed that it pulled the chaff. He also

realized that when it was pulled over a human body in long term rubbings, the amber produced small sparks. As a result of his experiments, he observed that mat and similar materials showed the same characteristics. Thales examined today's static electricity and the first mention of static electricity started during the Ancient Greek period of Thales. This is the first observation of static electricity by man. [1], [2].

All material in the environment consists of protons containing positive charges in the nucleus and containing an equal number of electrons surrounding the nucleus. The contact of two different materials allows the transfer of electrons across the interface. It causes the formation of charges on both materials after two materials have been separated. As a result, one material has negative charge (excess electrons) and the other material has positive charge (insufficient electrons). This is called static electrification. If the two materials are conductive, the charges can equalize themselves by the backflow of electrons immediately after the separation of two surfaces [3].

Static loads on the textile surface can lead to serious consequences. For example, loaded fibers and yarns may push each other, which makes processing difficult or impossible. Charges generated on fibers and fabrics can make sensitive electronic equipment difficult to operate and can sometimes overload and damage these devices. Discharges of sufficient magnitude may cause fires or explosion in an operating room. Therefore, it is necessary to prevent the formation of static charges and it is important to develop antistatic and conductive textiles.

Conductive textiles are also important for wearable electronic clothing, which is also a branch of smart textiles. Electronic textiles or e-textiles are used to specify fabric structures that integrate electronic elements into the textile, detect and respond to changes in the environment. These clothes are used such as defense, medicine, space, industry and so on. Conductive fibers, yarns and fabrics have functions such as sensor, electromagnetic protection, actuator, imaging, dust and bacteria prevention, static charge discharge, data management, communication [1], [4], [5].

Using wearable computers, we can communicate with the environment, receive and transmit data. The equipment designed for the desktop needs to be designed in a way that will fit the garment [6]. The Massachusetts Institute of Technology (MIT) issued a manifesto for this purpose:

> To date, personal computers have not lived up to their name. Most machines sit on the desk and interact with their owners for only a small fraction of the day. Smaller and faster notebook computers have made mobility less of an issue, but the same staid user paradigm persists. Wearable computing hopes to shatter this myth of how a computer should be used. A person's computer should be worn, much as eyeglasses or clothing are worn, and interact with the user based on the context of the situation. With heads-up displays, unobtrusive input devices, personal wireless local area networks, and a host of other context sensing and communication tools, the wearable computer can act as an intelligent assistant, whether it be through a Remembrance Agent, augmented reality, or intellectual collectives [7].

In this work, we focus on the properties of antistatic and conductive fibers. The fundamental principles of conductive textiles, conductive fiber production and types, future applications will be explained.

2. BASIC PRINCIPLES OF ANTISTATIC AND CONDUCTIVE TEXTILES

Fibers, yarns and fabrics are organic products that are not conductive. For this reason, the most important principle for antistatic and conductive textiles is to increase the ionic or electronic conductivity of the materials. Pure water is not conductive, but it has water conductivity that contains dissolved minerals, which plays a key role in ensuring conductivity to textile products. The

conductivity of these products can increase considerably with the presence of water molecules present in the textile materials [3], [8].
Antistaticity and conductivity can be imparted to a textile product using different methods. These methods are given below:

- During extrusion melting a synthetic polymer (PES, PA etc.) by adding conductive carbon or a metallic material,
- The production of yarns as a result of blending of stainless steel fibers or filaments with natural or synthetic fibers,
- Using conductive fibers made of metals such as stainless steel, aluminum, copper and carbon in production,
- Method of applying antistatic agents in a solution bath or by sputtering
- Electrolytic coating of the surface with metal or carbon [3], [9].

3. CONDUCTIVE FIBERS

The first step in the development of wearable electronic devices is to use electrically conductive fibers or yarns. Conductive fibers can be self-conducting or can be subsequently added. Carbon fibers are at the head of spontaneously naturally conductive fibers [1], [10]. In addition, fibers made from metallic materials such as stainless steel, ferro alloys, nickel, titanium, aluminum, copper wire are also used [5].

3.1. Carbon Fibers

Carbon fibers were first produced from cellulosic precursors by Edison and Swann more than 100 years ago [11]. Carbon is the nonmetal that forms the main element of coal and organic compounds. The raw materials of the carbon fibers are polymeric precursors materials such as polyacrylonitrile (PAN), cellulose, pitch and polyvinylchloride. The density of carbon fibers is in the range of 1.6-2.2 g / cm^3. Fatigue behavior of carbon fibers is better than all known metals. At the same time, the conductivity of tar-based carbon fibers is 3 times higher than copper. Major uses of carbon fibers include defense, space, automotive, and medical. [10], [12], [13].
Carbon filaments have high conductivity and good wear resistance. Carbon fiber can be produced singly or carbon particles can be incorporated in the extruder during fiber spinning (Figure 1). However, the conductivities of these fibers are limited. Homogeneous carbon fibers have high electrical conductivity in the range of 10^{-3}-10^{-5} Ohm.m. [6], [14].

Fig. 1 *Filament carbon fiber (HexTow®)*

3.2. Metallic Fibers

The first use of metallic fibers goes back 3000 years. Contrary to what is believed, the first man-made fibers are metallic fibers, not nylons or rayon [15]. 100% continuous metal wire causes various problems in the production and use of the fabric. It is also aesthetically undesirable. Because of this, it is preferred to use composite yarns, which are combined with various synthetic / natural fibers and yarns by different methods, in fabric production. Blending non-conductive fiber bands and metal bands can result in high-conductivity yarn. Blending of synthetic or natural fibers with metal fibers is successfully accomplished especially in staple spinning processes. Metallic fibers are typically produced either by a bundle drawing or a shaving operation. [1], [6], [5], [16]. The bundle-drawing process consists of bundling several fine metal wires then drawing them continuously and simultaneously from source metals. During shaving, the edges of a metal plate are shaved and afterwards winding in hanks or bobbins. This method is advantageous in that it requires less time and is less costly. At the same time, the section of the fibers obtained by this method is rectangular and is more crimp and finer than bundle-drawing method. The thickness of the metal fibers can be in the range of 1-80 μm. This value is lower than that of human hair with an average thickness of 70-100 μm. (Figure 2) [5], [14].

Fig. 2 *Metallic fiber diameters compared to human hair [17]*

3.3. Conductive Polymers

Polytiophene (PT), polyaniline (PANI) and polypyrrole (PPy) based polymers are conductive polymers. Conductive fibers were obtained using two experimental processes (melt spinning and coating process). The electrical conductivities of these polymers result from the fact that they have conjugated double bond structures. Polyaniline (PANI) is the most attractive conductive polymer because of its good environmental, thermal, chemical stability and economic properties. [5], [18].

3.4. Making Conductive Coating on Fibers

Electrically conductive fibers can be obtained by coating with conductors such as metal, metal oxides and metal salts. For this purpose, such coating methods as non-electric coating, vapor deposition, spraying can be applied without changing the existing properties of the textile products [1], [19].

Physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques have wide range of applications in industrial applications. Physical and chemical vapor deposition methods are effective methods for imparting conductivity to textiles. Metals such as Zn, Ti, Cu, Ag and Al; conductivity can be imparted to fibers. Silver (Ag) is a coating material that can impart conductivity, antibacterial, UV protection and hydrophobic properties to textile products (Figure 3) [20].

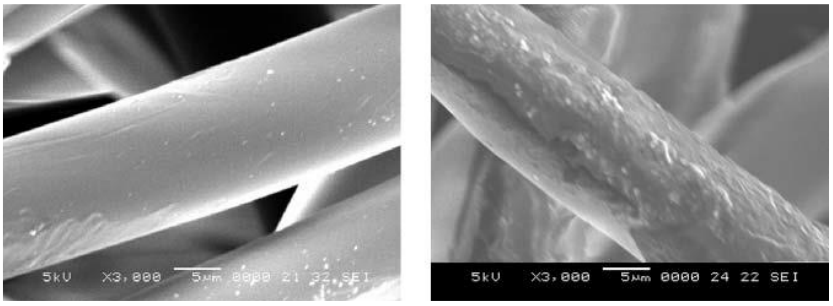


Fig. 3 *SEM images, (a) Original PP fibers, (b) 3 nm thick silver coated PP fibers [20].*

4. DISCUSSION

For the textile products to be conductive, the fibers from which they are made of need to be conductive. Depending on their raw materials, the fibers (carbon, metal fibers etc.) are spun in a way that will enable them to become conductive or this feature can be imparted to them later. It is important that the textile products used in clothing industry need to have some specific features that will provide the users with comfort. Metallic or carbon fibers are not suitable fibers because of their rigid properties. For this reason, it would be more appropriate to use conductive materials in extruder during fiber spinning or coat the surface with a conductive material so that the conductive fibers to be used in clothing production can fulfill their comfort features, which will consequently affect the comfort of clothes.

5. CONCLUSION

Being fast and practical is one of the most important factors in today's world. It is not possible for textile products not to be affected by this changing trend. For this reason, the importance of conductive textiles is continuing to increase day by day. Conductive textiles are now attracting considerable attention thanks to their innovative and life-promoting effects on human life.

Global competition is requiring antistatic and conductive textiles that can be produced at lower cost and greener production. It would be also advantageous to have textiles that are not only antistatic, but also have other functionalities such as soil and stain resistibility, retarding flame, water and/or oil repellency and antimicrobial ability.

In this work, the fundamental principles of conductivity and the conductivity of the fibers have tried to be explained. With the progress of technology, it is foreseen that the conductive polymers and coating technology will continue to develop in conductive fiber production.

REFERENCES

[1] A. C. Bedeloglu, N. Sunter and Y. Bozkurt, "*Elektriksel Olarak İletken Tekstil Yapıları, Üretim Yöntemleri ve Kullanım Alanları*", The Journal of Textiles and Engineer, vol. 17, pp. 7-17, 2010.

[2] M. Karayaman. (2013, March) "*İlkler Şehri Uşak'ta Elektriğin Serüveni*", [Online]. Available:https://www.academia.edu/10339782/%C4%B0lkler_%C5%9Eehri_U%C5%9Fakta_Elektri%C4%9Fin_Ser%C3%BCveni

[3] X. Zhang, "*Antistatic and Conductive Textiles*", in Functional textiles for improved performance, protection and health, Ed. N. Pan, G. Sun, Woodhead Publishing Ltd., 2011, pp. 27-44.

[4] S. Lam and P. Tang, "*Recent developments in flexible wearable electronics for monitoring applications*", Transactions of the Institute of Measurement and Control, vol. 29, pp. 283–300, 2007.

[5] M. G. Honarvar and M. Latifi, "*Overview of wearable electronics and smart textiles*" The Journal of the Textile Institute, 108:4, pp. 631-652, 2016.

[6] D. J. Tyler, "*Joining of wearable electronic components*", in Joining textiles Principles and applications, Ed. I. Jones, G. K. Stylios, Woodhead Publishing Ltd. 2013, pp. 507-535.

[7] Available: https://www.media.mit.edu/wearables/

[8] O. Kayacan and E. Y. Bulgun, "*Akıllı Tekstiller ve Elektriği İleten Tekstil Esaslı Malzemeler*", The Journal of Textiles and Engineer, vol. 58, pp. 29-34, 2005.

[9] D. Cukul, "*Teknik İpliklerde Son Yıllardaki Gelişmelere Örnekler*", The Journal of Textiles and Engineer, 20: 91, pp. 50-63, 2013.

[10] B. Yalcinkaya, D. Yilmaz, "*Elektronik Tekstillerin, Tekstil Endüstrisindeki Yeri ve Giyilebilir Tekstilde Kullanılan İletken Lifler*", Tekstil Teknolojileri Elektronik Dergisi, vol. 5, pp. 61-71, 2011.

[11] B. A. Newcomb and H. G. Chae, "*The properties of carbon fibers*", in Handbook of Properties of Textile and Technical Fibres, Ed. A. R. Bunsell, The Textile Institute Book Series, 2018, pp. 841-871.

[12] N. Yaman, T. Oktem and N. Seventekin, "*Karbon Liflerinin Özellikleri ve Kullanım Olanakları*", Tekstil ve Konfeksiyon, vol. 2, pp. 90-95, 2007.

[13] P. Morgan, "*Carbon Fibers and Their Composites*", Taylor & Francis, 2005.

[14] N. Sunter, "*İletken İpliklerin Üretim Yöntemlerinin ve Özelliklerinin İrdelenmesi*", Dokuz Eylül Üniversitesi Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi, İzmir, 2011.

[15] L. Guo, T. Bashir, E. Bresky and N. K. Persson, "*Electroconductive textiles and textile-based electromechanical sensors—integration in as an approach for smart textiles*", in Smart textiles and their applications, Ed. V. Koncar, Woodhead publishing in textiles no. 178, 2016, pp. 657-693.

[16] H. G. Ortlek, G. Kilic, G. Okyay and O. Bilget, "*Paslanmaz Çelik Tel İçerikli Özlü İplik Üretimi İçin Farklı Ring Eğirme Metodlarının İncelenmesi*", Textile and Apparel, vol. 3, pp. 225-235, 2011.

[17] E. J. Leavline, D. A. A. G. Singh, S. Prasannanayagi and R. Kiruthika, "*A Compendium of Nano Materials and their Applications in Smart Nano Textiles*", Research Journal of Nanoscience and Nanotechnology, vol. 5, pp. 44-59, 2015.

[18] B. Kim, V. Koncar, E. Devaux, C. Dufour and P. Viallier, "*Electrical and morphological properties of PP and PET conductive polymer fibers*", Synthetic Metals, vol. 146, pp. 167–174, 2004.

[19] B. J. Munro, J. R. Steele, T. E. Campbell and G. G. Wallace, "*Wearable biofeedback systems*", in Intelligent textiles and clothing, Ed. H. Mattila, Woodhead Publishing Ltd., 2014, pp. 450-470.

[20] I. Yuce, S. Canoglu, M. Yukseloglu, "*Textile Surface Modification by Pyhsical Vapor Deposition – (Review)*", Annals of the University of Oradea Fascicle of Textiles, Leatherwork, pp.123-128, 2017.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THERMAL CONDUCTIVITY OF CHICKEN FEATHER AND PUMICE STONE REINFORCED THERMOPLASTIC COMPOSITE MATERIALS

YUKSELOGLU S. Muge[1], UZUN Muhammet[1], OVALI Sabih[2]

[1] Marmara University, Faculty of Technology, Department of Textile Engineering, Goztepe 34722, Istanbul, Turkey

[2] Adıyaman University, Faculty of Technology, Department of Textile Engineering, Adıyaman, Turkey

E-Mail: myukseloglu@marmara.edu.tr , m.uzun@marmara.edu.tr , sabih.ovali@gmail.com

Corresponding author: myukseloglu@marmara.edu.tr

Abstract: *Natural fibres are green materials and have some advantages i.e. are renewable, reasonably cheap, biodegradable and ecologically freindly. Conversely, composites made of natural fibers can be used as a reinforcement material either long or short forms or recycled fibres. In the production of this NFC materials are made from a combination of natural fibers and polymeric matrice. In this study, thermoplastic-based polypropylene chips composites were produced by making use of pumice stone with different grain structures and chicken feather as reinforcement. In the composite production process hot-pressing machine was used to develop novel composites. Prior to the production process, the pumice stones were determined in the sizes of 0-1mm, 1-2mm and 2-3mm by passing them through a regular sieve. Later, chicken feathers with 0-1 mm granule structure were chopped in a blender and mixed with pumice stones separately. These mixtures were sewn in between polypropylene nonwoven fabrics. The composite plates were obtained by placing polypropylene chips on top and bottom of the sewn fabric. The samples for thermal conductivity tests were cut with a diameter of 28 mm from these plates. And heat conductivities of these samples were tested on the P.A. HILTON LTD. H940. By reinforcement materials such as chicken feather and pumice stone, it is aimed to improve the heat conductivity properties of the produced composites. Overall results showed that an increas in particle size of pumice stone has negative effect on the thermal conductivity of natural fiber composites.*

Keywords: *Pumice, chicken feather, polipropilen, composite, heat conductivity*

1. INTRODUCTION

Technological innovations have helped the humanbeings to improve their living standards, with the pace of development and research throughout the history. However, some technological improvements have also a negative environmental impact. Therefore, nowadays more efforts are being made to use natural-based biological and sustainable materials that exist in nature instead of creating new materials. The engineering and technical applications of textile structures have gained importance in fiber reinforced composite production, especially due to their lightness, strength, durability, thermal resistance, low density and stability [1-3]. CFF (Chichen Feather Fiber) is often defined as a waste by-product and contributes to environmental pollution due to disposal problems. There are two main chicken feather removal methods available in industry, which are burning and

embedding. Unfortunately, both have negative effects on the environment. Recent studies on chicken feather wastes have shown that they can be a potential composite reinforcement material. The CFF composite reinforcement application offers a more efficient way to solve environmental problems compared to conventional disposal methods. There are some advantages of CFF, they are cheap, renewable and readily available. CFF as a composite reinforcement material has desired features such as being light, having high thermal isolation and excellent acoustic properties, non-corrosive behaviour and excellent hydrophobic properties. CFF has the lowest density value compared to other all natural and synthetic fibers [4-7]. Castano et al reported that CFF keratin biofuels provide a uniform distribution and adhesion between polymers due to their hydrophobic nature and CFF-reinforced composites have good thermal stability and low energy distribution [8-9]. In composite structures, properties such as lightness, strength and modulus, fatigue strength, electricity and heat conductivity and also their economy play a role in the selection of reinforcing material. Properties like providing tension transfer between fiber and matrix, fiber corrosion, oxidation, environmental impact and protection of matrix material are the important selection criterias of the composites. The advantage of composite materials is that it combines the best features of its components [10]. Pumice-based products are resistant to fire, mould and pests. Fine-grained, pure white, hard, light and neutral pumice stones are used as natural puzzlers in Portland cement production as mineral additives. In this study, heat permeability values of produced composite materials were tested. Chicken feathers and pumice stones were added into polypropylene to produce composite materials [11]. Some researchers [12] also indicate that, in natural fibre composites (NFCs) novel manufacturing processes and surface modification methods can be developed in future studies; therefore in this study we first aimed to produce reinforced composite materials both made of pumice stone with different grain structured and chicken feathers. Later, we will highlight its thermal conductivity properties.

2. MATERIAL AND METHOD

In this study, pumice stone and chicken feathers were used as a reinforcing material. Polypropylene nonwoven fabrics have been used in the upper parts of the chips to prevent slippage in the composite. In addition, polypropylene sewing threads were used to sew the fabrics. Thermoplastic-based composites are manufactured by reinforcing the chicken feathers and pumice stone into polypropylene chips as polymer matrix material.

In the hot press machine, the upper and lower tables pressed the reinforcement materials with 200^{o}C temperature under 1.00 bar pressure to obtain composite structures as shown in Figure 1. Pumice stones with 0-1 mm, 1-2 mm and 2-3 mm sizes were determined by passing through sieves. Later, they were mixed separately with chicken feathers having a grain structure of 0-1 mm by passing through the blender. These blended materials were planted by placing them between polypropylene and nonwoven fabrics. Composite plates were obtained by placing polypropylene chips on the upper and lower parts of the fabric. Heat samples were cut in 25 mm diameters from these plates for the heat permeability tests.

Fig 1: *Production stages of composites in hot press machine*

3. HEAT CONDUCTIVITY ANALYSIS

Heat conductivity tests of the samples were performed with P.A. HILTON LTD. H940 heat transmission device. Composite material samples for the heat conductivity test were cut in a circle form with a 25 mm diameter and placed in the device. Linear conduction module is applied on the heat conduction device.

The heat flow rate (Q) can be obtained from the digital display unit of the device. The K (heat transfer coefficient) value is determined by placing the values in the formula at Equation 1.

$$K = (Q \cdot Dx) / (A \cdot Dt) \quad \textbf{(1)}$$

$$Dt = T3 - T7$$

A: area of the field (m^2), Dx: thickness of material (m), Q: heat flow rate (w), T3: given heat (^oC), T7: received heat (^oC), Dt: temperature difference (^oC), K: heat transfer coefficient (W/m^oC)

Fig.2: *Heat transmission device and a tested sample*

As a result of the testing operation, the heat transfer coefficient (K) was calculated in W/m^oC unit. The test samples used in the heat testing is as shown in Figure 2. Before starting the heat conductivity measurement test, the machine has been calibrated. The temperature was fixed at 22°C and test procedures were performed.

4. RESULTS AND DISCUSSION

The results of heat conductivity test for 4 different pumice and chicken feather reinforced composite materials with 25 mm diameter and 2 mm thickness are given in Table 1. The results of the heat conductivity tests are as given in Table 1.

Table 1. *Heat transfer coefficients of composite materials*

Pumice stone and chicken feather reinforced composite materials	**Heat transfer coefficient (k)(W/m^0C)**
1-2 mm grain structured Chicken feather reinforced composite	1,48259114
Chicken feather and 0-1 mm pumice stone reinforced composite	1,452339317
Chicken feather and 1-2 mm pumice stone reinforced composite	1,425868972
Chicken feather and 2-3 mm pumice stone reinforced composite	1,474218864

The best heat conductivity value of the produced material was the reinforced composite material with chicken feather and 1-2 mm of pumice stone sample.

5. CONCLUSIONS

In the produced reinforced composite materials, the particle size of the reinforcement material is one of the important factors in heat isolation. Thermal transition increases or decreases according to the grain size. Effects on heat conductivity values were determined by adding pumice and chicken feathers to polymer materials. The increase in particle size of pumice stone negatively affected the heat permeability values.

The tensile and flexural properties of the control (0%) composites for the resins, vinylester and polyester, have significantly superior properties to the CFF reinforced composites. The tensile and flexural values decrease when the fibre loading percentage increases. The control (0%) composite tensile strength was found to be 5000N whilst the CFF reinforced vinylester composite tensile strength was at maximum 1891N. It is evident that the reinforcement material decreases the tensile property of the composites almost three times. For the flexural property, the reinforced composites indicate around two times lower value than the control composite. Only the Charpy impact values of the CFF reinforced composites are considerable better when compared with the control (0%) composites [12].

REFERENCES

[1] Drzal LT, Rich MJ, and Lloyd PF, "*Adhesion of graphite fibers to epoxy matrices. Part 1. The role of fibre surface treatment"*, J. Adhesion 16, 1-30

[2] Hsie M, Tu C, Song PS, "*Mechanical properties of polypropylene hybrid fiber-reinforced concrete*" Materials Science and Engineering A 494 (2008) 153-157

[3] Shibata S, Cao Y, and Fukumoto I, "*Lightweight laminate composites made from kenaf and polypropylene fibres*" Polymer Testing (2006), 142-148

[4] Barone JR, Schmidt WF, Liebner FE, "*Compounding and molding of polyethylene composites reinforced with keratin feather fiber*" Com. Science and Technology 65 (2005) 683-692.

[5] Bullions TA, Hoffman D, Gillespie RA, O'Brien JP, Loos AC, "*Contributions of feather fibres and various cellulose fibres to the mechanical properties of polypropylene matrix composites*" Composite Science and Technology 66 (2006) 102-114.

[6] Huda S, Yang Y, "*Composites from ground chicken quill and polypropylene*" Composites Science and Technology 68 (2008) 790-798.

[7] Reddy N, Yang Y, "*Structure and properties of chicken feather barbs as natural protein fibres*" Journal of Polymers and The Environment 15(2) (2007) 81-87.

[8] Uzun M, Sancak E, Patel I., Usta I., Akalın M., Yuksek M. "*Mechanical Behaviour of Chicken Quills and Chicken Feather Fibres Reinforced Polymeric Composites*", Archives of Materials Science and Engineering, 52(2), 82-86, (2011).

[9] Hernandez A.L.M., Santos C.V., de-Icaza M., Castano V.M., "*Dynamical-mechanical and thermal analysis of polymeric composites reinforced with keratin biofibers from chicken feathers*" Composites: Part B 38 920070 405-410.

[10] Ulusoy, G., "*Pomzanın İzole Monomilitik Malzeme İmalinde Kullanılması"*, MTA Dergisi, Ankara, Türkiye ,129, 89-96, (2004).

[11] Bulut, Y., Erdoğan, Ü.H., "*Selüloz esaslı doğal liflerin Kompozit üretiminde takviye materyali olarak kullanılması*", Tekstil ve Mühendis, İzmir, Türkiye, 18-82 ,2011.

[12] Yukseloglu S.M., Canoglu S., "*Natural fibre composites: A review on flax fibres*", in Annals of the University of Oradea Fascicle of Textiles, Leatherwork, Oradea, 2017.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE ANALYSIS OF TURKISH LEATHER INDUSTRY'S COMPETITIVENESS

ATILGAN Turan[1], OFLUOGLU KUCUK Pelin[1]
ORK Nilay[2], MUTLU Mehmet Mete[2]

[1]Ege University, Engineering Faculty, Department of Textile Engineering, 35040, Izmir, Turkiye
pelin.ofluoglu@ege.edu.tr, turan.atilgan@ege.edu.tr

[2]Ege University, Engineering Faculty, Department of Leather Engineering, 35040, Izmir, Turkiye
nilay.ork@ege.edu.tr, mete.mutlu@ege.edu.tr

Corresponding author: Mutlu, Mehmet Mete, mete.mutlu@ege.edu.tr

Abstract: *Considering its export-oriented performance and the close relationship with various branches, the Turkish leather industry is one of the most important sectors of Turkey. Turkey is also a well-known leather and leather products manufacturer in the global market. Thus, Turkish leather industry is faced with a constant competition pressure. Analysing the developments and the factors that are driving the industry, and contributing industry's sustainable competitive advantage are important for both the industry and the country's economy. In this study, analysis of Turkish leather industry's competitiveness was discussed by using Porter's Diamond Model. For this purpose, both primary and secondary research methods have been utilized. Interviews consisting of open-ended questions prepared in the light of data surveys were made with two researchers who are experts in leather industry and three large-scale leather apparel companies in Izmir and Istanbul. As a result of the analysis, the main elements of the competition structure of the industry were described under the titles of Input conditions, Demand conditions, Relevant and Supporting authorities, Strategy and competitive structure of company, State activity and chance by analysing the results of respondents; and various suggestions have been made in order to let Turkey have a more competitive position on the world leather industry platform.*

Key words: *Leather industry, Porter diamond model, competitiveness analysis*

1. INTRODUCTION

Turkish leather industry has made important contributions to the development of Turkey industry, especially after the 1980's; Turkish leather industry's name also has begun to be mentioned in global markets by the export-based production model. However, because of the increasing market share of the low-priced and low-quality products coming from the Far East, the leather industry has faced with a constant competition pressure. Thus, increasing competition and sustainability of this industry is of major importance.

Surviving of Turkish leather industry in these competitive conditions and increasing its share in the international markets will be possible by correctly analysing and interpreting the dynamics of the industry, and taking strategic steps towards the future. Porter's diamond model allows systematic evaluation of the elements of competition together. For this reason, in this study, the competitiveness of the leather industry was analysed by the Porter approach, and some prospective deductions and suggestions were made. Furthermore, competitiveness analysis studies

based on the diamond model are available for different industries but it is not studied for the leather industry yet. Consequently, it is thought that this study will also contribute to literature in this issue.

1.1. Diamond Model Approach in Competitiveness Analysis

Porter has developed a model, namely diamond model, to analyse the competitive power of an industry or a country. The model analyses the elements of global competition in a system approach in order to systematically reveal the determinants of national competitive advantages. Four major factors affecting the competitive advantage of an industry in the diamond-designed model have been identified. These basic variables are the factor conditions, firm strategy and competitive structure, demand conditions and supporting industries, which are composing the diamond's corners. In response to these four internal variables, there are two external factors in the system, namely government and chance. In this model, the basic variables determine the competitive advantages together, not individually. Hence, the variables influence each other's and form a whole. The diamond model is used to determine industries' competitiveness positions by explaining how a factor is affected by three other factors [1]. Figure 1, shows the model and dynamics that form the model.

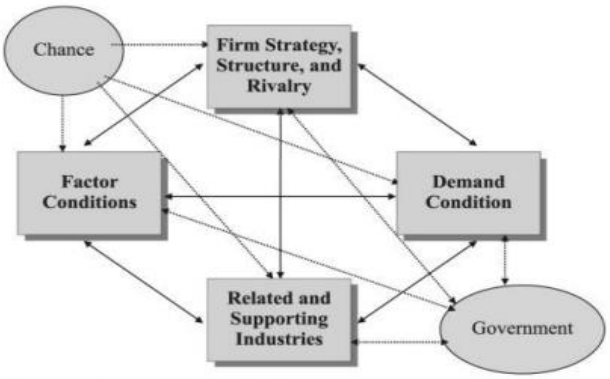


Fig. 1: *Porter Diamond Model*

2. METHOD

In this study, the competitiveness of the Turkish leather industry was analysed by Porter's Diamond Model method. The elements that constitute the competitiveness of the industry have been evaluated within this framework. The researchers have utilized primary and secondary data collection techniques during the data collection step. In the secondary data collection method, sources that related with the industry and the method (industrial reports of public institutions and organizations, databases of these institutions, relevant internet resources, scientific articles, company catalogues, etc.) have been examined.

In the primary data collection method, interviews consisting of open-ended questions were made with two researchers who are experts in leather industry and three large-scale leather apparel companies in Izmir and Istanbul. The questions in the questionnaire were prepared in the light of the secondary data survey and these questions were used in the interviews.

3. RESULTS

Information and data obtained for the competitiveness of the leather industry are given in the light of the findings obtained by primary and secondary data collection methods. In this context, the sub-headings that constitute the model are summarized by numerical and interpretive data, and the

"high-moderate-weak (low)" triple scale is used in order to base the interpretations on a common classification [2].

3.1. Input conditions

Labour: Leather industry has a 2% share in employment in Turkey. The average daily earnings of these people are 50.93 TL (9.93Euro) [3]. According to the enterprises, there is a significant decrease in the number of students who go to the leather-related schools, which negatively affects the supply of qualified labour force. Moreover, it was emphasized that many employees changed leather industry due to the economic problems experienced. For these reasons, the level of qualified labour force in this industry is considered as "weak". It is observed that the average wage level of the employees is 2000 TL (389.88 Euro) and recruitments are made by references or advertisements on the internet.

Raw material: leather industry have share in production costs of 60% of raw material, 20% of labour, 7% of auxiliary materials, 7% of energy, 4% of financing and 2% of another components. Therefore, raw material costs constitute an important input item [4]. As is known, production costs are increasing in leather industry. The increase in raw material prices is one of the main reasons for this situation. Company officials and experts have stated that they have experienced "low" in terms of quantity in the supply of raw materials and "moderate" in terms of quality and cost. It is stated that almost 70% of the raw materials are imported from abroad.

Capital: Firms in the leather industry indicate that new investment incentives are limited for them and that existing clusters are not adequately supported [5]. Industry experts and businesses classify financing sources on average at 50% bank loans and 50% equity. It is believed that cost of capital is considered to be "high".

Energy: Industry staffers have stated that they don’t experience any quantity and quality problems in supplying the energy they need, so they see problems in this area at a "low" level.

3.2. Demand conditions

Domestic demand: It is thought that domestic demand is insufficient and "weak" compared to external demand, and the demand variability in this market is considered to be "weak". It is argued that insufficient purchasing power and the changing weather conditions due to global warming cause low demand of leather; and leather products in the domestic market are mostly export leftover and second quality products.

Foreign demand: According to experts, foreign demand for Turkish leather products is increasing. Among the main reasons for this are the geopolitical position and its high quality and experienced production infrastructure. The foreign demanding level is stated "moderate" and this demanding variance is at "high" level. Parameters affecting external demands are economy, politics, fashion, climate change and instability in the country.

The status of the related industries: Leather industry performs activities in close relationship with many different sectors such as, animal husbandry, textile, chemistry [4]. According to experts, changes in demand in the related industries are not widely reflected in the leather sector and are "moderate" level of influence. It is thought that other concepts such as economy and fashion direct demand more.

3.3. Relevant and Supporting authorities

Industry is in contact with the Ministries of Economy, Customs and Trade, Development and many others. In addition, occupational and non-governmental organizations like Turkish Association of Leather Industrialists, Turkish Leather Foundation, Footwear Industrialists Association of Turkey, Turkish Leather Garments Manufacturers' Association, and Turkish

Exporters Assembly can provide many possibilities and advantages such as education, labour force, and cooperation. In addition, Turkish Leather Brands carries out activities aimed at increasing exports of Turkish leather, leather goods and footwear industry, developing its image and branding it abroad. Ege University Leather Engineering Department trains engineers for leather industry and carries out projects and R&D studies jointly with companies in the industry. However, according to the interviews, the experts find the university-industry cooperation as "moderate". Looking at international cooperations, companies participating in international fairs and leather companies can strengthen their cooperation and market share. Cooperation capability in the logistic infrastructure is considered adequate at the "moderate" level in terms of technology, cost and time opportunities.

3.4. Strategy and competitive structure of company

The situation of the SMEs: The leather processing industry is concentrated in Istanbul-Tuzla, İzmir-Menemen, Tekirdag-Corlu, Usak, Bursa, Balikesir-Gonen, Bolu-Gerede, Isparta, Hatay and Manisa-Kula. The distribution of shoe supplier firms is 50% in Istanbul and the other firms are located in cities like Izmir, Konya, Gaziantep, and Bursa. Leather apparel firms are mostly located in Istanbul and Izmir [6]. According to experts, firms are mainly small and medium sized enterprises, and the proportion of these firms is 90%. According to industry workers and experts, leather firms' strategies are more cost-oriented.

The situation of R&D, design and branding activities: There is one R&D center in the leather industry. There is no leather factory with a design center [7, 8]. The companies in the industry are also signing various R&D projects with universities. According to managers and experts, R&D, design infrastructure and branding in leather industry are seen at "low" level. Concentrated areas of R&D projects are indicated as new technologies in production, technologies for the environment and productivity increasing methods. Especially design becomes recently an important fact at firms. It is emphasized that this situation is reflected in the branding and that the branding is inadequate especially in the foreign market.

Capacity utilization (ratios): According to the data of Central Bank, the production capacity utilization ratio of leather and related products is 57.4% by 2016 [9]. This ratio proves that the capacity cannot be used efficiently.

Production range: By means of know-how, craftsmanship, high collection and design capacity of double-face production, the leather garment area is known internationally. In the footwear industry, production and product quality are rapidly improved, and design and R&D capacity develops to produce higher added value products [5]. It is thought that the Turkish leather is among main players in footwear and garment area, while main competitors are Italy in leather garments and China in footwear. According to experts, Turkish leather is seen as high quality but also high cost according to Far East market and low cost and moderate quality according to European market.

3.5. State activity

Social security payments: Taxes on labour costs and employment in Turkey are an important part of production costs [4]. The minimum wage in Turkey was 277.18 Euro, the total cost to the employer together with other expenses 412.31 Euro stands out [10]. This situation can cause informal employment in the sector.

Tax rates: The rate of VAT on leather and shoe upper leather made by a subcontractor has been reduced from 18% to 8% starting 25 November 2016 by Decree No 2016/9542 [11]. Industry executives and academics agree that tax rates for Turkey's manufacturing industry are "high".

Incentives: There are many incentive schemes closely followed by the leather industry [12]. According to experts and academicians, the effect of incentives and tax policies provided by the government on competitiveness level is "moderate".

Audit: The leather industry, which moved from an environmental point of view, signed an "Environmental Protocol" with the Ministry of Environment in 1994. Protocol is required that the enterprises either take part in any organize industrial zone with a treatment system or establish their own treatment systems. As a result of the efforts of industry to adapt to the environment, 70% of the goods produced are produced by environmentally sensitive methods today [13]. It is argued that the practices in the regulation of intellectual property rights in the fight against counterfeiting should be activated [5]. Representatives of industry have stated that the efficiency of the state control systems is "moderate".

Informality: Informal employment has become widespread, wage levels have fallen, and long working hours have been used as the most known way to lower the labour [14]. One of the important means of reducing costs is to employ uninsured workers, so industrial representatives particularly point out that informal employment is at a "high" level.

3.6. Chance

It is also a factor that affects the competitiveness of the leather industry, like every industry both nationally and internationally. The Turkish leather industry has a structure that is influenced by economic and political developments due to its commercial relations especially with other foreign markets in other fields. Managers and academicians interviewed within the scope of the study see the leather industry as "moderately bright" for the future of Turkey.

4. CONCLUSIONS AND SUGGESTIONS

Turkish leather and leather goods industry is one of Turkey’s important industries in international markets in terms of competitiveness. The leather industry has been on a rising trend for the last two years, although it has followed a long period of ups and downs. The export target of the industry is 5.2 billion dollars in 2023. When the leather industry is examined, it is seen that it is composed of shoes, leather and fur garments, finished leather and furs and saddlery product groups. Leather shoes has 51% share of the leather industry in export; leather apparel, finished leather and furs saddlery product groups have 19%, 17%, 13% respectively. According to Porter's Diamond Model, the competitive power of the industry appears to be "moderate". While the industry is weak in terms of input conditions, it has moderate competition power in terms of demand conditions. When we look at the strategies and structure of the companies in the industry, it is seen that there is a low competitive power except from the product variety. The reason for this is that firm strategies are largely based on cost strategies due to the fact that 90% of the company structures are composed of SMEs, low capacity utilization rates (57.4%), low level of R&D, design and branding. Product range is seen as the most important success of leather industry and it is at a high level.

When we look at the efficiency of the government, it is seen that it is a moderate effect of competition power. The most significant weaknesses in terms of industry are shown as high tax and social security payments that state implements. It is also seen that government incentives and supervision are moderate.

It can be said that the competitiveness of the Turkish leather industry is at a moderate level. In order to increase the competitive power, it is necessary to improve the weak and moderate competition elements. According to this;

• Input conditions need to be improved. In this regard, the industry and the government should give more support to the vocational schools and University that provide intermediary and

expert personnel for leatherworking in order to solve the problem of qualified personnel. Also; government incentives need to be developed to lower energy costs. Likewise, remedial measures should be considered for high capital costs and public measures should be taken to reduce credit interest.

• Foreign alternative markets should be emphasized in demand conditions. In particular, markets such as the USA, Africa and Iran should be evaluated.

• Turkish companies should focus more on marketing, innovation, design and branding-oriented strategies than on cost and production-oriented strategies.

• As with all of industries, the most important problems of the leather industry are high tax rates and social security payments. These costs need to be removed from the factors that have an adverse effect on competition power of Turkish firms. Likewise, the emphasis should be given on incentive system to industry-oriented by reviewing.

• One of the most important problems of the industry is informality, which has also a great effect to unfair competition. In this regard, necessary regulations and inspections must be done urgently.

The improvements to be done on these terms will provide significant contributions to leather industry's ability to increase its competitive power and achieve its goals for the year 2023.

REFERENCES

[1] İ.H. Eraslan, A. Karataş, H. Kaya, "*Türk Plastik Sektörünün Rekabetçilik Analizi*", Istanbul Commerce University Journal of Social Science, vol. 6(11), pp. 203-219, 2007.

[2] Ö. Öz, "*Assessing Porter's framework for national advantage: the case of Turkey*", Journal of Business Research, vol.55, pp. 509-515, 2002.

[3] Republic of Turkey Social Security Institution, "*Statistical Annals*", http://www.sgk.gov.tr/wps/portal/sgk/tr/kurumsal/istatistik/sgk_istatistik_yilliklari, 2015.

[4] Republic of Turkey Ministry of Development, Tenth Development Plan 2014-2018: Textile-Leather-Ready-Wear Working Group Report, pp. 184, 2014.

[5] Istanbul Chamber of Industry, "*Deri ve Deri Ürünleri İmalatı Sanayi*", Istanbul, 2015.

[6] E. Ekti, "*Tekstil Sektörü Raporu Sektörel Raporlar Serisi V*", Doğu Marmara Kalkınma Ajansı Düzce Yatırım Destek Ofisi, 2013.

[7] Republic of Turkey Ministry of Science, Industry and Technology, "*Ar-Ge Merkezi İstatistikleri*", https://agtm.sanayi.gov.tr/Upload/SingleFile/Dosya-473-356.pdf, 2017.

[8] Republic of Turkey Ministry of Science, Industry and Technology, "*Tasarım Merkezi İstatistikleri*", https://agtm.sanayi.gov.tr/Upload/SingleFile/Dosya-48-655.pdf, 2017.

[9] Central Bank Statistics General Directorate, "*İmalat Sanayi Kapasite Kullanım Oranı*", http://www.tcmb.gov.tr/wps/wcm/connect/bbd84449-6725-4cdd-ac34-8b70525c27e7/KKO-RaporTablo-Int.pdf?MOD=AJPERES-CACHEID=bbd84449-6725-4cdd-ac34-8b70525c27e7, 2017.

[10] Ministry of Labour and Social Security, "*Asgari ücretin net hesabı ve işverene maliyeti*", https://www.csgb.gov.tr/home/Contents/Istatistikler/AsgariUcret, 2017.

[11] A. Tolu, "*KDV Oranlarında Yapılan Son Değişiklikler*", http://muhasebedr.com/kdv-oranlarinda-yapilan-son-degisiklikler-2016/, 2016.

[12] Aegean Leather and Leather Products Exporters Association, "*2016-2017 Dönemi Çalışma Raporu*", 2017.

[13] Republic of Turkey Ministry of Economy, "*Deri ve Deri Mamulleri Sektörü Raporu*", 2016.

[14] Republic of Turkey Ministry of Customs and Trade, "*Esnaf ve Sanatkarlar Özelinde Sektör Analizleri Projesi: Deri, Giyim ve Ayakkabı Sektörü*", 2017.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE INFLUENCE OF TEMPERATURE AND RECIPE FORMULATION ON THE DIELECTRIC BEHAVIOUR OF PLASTIFIED PVC FILMS

BĂLĂU MÎNDRU Tudorel[1], BĂLĂU MÎNDRU Iulia[1], BUCIȘCANU Ingrid[1]

[1] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Textiles, Leather and Industrial Management, Str. Prof. Dr. Doc. Dimitrie Mangeron Avenue, No. 28, 700500 Iaşi, Romania, E-Mail: decanat@tex.tuiasi.ro

Corresponding author: Bălău Mîndru Iulia; E-mail: ibalau@tex.tuiasi.ro

Abstract: *Radio frequency fields (RF fields) have well-established uses in the manufacturing industries, as environmentally friendly heat sources. Synthetic polymer films can benefit from RF fields in several operations of the processing train, like gelification and blowing. Plastified polyvinyl chloride (PVC) films are some of the most popular products of this kind and have different applications in consumer goods, like clothing and footwear. Films properties depends on the recipe of the plastisol blend and on the processing parameters. This paper presents the combined influence of temperature and the nature of some auxiliaries, added to the plastisol blend, upon dielectric characteristics of plastified PVC films, obtained in high electric frequency field. The chemicals used as additives in the recipe formulation were: polydimethylsiloxane (PDMS) polymethylhydrosiloxane (PHDMS), nonylphenol ethoxylate emulsifier NF10 (NE) and collagen hydrolizate (CH). The RF field was provided by a high capacitive generator with 380 V supply voltage, and 13.56 MHz working frequency. Variation of dielectric loss angle, tg δ and dielectric permittivity, ε_r' were recorded over a temperature range of 20°C-160°C, in the frequency range 50 KHz-14.8 MHz. The phenomena of polarization, appeared in RF field, are either dipole - elastic or dipole-radical type. Attainment of resonance frequency determines an accelerated "internal friction" that produces heat, which causes the thermal decomposition of the blowing agent and the emergence of the porous structure. The losses factor presents a significant increase, passes through a maximum, and decreases with temperature, except the ternary mixture. For all the studied mixtures, a slight increase of ε_r' at temperatures above 110°C was noticed.*

Key words: *unconventional heating, radio frequency field, polymer film, polymer dielectrics, leather substitutes*

1. INTRODUCTION

Specialty literature and research carried out in the last decades emphasize the advantages of using the radio-frequency fields (RF fields) in different areas of activity, like machinery manufacturing, agriculture, pharmaceutical and plastics industries [1-3], clothing and leather industry, bioengineering, etc. [4-6]. In the production of leather substitutes, the use of high frequency field is relatively recent, mainly for the obtaining of different porous material for the lower parts of footwear, like heels and soles [7]. Recent international and national research confirmed once again the advantages of this unconventional treatment technique, as compared with the conventional ones, for the obtaining of synthetic polymer films [8]: increased efficiency (63%), as compared with 32-34% for the classical heating techniques; higher productivity; lower utilities

(water, steam, and electric energy) consumption; reduced number of maintenance personnel; reduced treatment time (by 3-4 times shorter than those of conventional procedures); the possibility of performing different operations involving heat transfer and change of material structure on the same machine: gelification, foaming, grafting, polymerization, cross-linking, drying, dyeing, impregnation, etc.[9].

In accordance with the electromagnetic field theory applied to a dielectric material, the result of the material-field interaction, at macroscopic level, is a perceivable heating of the material. In fact, heat generation is produced due to some simultaneous phenomena, like dipole rotation, ionic conduction, interface polarization, dipole elongation, dipolar electric resonance, etc. From all of these, the preponderant for the observed processes is that of ionic conduction, and especially that of dipolar rotation and dielectric resonance. These phenomena are more or less strongly manifested, depending on the chemical structure of the material constituents [10]. As presented in previous articles, [11, 12] the addition of certain chemical auxiliaries to the recipe of plastified PVC films, can significantly improve the physical-mechanical and hygienic properties of the expanded films. It is difficult to establish the predominant phenomenon from those previously mentioned, because these components are not separated in the studied mixtures, but they evolve in continuous interaction until the end of thermic processes which take place under the action of the extern electric field [13]. In this context, it is the aim of this paper to study the effect of plastisol blend formulation and temperature upon some dielectric characteristics of plastified PVC films; *in accordance with the REACH Regulation (EC 1907/2006) wich imposes some restrictions on the use of certain chemicals (such as nonylphenol ethoxylate or dioctylphtalate in the blend formulations), the resulting PVC films can be used to obtain products that are not subject to washing cycles or do not come in direct contact with the body, such as artificial leather for shoe upper or some leather goods [14]*.

2. MATERIALS AND EQUIPMENT

The constituents of the basic recipe are: Polyvinyl chloride, PVC (Sigma Aldrich), with the following chemical and physical characteristics: molecular weight M= 4000 g/mol, viscosity index Kwert = 65– 67, density 0.48–0.56 (powder PVC emulsion type); Dioctylphthalate, DOP (Limited England), with a viscosity of 74-76 cP and M = 390 g/mol; thermal stabilizer of Cd–Zn type KZII (România). The chemical auxiliaries used in the recipe formulation were: polydimethylsiloxane, PDMS (Sigma Aldrich) with M=17537 g/mol; polymethylhydrosiloxane, PHDMS (Sigma Aldrich) with M=16180 g/mol; nonylphenol ethoxylate emulsifier emulsifier NF10, NE (România); collagen hydrolizate, CH with M=30000 g/mol and pH_{iz}=10.8 (România). The auxiliary agents were added as mono, binary, ternary or quaternary mixtures. The following laboratory equipment was used: laboratory Roll Mill Type W 110 E for mixture preparation; Werner Mathis type LTE-S-B apparatus for film forming; vaccum oven type Horyzont (Germany) for films gelification.

The high frequency electric field for treatment of PVC plasticized films was provided by a high frequency capacitive generator with 380 V supply voltage, and 13.56 MHz working frequency. Temperature was controlled by a non-contact infrared (IR) thermal sensor. The dielectric loss angle was measured with a Q-meter type LCR-Q (Model HP4284), with variable capacity, in the range 50 KHz-14.8 MHz.

3. EXPERIMENTAL

Mixtures for the preparation of plasticized PVC films were obtained accordingly with the following recipe: PVC (polyvinyl chloride) - 100 parts, DOP (dioctylphtalate) - 60 parts, thermal

stabilizer (KZ II) - 3 parts, auxiliary agents (CH-collagen hydrolizate, polydimethylsiloxane (PDMS), polydimethylhydroxisiloxane (PHDMS), Nonionic emulgator type NF10 (NE): 4 - 6 parts.

The plasticized PVC films samples tested in this study were as follows:

1. Control sample, prepared only with the constituents of the basic recipe (PVC, plasticizer, blowing agent, thermal stabilizer) ;
2. Samples prepared by the addition of a binary mixture of CH + PDMS;
3. Samples prepared by the addition of a ternary mixture of PDMHS + CH + NE;
4. Samples prepared by the addition of a quaternary mixture of PDMHS+HC+NE+PDMS.

At laboratory scale, the plastified PVC films were obtained as follows: a homogenous blend was firstly prepared in accordance with the basic recipe, by thoroughly mixing in a mortar and pestle the PVC powder, the plasticizer, and the thermal stabilizer. Recipes containing auxiliaries were prepared from portions of the basic recipes, by adding the corresponding binary, ternary and quaternary mixtures. The resulting blends were then homogenized and deaerated on the roll mill. Films of 0.5 mm thickness were drawn on a Teflon antiadherente plate in the Werner Mahis apparatus. The films thus obtained were pre-gelified at 120°C for 4 min and gelified at 130 ^{o}C -160 ^{o}C for 2-3 min. Both pre-gelification and gelification were performed in RF field, at 13.56 MHz working frequency; during gelification, temperature values were recorded with the IR pyrometer.

Rectangular (20×100 mm) and circular (60 mm diameter) test specimens were cut from the PVC films for measuring dielectric properties. Experimental determinations were made on representative samples (containing mono, binary, ternary and quaternary mixture of chemical additives) in order to determine the dependence of dielectric loss angle (or loss factor), tg δ and dielectric permittivity, ε_r' on temperature. Variation of loss factor was recorded over a temperature range of 20°C-160°C, with a variable capacity Q-meter, type LCR-Q meter (Model HP4284), in the frequency range 50 KHz-14.8 MHz, using the resonance method on an oscillate capacitive circuit, in accordance with a methodology described in other works [15-17].

4. RESULTS AND DISCUSSIONS

The fluid components with polar structure exhibit an increased freedom of movement under the external electric field action; the higher the frequency of the external field, the higher tendency for dipole orientation. On the other side, under the high frequency field action, this mobility that induces a so-called supplementary internal plastifying, which contributes to the reduction of the loss factor, is counteracted by the interaction between the mixture constituents. Among unreacted remnants of the auxiliary and blowing agents free radicals or interactions (because of the vibration frequency in resonance with the extern electric field) may appear, which result in the increase of losses factor value of the dielectric material, up to a value that corresponds to a critical current intensity, termed as breakdown current.

Even if initially the material contained components whose concentration corresponded to the domain of optimal dielectric losses, an amplification of vibration frequency of the dipoles from the mixture took place, (because of electric resonance phenomena), that determined an accelerated dielectric loss increase till dielectric breakdown, due to the formation of an electric arc that brought out the installation from the circuit [18, 19]. This phenomena can be counteracted either through the control of the geometrical factors (the geometry of the condenser fitting in the case of the high frequency field) or through the control of the intensity of the applied electric field, introducing IR pyrometer into the circuit. Beside the above mentioned phenomena, another one can be noticed: due to lower relaxation frequency of some of the mixture constituents (like collagen hydrolyzate, polysiloxanes, polyvinylchloride) as compared with the frequency of the external electric field, rapid

growth of the material temperature takes place; this can be explained by the emergence of the resonance frequency in the mixture molecules, which determines an accelerated "internal friction" having as a final result a significant heating of the material. Finally, this heating will cause the thermal decomposition of the blowing agent and hence the apparition of the porous structure, or only gelification and consolidation of the film in the absence of the blowing agent.

During the films treatment in the RF field, rapid shifting of the component dipoles from the mixture are produced, which have the following effects: structural transitions from an ordered form to another one; local movement of side groups or free radicals (-NH_2, -COOH, -OH, -CH_3 etc.) similar to Brownian movement, which is reflected in a change of the dielectric permittivity, ε_r' and of the loses factor, tgδ values.

From the examination of the dielectric spectra (fig.1-4), which presents the variation of tgδ and ε_r' with temperature, the following comments can be made:

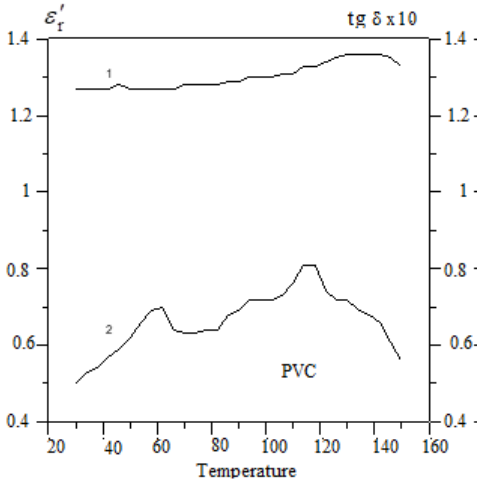


Fig. 1. *The variation of ε'r (1) and tg δ (2) with temperature for PVC film (control sample)*

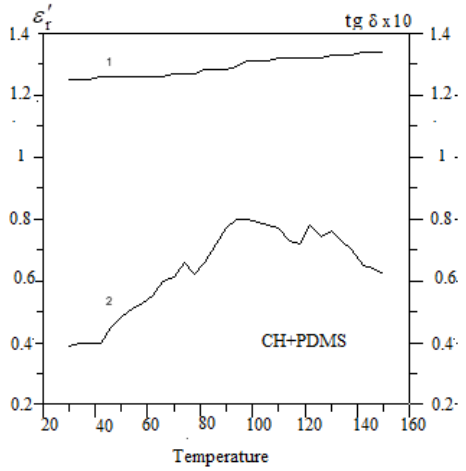


Fig. 2. *The variation of ε'r (1) and tg δ (2) with temperature for the (CH+PDMS) mixture*

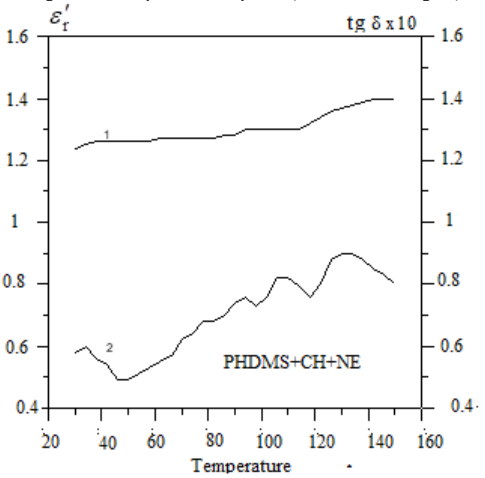


Fig. 3. *The variation of ε'r (1) and tg δ (2) with temperature for the (PHDMS+CH+NE) mixture*

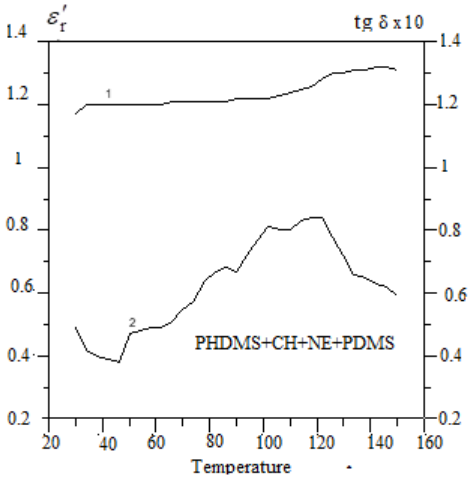


Fig. 4. *The variation of ε'r (1) and tgδ (2) with temperature for the (PHDMS+CH+NE+PDMS) mixture*

For all the studied mixtures, a slight increase of the dielectric permitivity, ε_r' at temperatures above 110°C can be noticed, which is characteristic for the dielectrics with attenuated relaxation phenomena. The losses factor (tgδ) presents a significant increase with temperature rising, passes through a maximum, and decreases with temperature increase, except the ternary mixture. On the variation curves of the losses angle tangent and of the dielectric constant by the temperature, the relaxation state τ_c (the characteristic relaxation time) corresponds to the inflexion point on the ε_r' curve and to the maximum on the tgδ curve. Depending on the mixture composition, the tgδ variation with temperature presents characteristic peaks, which correspond to a relaxation processes with different kind of molecular mechanism. In the case of the control sample, two characteristic peaks can be observed, which correspond to some relaxing processes with molecular mechanisms of different nature. The presence of a peak at 110^0C can be noticed, which corresponds to the α type relaxation (around the vitreous transition) and another peak at the 60^0C, corresponding to β type relaxation (determined by damping of oscillation of the chain ramification around the equilibrium point).

Because of the mixtures complexity and the polar character of most of them, the existence of more dipole types must be taken in consideration, each one with its own characteristic relaxation time, which determines the apparition of peaks in the dielectric relaxation spectrum of studied films.

In the case of binary mixture, a shifting of α transition to a lower temperature occurs, which indicates a plasticizing effect mainly due to the alkyl radical from the polysiloxane component, which slows down the intermolecular relaxation. For the other mixture, the chain mobility decreases, because of the new polar groups introduced in PVC base mixture and the increase of macromolecular interaction; consequently, the α transition is shifting to higher temperature. This effect is most obvious in the ternary mixture. For all mixtures an attenuation of the peak can be noticed, which is characteristic to β transition compared to the control sample, with more obvious shifting to higher values, in the case of ternary mixture, too.

5. CONCLUSIONS

The obtaining of plastified PVC-based films with improved dielectric characteristics is significantly favoured by the addition of auxiliaries such as hydrolyzed collagen, siloxane polymers (polydimethylsiloxane, polydimethylhydroxysiloxane), or non-ionic emulsifiers to the plastisol recipe.

The binary mixture shows a shifting of α transition to a lower temperature which indicates a plasticizing effect mainly due to the alkyl radical from the polysiloxane component, which slows down the intermolecular relaxation, while in the ternary mixture the α transition is shifting to higher temperature due to the increase of macromolecular interaction.

With the variation of the temperature the apparition of α or β types relaxation phenomena, characteristic to the dipole-elastic or dipole-radical losses can be noticed.

REFERENCES

[1]. H. Djidjelli, D. Benachour, A. Boukerrou, O. Zefouni, J. Martinez-Véga, J. Farenc, M. Kaci, "*Thermal, dielectric and mechanical study of poly(vinyl chloride)/olive pomace composites*", Polymer Letters Vol.1, No.12 , 2007, pp., 846–852.

[2]. I. Mitelea, I. Bordeasu, N. Varzaru, I. Dragos, "*Research of the Thermal Gradient and Quality of Welded Joints from PVC Thermoplastics Foils at High Frequency Symmetric Welding*" Rev. Materiale Plastice vol. 54, No. 3, 2017, pp.461-465,

[3]. M. Heinola, P. Lätti, P. Silventoinen, P. Ström, M. Kettunen, *"A Method to Evaluate Effects of Moisture. Absorption on Dielectric Constant and Dissipation Factor of Printed Circuit Board Materials,"*IEEE 9th Int'l Symposium on Advanced Packaging Materials, pp., 241-246, 2004.

[4]. B. Vairamohan, I. Bran, G. Meric de Bellefon,"*What's New in Electrotechnologies for Industrial Process Heating?*", ACEEE Summer Study on Energy Efficiency in Industry, ©2011, pp.156-164,

[5]. T. Tanaka, G.C. Montanari, R. Mülhaupt, "*Polymer Nanocomposites as Dielectrics and Electrical Insulation- Perspectives for Processing Technologies, Material Characterization and Future Applications*", IEEE Transactions on Dielectrics and Electrical Insulation, Vol.11, No. 5, pp. 763-784, 2004.

[6]. D. E. Gavrilă, "Studies of Degradation of Plasticized Polyvinyl Chloride", Int. Journal of Engineering Research and Applications, www.ijera.com, Vol. 6, Issue 1, (Part -3) January 2016, pp.56-63].

[7]. Whitfield & Associates, The Vinyl Institute Inc.,"*The Economic Benefits of Polyvinyl Chloride in the United States and Canada"* dec.2008, pp., 3-22.

[8]. E. R. Kolbe, J. W. Park,J. H. Wells, B. A. Flugstad, Y. Zhao, "*Capacative dielectric heating system"*, US Pat. No., 6303166B1, 2001-10-16.

[9]. F. E. Kennedy, X.Tian,"*The effect of interfacial temperature on friction and wear of thermoplastics in the thermal control regime*". Tribology Series 27 (C) 1994, pp., 235-244.

[10]. J.Andraj, G.M. Joshi,"*Preparation and characterization of low dielectric constant soft polymer blends for engineering applications*", Indian Journal of Pure&Applied Physics, Vol.55, May 2017, pp.313-323.

[11]. T. Bălău Mîndru, I. Bălău Mîndru,E. Popa, M. Pruneanu, A. Mureșan, *"Study concerning the influence of certain hydrophilic auxiliaries on the properties of the plasticized polyvinyl chloride porous films,part 1 - moisture sorption"*, Annals Of The Oradea University. Fascicle of Textile- Leatherwork", Vol. XVI, 2015, pp. 99-105.

[12]. T. Bălău Mîndru, I. Bălău Mîndru,E. Popa, M. Pruneanu, A. Mureșan, *"Study concerning the influence of certain hydrophilic auxiliaries on the properties of the plasticized polyvinyl chloride porous films,part 1I – hygienic properties"*, Annals Of The Oradea University. Fascicle of Textile- Leatherwork", Vol. XVI, No.1/2015, pp. 105-111.

[13]. H. Djidjelli, M. Kaci, A. Boukerrou, D. Benachour, J. J. Martinez, "*Hydrothermic Aging of Plasticized Poly(vinyl chloride): Its Effect on the Dielectric, Thermal, and Mechanical Properties*", Journal of Applied Polymer Science, Vol. 89, 2003, pp., 3447–3457.

[14]. *** Official Journal of the European Union, no. L 396, Volume 49, 30 December 2006

[15]. V. Komarov, S. Wang, J. Tang,"*Permittivity and Measurements*", Copyright © 2005 by John Wiley & Sons, Inc., Published Online: 15 Apr. 2005, pp.3693-3711.

[16]. S. O. Nelson, *"Improved Sample Holder for Q-Meter Dielectric Measurements"* American Society of Agricultural and Biological Engineers, St. Joseph, Michigan **www.asabe.org**, doi: 0.13031/2013.35132) @1979

[17]. G. L. Johnson,*"Solid State Tesla Coil"*, Chapter 3—Lossy Capacitors, pp.1-24, Kansas State University Press. Manhattan, Kansas, pp. 3_1-3_24, December 2001.

[18]. I. Mitelea, I. Bordeasu, N. Varzaru, I. Dragos,*Research of the Thermal Gradient and Quality of Welded Joints from PVC Thermoplastics Foils at High Frequency Symmetric Welding,*Rev. Materiale Plastice Vol. 54, No. 3, 2017, pp. 461-465.

[19]. M. Birle, C. Leu, *"Dielectric heating in insulating materials at high dc and ac voltages superimposed by high frequency high voltages"* , Seoul Coreea ISH 18th International Symposium of high Voltage Engineering, 25-30 Aug., 2013, pp. 1025-1030.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

FOOTWEAR DIVERSIFICATION BY TYPIFICATION OF COMPONENT PARTS

HARNAGEA Marta Catalina [1], SECAN[2]Cristina

[1]Advanced Intelligent Mechatronics, ENS des Mines, 880 Route de Mimet, 13120 Gardanne, France,
E-Mail: martaharnagea@yahoo.com

[2] University of Oradea, Faculty of Energy Engineering, Department of Textiles-Leather and Industrial Management,
B.St.Delavrancea str., No. 4, 410087, Oradea, Romania, E-Mail: cris_secan@yahoo.com

Corresponding author: Harnagea, Marta, mail: martaharnagea@yahoo.com

Abstract: *Diversification of a footwear product, constructively designed in a basic model, can be assured by putting into practice several diversification criteria. With this respect, the paper presents the results of the research on the diversification of a footwear product by typification of component parts. Thus, starting from a leisure time model of men shoe with vamp and whole quarters, diversification was made by detailing the basic patterns of the uppers. The detailing of the basic drawing of the uppers was made so that the outer contour of the two parts (the vamp and quarter) remains unchanged even in the case of patterns consisting of several components. Also, the vamp-quarter merging line will keep its position on the shoe last, its length, and its configuration unchanged. Under these circumstances, by detailing the vamp and the quarter, several variants of these fragmented parts resulted, which are considered typified parts. The use of typified parts for uppers will ensure the diversification of the basic model. The analysis of the resulting model variants led to highlighting the influence of the number of component parts of the uppers and of the set area on the usage index of the leather surface and the specific consumption at cutting.*

Key words: *diversification, footwear, waste, usage index, specific consumption*

1. INTRODUCTION

Nowadays, the continuous increase of the consumers' requirements and exigencies regarding the footwear products implies a demand of rapid diversification. In parallel with the diversification, the footwear manufacturers also aim at rationalizing the production in order to increase the economic efficiency.

Diversification of footwear is done mainly by changing the look and the composition of the uppers. This change is possible by adopting certain criteria of diversification, given that several criteria are possible, such as: the detailing of the basic drawing of the uppers, the detailing of the basic drawing of the outer linings, decorating the uppers, appearance and finishing of upper materials, the way of fixing footwear on the foot, etc. [1], [2]

As the detailing of the basic drawing of the uppers is an important criterion for diversification, in the present paper, this criterion is applied to a model of men's footwear, for leisure time, with vamp and whole quarters.

Thus, the following restrictive condition was imposed: the outer contour of the two parts (the vamp and quarter) remains unchanged, even in the case of a pattern composed of several pieces. Also, the vamncp-quarter merging line will keep the position on the shoe last, the length, and the configuration uhanged.

Under these circumstances, by detailing the vamp and the quarter several variants of these fragmented parts have resulted.

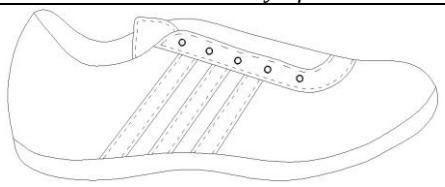
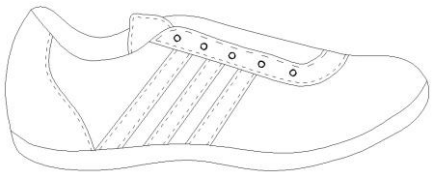
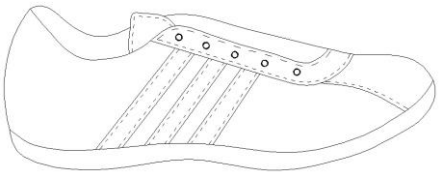
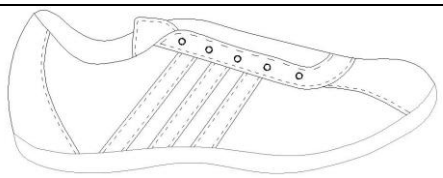
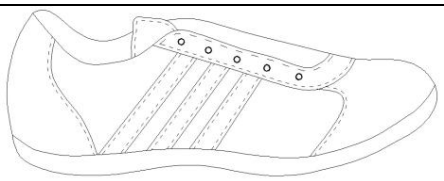
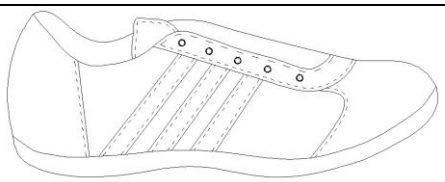
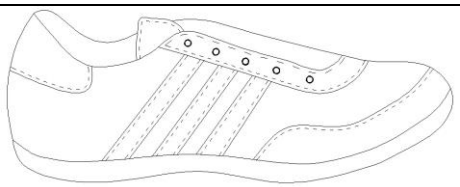
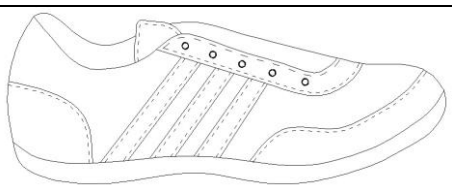
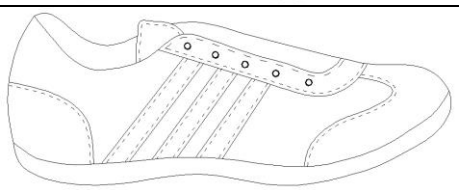
The association in a different way of the fragmented vamp and quarter has allowed a large number of variants of patterns to be grouped in a family [2], [3].

The component parts of the wamp and quarter were considered typified parts. Their use in the uppers will ensure the diversification of the basic model.

2.OBTAINING THE TYPIFIED COMPONENT PARTS

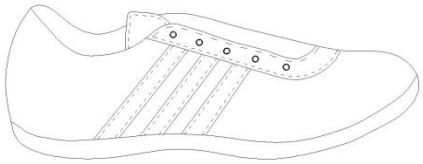
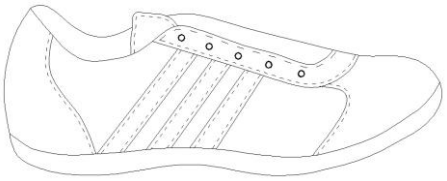
The vamp and the quarter were detailed, obtaining the family of models out of which were selected the models presented in Table 1.

Table 1. *Family of models*

<table>
<tr><td colspan="4"> 
Basic model M1</td></tr>
<tr><td>No.</td><td>Model variant</td><td>No.</td><td>Model variant</td></tr>
<tr><td>M2</td><td>  </td><td>M3</td><td>  </td></tr>
<tr><td>M4</td><td>  </td><td>M5</td><td>  </td></tr>
<tr><td>M6</td><td>  </td><td>M7</td><td>  </td></tr>
<tr><td>M8</td><td>  </td><td>M9</td><td>  </td></tr>
</table>

The parts: anchor, tongue, strap I, II and III are found in all model variants.
For example, for the M1 base model and the M5 model, the composition of the uppers is shown in table 2.

Table 2. *The patterns of the product*

Model variant		Pattern's name	Pattern Code	No. of patterns, ns
M1		anchor	01	2
		tongue	02	2
		strap I	03	4
		strap II	04	4
		strap III	05	4
		vamp	06	2
		quarter	07	4
		Total		22
M5		anchor	01	2
		tongue	02	2
		strap I	03	4
		strap II	04	4
		strap III	05	4
		toe cap	08	2
		vamp without toe cap	09	4
		quarter without heel counter stiffener	10	4
		heel counter stiffener	11	2
		Total		28

3. THEORETIC CALCULUS OF SPECIFIC CONSUMPTION

The hypothesis was that the models considered in this paper will be manufactured with 180 of dm^2 box calf leather. Knowing the surface areas and the perimeters of the patterns per model variant, theoretical variants of layout are done [4].

Once done the theoretical layout of patterns, the primary values necessary for calculating the leather consumption are obtained for each model variant, namely the area of the set, Aset, the area of the paralleogram of the set Aps, the perimeter of the set Ps and the theoretical factor F_A [5, 6].

The elements and calculus relationships necessary for establishing the specific consumption are presented in table 3.

Table 3*. Calculus relationships for estimating the specific consumption*

Calculus element	U.M.	Calculus relationship	Calculus element	U.M.	Calculus relationship
ns	-	-	a_{Dm+Dt}	%	$a_{Dm+Dt} = \frac{a}{\sqrt[4]{f_A}}$
$\overline{F_A}$	%	$\overline{F_A} = \frac{\sum A_s}{\sum A_{ps}} \cdot 1$	a_{Dp}	%	$a_{Dp} = \frac{pP_s}{2A_s} \cdot 1$
a_{Dn}	%	$a_{DN} = 100 - \overline{F_A}$	a_{DT}	%	aDT =aDN+ aDp + aDm+Dt

$\overline{A_S}$	dm^2	$\overline{A_S} = \frac{A_S}{n}$	IU	%	100-aDT=100-(aDn+aDm+t + aDp)
fa	-	$f_A = \frac{\overline{A_p}}{\overline{A_S}}$	CS	dm^2	$C_S = \frac{A_S}{I_U} \cdot I_C \cdot 10$

4. ANALYSIS OF MODEL VARIANTS

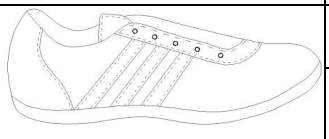
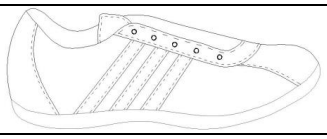
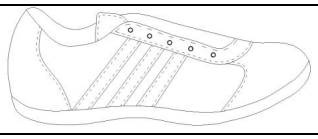
The number and configuration of the typified parts of the patterns of each model variant has led to different values of the average layout factor and of the size of the normal wastes (a_{Dn}), through bridges (a_{Dp}), marginal and pattern (a_{Dm+Dt}), table 4.

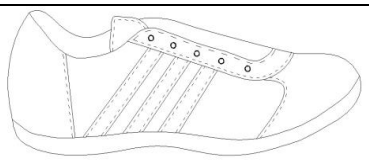
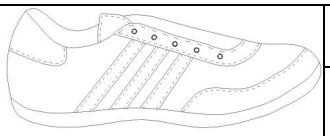
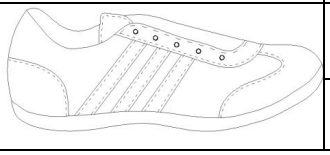
Table 3. *Average values for wastes*

	M1	M2	M3	M4	M5	M6	M7	M8	M9
ns	22	24	26	28	28	28	28	28	28
As	14.39	14.75	14.77	15.15	15.16	15.18	15.21	15.28	15.05
Aps	15.61	15.94	16.41	16.79	16.94	17.11	17.23	17.27	16.92
Ps	87.33	93.04	95.34	102.13	103.77	101.31	104.13	108.10	106.44
$\overline{F_A}$	92.18	92.53	90.01	90.23	89.49	88.72	88.27	88.47	88.94
a_{Dn}	7.82	7.47	9.99	9.77	10.51	11.28	11.73	11.53	11.17
$\overline{A_S}$	0.65	0.61	0.57	0.54	0.54	0.53	0.54	0.55	0.54
f_a	276.9	295.1	315.8	333.3	333.3	339.6	333.3	327.3	333.3
$\sqrt[4]{f_A}$	4.08	4.14	4.22	4.27	4.27	4.29	4.27	4.25	4.27
a_{Dn}	7.82	7.47	9.99	9.77	10.51	11.28	11.73	11.53	11.17
a_{Dp}	6.07	6.31	6.45	6.74	6.84	6.81	6.93	7.07	7.08
a_{Dm+Dt}	9.56	9.42	9.24	9.13	9.13	9.09	9.13	9.17	9.13
a_{Dt}	23.45	23.20	25.68	25.64	26.48	27.18	27.79	27.77	27.38
Iu	76.55	76.80	74.32	74.36	73.52	72.82	72.21	72.23	72.62
Cs	18.80	19.20	19.87	20.37	20.62	20.84	21.06	21.09	20.72

The values of usage indices and specific consumption, calculated on the basis of the theoretical layouts for model variants, are shown in Table 5.

Table 5. *Usage indices and specific consumption*

Model	Iu, %	Cs, dm^2/pair	Model	Iu, %	Cs, dm^2/pair
				M1	
				76.55	18.80
	M2			M3	
	76.8	19.2		74.32	19.87
	M4			M5	
	74.36	20.37		73.52	20.62

	M6			M7	
	75.55	19.68		21.72	69.08
	M8			M9	
	70.73	21.6		72.62	20.7

In the family of models created by the detailing differently the vamp and the quarter, there is registered an increase in the number of component parts of the uppers and implicitly of the area of the parts set. By detailing the vamp and quarter, the number of patterns in the set varies from 22 to 28 patterns in 6 model variants, having a significant influence on the average layout factor.
The highest average layout factor was obtained for the model M2, and the lowest for the model M7, figure 1.

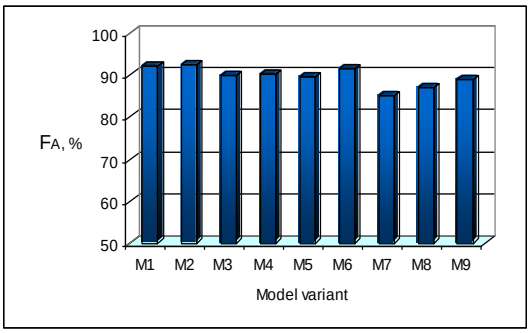


Fig.1 *Variation of average layout factor*

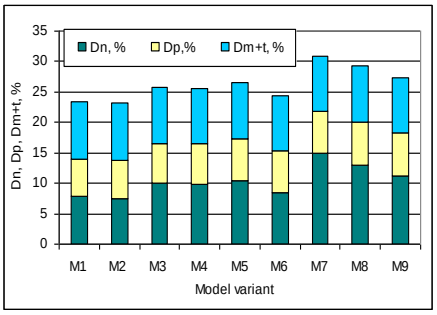


Fig.2. *Variation of total wastes*

The highest average layout factor was obtained for the model M2, and the lowest for the model M7, figure1. The variation of total wastes is illustrated in figure 2 as a sum of all wastes: normal, by bridges, marginal and pattern. The total waste varies in the range (23.75 - 27.77)%.

According to figure 2, within the three categories of waste, the highest differences are encountered for the normal waste.

The usage index of the leather varies for the model variants, between 72.21% and 76.80%. By detailing the component parts, Iu for M2 model is larger compared to the basic model.

The highest average layout factor was obtained for the model M2, and the lowest for the model M7, figure1. The variation of total wastes is illustrated in figure 2 as a sum of all wastes: normal, by bridges, marginal and pattern. The total waste varies in the range (23.75 - 27.77)%.

According to figure 2, within the three categories of waste, the highest differences are encountered for the normal waste. The usage index of the leather varies for the model variants, between 72.21% and 76.80%. By detailing the component parts, Iu for M2 model is larger compared to the basic model.

The number and shape of the component parts of each model variant influences the amount of specific consumption; the variation of the specific consumption is illustrated in figure 3.

Compared to the basic model M1, from the specific consumption point of view, the model variants can be grouped as it follows:

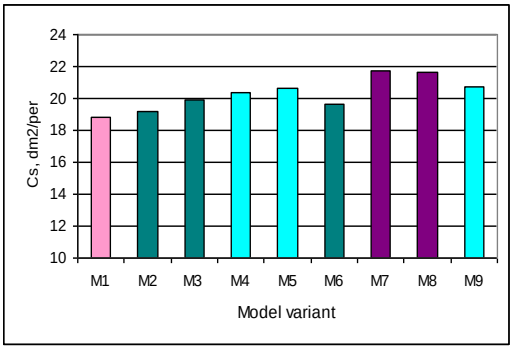


Fig.3 *Variation of specific consumption*

M2 and M3 : Cs= 19.20-19.87 dm^2/pair
M4 , M5, M6 and M9 : Cs=20.37-20.87 dm^2/pair
M7 and M8 : Cs=21.06-21.09 dm^2/pair

Variants of models with the same number of patterns in the set show higher values of specific consumption.

The graphical representations confirm the expectations regarding the estimate influence of the model variant on the efficient usage of the material while cutting-on.

4. CONCLUSIONS

In the case of the analyzed models, the following conclusions can be drawn:

- ✓ Different detailing of the uppers allows obtaining of typified patterns, and their use in the uppers is a manner of diversification of the footwear.
- ✓ The complexity of the uppers - given by the number of component parts - influences the size of the total wastes (23.75 - 27.77%), the biggest differences are found for normal wastes.
- ✓ The size of normal wastes is influenced by the size and the shape of the typified patterns, varying between 7.82 and 11.73%.
- ✓ The index of usage at leather cutting varies between 72.21% and 76.80% per model variant, being influenced by the configuration of the parts and the size of the set.
- ✓ The set area and usage index influence the specific consumption.
- ✓ Compared to the basic M1 model, from the point of view of specific consumption, the model variants can be grouped into three groups as it follows: M2 and M3 - Cs = 19.20-19.87 dm^2 / pair; M4, M5, M6 and M9 - Cs = 20.37-20.87 dm^2 / pair and M7 - M8 - Cs = 21.06-21.09 dm^2 / pair.

The conclusions are valid in the concrete case study and can be generalized for other types of footwear products through similar studies.

REFERENCES

[1] A.Mihai, A.Curteza, *Designul produselor din piele*, Ed. Performantica, Iasi, 2005, pag.232-236, ISBN 973-730-061-0

[2] Harnagea F., Harnagea M.C., *Diversification through development of the shoe uppers***,** Leather and Footwear Journal 2010, 10th volume, nr.3, ISSN nr.1583-4433, p.25-38 **,** *www.icpi.ro*

[3] A.Mihai,s.a., *Metode utilizate în conceptualizarea şi dezvoltarea produselor de încălţãminte*, Ed. Ed.Performantica, 2010, ISBN 978-973-730-648-7, pg.137-138

[4] M. Cocea, D.Croitoru – "*Proceduri CAD destinate proiectarii încălţãmintei*", Ed.Gh. Asachi, Iaşi, 2003, ISBN 973-621-035-9, pag.40-48

[5] A.Mihai s.a. - "*Proiectarea încălţămintei*", Editura Performantica, Iaşi, 2009, pag 29 – 44, ISBN 978-973-730-465-6

[6] Harnagea F., Harnagea M.C, *Bazele tehnologiei confecţiilor din piele şi înlocuitori. Lucrãri practice,* Ed.Performantica, 2013, ISBN 978-606-095-7; pg.7-18

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

DYE REMOVAL FROM AQUEOUS SOLUTION BY MAGNETIC HYDROGEL

NARİN Güler[1], KİRAZ Uğur[2], TEBER Sena[2], KILIÇ Eylem[2]

[1] Usak University University, Faculty of Engineering, Department of Chemical Engineering, 64200, Usak, Turkey, guler.narin@usak.edu.tr

[2] Usak University University, Faculty of Engineering, Department of Material Science and Nanotechnology Engineering, 64200, Usak, Turkey, E-Mail: eylem.kilic@usak.edu.tr

Corresponding author: KILIÇ Eylem, E-mail: eylem.kilic@usak.edu.tr

Abstract: *For coloration of products, dyes are used in various industries such as pulp, paper, leather, pharmaceuticals, and textiles. Disposal of colored textile wastewater into the environment, without efficient treatment, imposes serious damages to aquatic life by reducing sunlight penetration to water. Different treatment techniques including chemical coagulation, electrochemical coagulation, advanced oxidation processes, membrane technology, and adsorption have been applied to remove dyes from industrial wastewater. Among these, adsorption is an easy-operating, effective, and cost-effective option. Activated carbon has been employed for removal of various pollutants from wastewater, but it has high cost of regeneration. Hence low-cost adsorbents alternative to activated carbon are gaining attention in recent years. In the present study methylene blue was selected as the model dye molecule. Methylene blue adsorption kinetics and equilibrium of poly(viny) alcohol hydrogel films containing different amounts of magnetic particles were investigated. The hydrogels were synthesised by freezing-thawing method. The amounts of dye adsorbed by the hydrogels at equilibrium were in the range of 2.5–3.4 mg/g almost independent of the hydrogel magnetic particle content. The MB adsorption kinetics of the magnetic hydrogels can be represented by the pseudo-second order kinetic model and the model parameters were determined. It was not possible to desorb all the adsorbed dye by contacting the saturated hydrogels with water at 25 ℃.*

Key words: *magnetic particles, magnetic hydrogel, dye adsorption, poly(vinyl) alcohol*

1. INTRODUCTION

Many industries including textile industry use dyes extensively in different unit operations to colour their products, and as a result they generate substantial amount of colored effluent. The removal of dyes from the effluents is extremely desirable, and adsorption of dyes by low-cost and efficient adsorbents was considered as a simple and economical method for this purpose [1, 2]. In recent years, magnetic adsorbents have received increasing attention due to their facile recovery by magnetic separation from the water after the adsorption [3-6]. In the present study, authors used previously synthesized and characterized magnetic PVA hydrogels [7] with different concentrations of magnetic particles (MPs) to investigate their dye removal efficiency. Methylene blue (MB) was selected as a model dye molecule. MB adsorption by the magnetic hydrogels was studied in batch mode by contacting 5 g of hydrogel with 1 liter of the dye solution with initial concentration of 25 ppm at 25 °C for 24 hours.

2. EXPERIMENTAL PART

2.1 Dye Adsorption

MB (3,7-bis{dimethylamino}-phenazathionium chloride, $C_{16}H_{18}ClN_3S$, C.I.52015, CAS number: 61-73-4)) was obtained from Merck. The magnetic hydrogels were prepared by freezing-thawing (freezing at -20 °C for 16 hours and thawing at room temperature for 8 hours) of aqueous poly(vinyl) alcohol (PVA) solutions containing different amounts of MPs. The MPs were synthesised by co-precipitation method. The dried hydrogel discs were contacted with aqueous MB solutions with the initial concentration of 30 mg/L in the adsorbent/solution ratio of 5 g/L in a thermostated water bath (NB303, N-Biotek) at 25 ºC and shaking speed of 180 rpm for 24 hours. During the adsorption 1 mL samples taken from the supernatants at specific time intervals were analysed using UV-VIS spectrophotometer (UV-1280, Shimadzu) and the absorbance values at 668 nm were recorded. The hydrogel with the highest MP content (Film 4) was also tested for MB adsorption capacity after chopping the film and then sieving to particle size range of 150-250 μm to investigate the effect of adsorbent particle size on the adsorption kinetics. The particles obtained in this manner were labelled as Film 4-s. The synthesized MP was also contacted with the MB solution under the same conditions as for the films. At the end of the adsorption period of 24 hours, the adsorbents were separated from the solution and dried at 40 ºC until constant mass.

The amount of MB adsorbed at any time (q_t, mg MB/g adsorbent) was calculated from the following equation:

$$q_t = \left(\frac{C_o - C_t}{m} \right) V \quad \textbf{(1)}$$

where C_t is the MB concentration in the solution at time t (mg/L), C_o is the initial MB concentration in solution (mg/L), V is the volume of the dye solution (mL), and m is the adsorbent mass (g).

Table 1:*Adsorption kinetic models investigated*

Kinetic model	Equation
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$
Intraparticle diffusion	$q_t = k_i \sqrt{t} + c$

Kinetic modelling gives information about adsorption mechanisms and possible rate-controlling steps such as mass transport or chemical reaction processes. For this purpose, the dye adsorption kinetics of the films was analysed using the kinetic models given in Table 1. The goodness of the fit of the experimental data to the models were deduced based on the linear regression coefficients (r^2) for the $\log(q_e\text{-}q_t)$ versus t, t/q_t versus t, and q_t versus $t^{1/2}$ plots, respectively for the pseudo-first, pseudo-second order and intraparticle diffusion models, respectively. In the model equations k_1, k_2 and k_i are the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic rate constants, respectively.

The percent MB removal at equilibrium was calculated as,

$$\text{Percent dye removal} = \left(\frac{C_e - C_o}{C_o} \right) \times 100 \quad \textbf{(2)}$$

where C_e is the dye concentration in solution at equilibrium.

2.2 Desorption Studies

To test the recyclability of hydrogels in dye adsorption, the films after the adsorption were immersed into 30 mL deionized water at 25 °C and agitated at 180 rpm. During desorption, the samples taken from the supernatants were analyzed for the absorbance values at 668 nm.Desorption efficiency (*DE*, %) was determined by the following equation,

$$DE(\%) = \frac{q_{des}}{q_{ads}} \times 100 \quad \textbf{(3)}$$

where q_{ads} and q_{des} are the amounts of dye adsorbed and desorbed by the films, respectively.

3. RESULTS AND DISCUSSION

3.1. Dye Adsorption

The MB concentration in the adsorption solution and amount of MB adsorbed by the films as well as by the MPs during the adsorption as a function of time are shown in Fig. 1. It can be seen that the adsorption equilibrium has been reached after the first hour of contact.

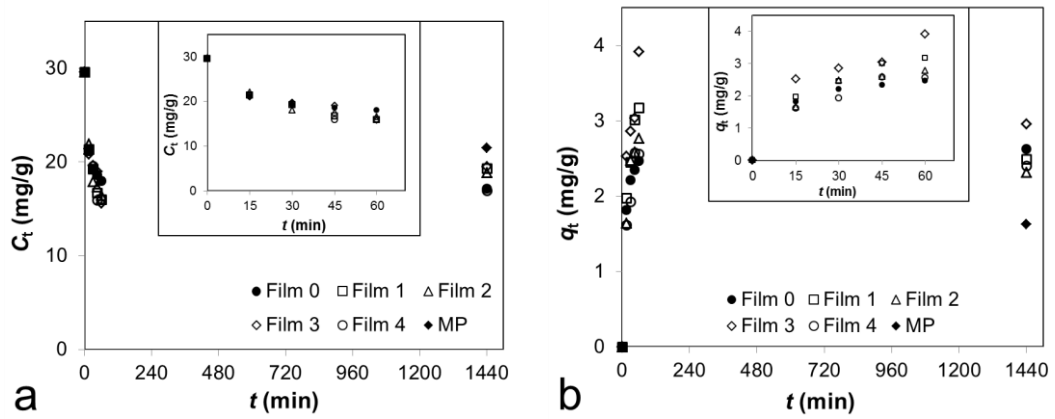


Fig. 1*: Solution MB concentration (a) and amount of MB adsorbed (b) as a function of time during adsorption (data for first 60 min of the adsorption is given in the insets).*

The amounts of adsorbed MB and percent removal values for the films and MPs at equilibrium (after 24 hours) are given in Table 2. Addition of MPs did not result in significnt change in the amount of dye adsorbed at equilibrium. Moreover the MPs added to the hydrogel did not affect the percent dye removal values remarkably. The equilibrium MB adsorption capacity of the synthesized MPs was 1.63 mg/g, lower than the PVA hydrogel without magnetic particles (Film 0). The reduction of the particle size of the Film 4 resulted in a significant decrease (46 %) in the dye adsorption capacity of the film.

Table 2: *Amounts of adsorbed MB and percent removal by the films and MPs at equilibrium*

Film	MP content of dry films (wt %)	q_e (mg/g)	removal (%)
0	0	2.55	40.4
1	2.1	2.83	40.4
2	4.0	2.56	40.4
3	6.2	3.44	40.7
4	8.1	2.52	44.2
4-s	8.1	1.37	25.7
MP	100	1.63	27.5

From the regression coefficients (r^2) for the investigated adsorption kinetic models (Table 3), it was concluded that the MB adsorption by the hydrogels can be represented by the pseudo-second kinetic model. This indicated role of interactions between the functional groups of the hydrogels and dye molecules [8]. The pseudo-second order kinetic model fittings are shown in Fig. 2 and the model parameters are given in Table 4. The data for Film 4-s was also reported.The initial dye adsorption rate (h) was calculated as follows,

$$h = k_2 q_e^2 \quad \textbf{(4)}$$

The rate of MB adsorption decreased with the MPs content of the films but increased with the size reduction of Film 4. The q_e values determined from the model fitting were found to be in good agreement with the experimental q_e values previously given in Table 2.

Table 3: *Regression coefficients (r^2) for the investigated adsorption kinetic models*

Film	Regression coefficients (r^2)		
	Pseudo-first order	Pseudo-second order	Intraparticle diffusion control
0	0.980	1.000	0.461
1	0.989	0.991	0.003
2	0.947	0.989	0.002
3	0.899	0.917	0.001
4	0.947	0.965	0.114
4-s	0.304	0.986	0.135

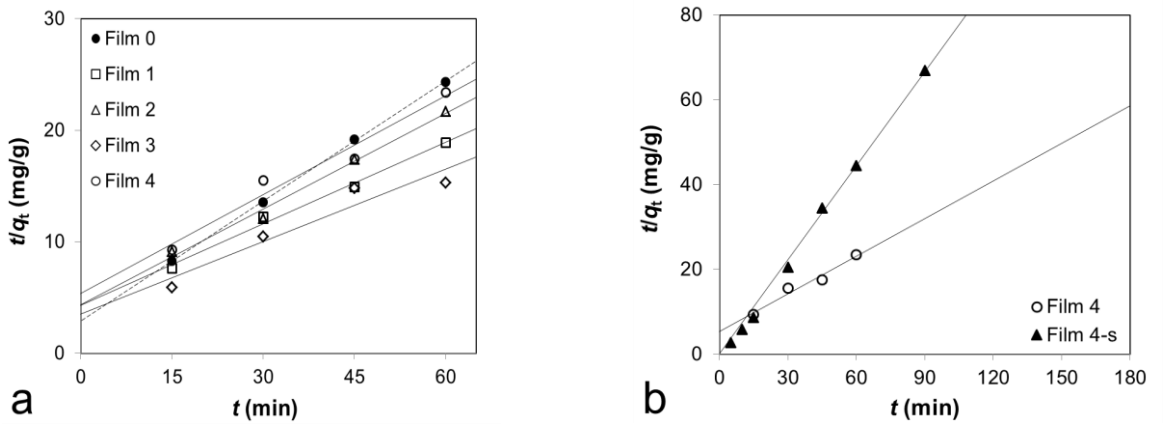


Fig. 2: *Pseudo-second order model fittings for the films (a) and for the two forms of Film 4.*

Table 4:*Pseudo-second order kinetic model fitting parameters*

Film	$q_{e,model}$ (mg/g)	k_2 (g/mg·min)	h (mL/g·min)
0	2.64	0.050	0.349
1	2.48	0.038	0.234
2	2.31	0.043	0.229
3	2.95	0.033	0.286
4	2.41	0.032	0.187
4-s	1.35	4.097	7.509

The photos of the films after crosslinking (wet), drying, swelling and MB adsorption are shown in Fig. 3. The volume of the films increased remarkably after swelling and the colourhas changed notably after the dye adsorption.

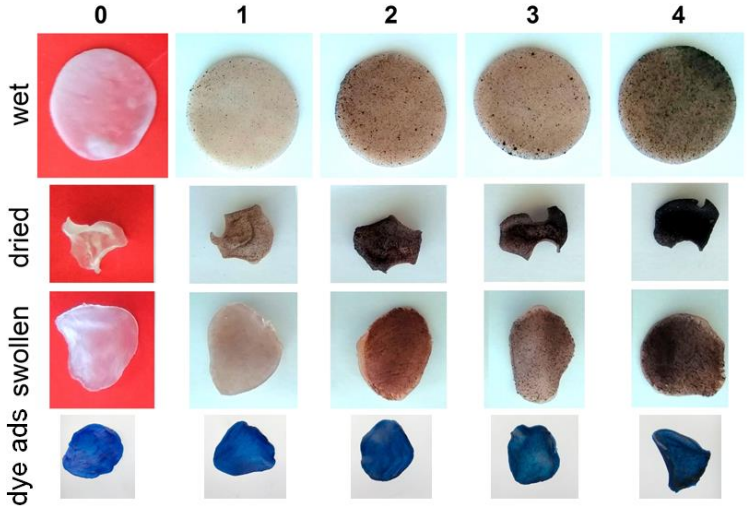


Fig. 3*: Photos of the films after crosslinking, drying, swelling and MB adsorption.*

3.2. Desorption Studies

The dye desorption efficiencies of the films were found to almost independent of the MP content (Table 5). Approximately 20 % of the dye adsorbed could be desorbed under the desorption conditions.

Table 5: *Desorption efficiency*

Films	Desorption efficiency (%)
0	19.0
1	19.5
2	22.5
3	18.4
4	19.5

4. CONCLUSIONS

The amounts of dye adsorbed by the hydrogels at equilibrium were between 2.5 mg/g and 3.4 mg/g, almost independent of the hydrogel MPs content. The equilibrium MB adsorption capacity of the synthesized MPs was 1.63 mg/g, lower than the hydrogel without the MPs. The MB adsorption kinetics of the magnetic hydrogels can be represented by the pseudo-second order kinetic model and the model parameters were determined.

REFERENCES

[1] V. K. Gupta, Suhas, *"Application of low-cost adsorbents for dye removal – A review"*, Journal of Environmental Management, 90(8), 2009, pp.2313-2342.

[2] K. R. Konduru, T. Viraraghavan, *"Dye removal using low cost adsorbents"*, Water Science and Technology, 36(2–3), 1997, pp.189-196.

[3] M. Pooresmaeil, Y. Mansoori, M. Mirzaeinejad, A. Khodayari, *"Efficient Removal of Methylene Blue by Novel Magnetic Hydrogel Nanocomposites of Poly(acrylic acid)"*, Advances in Polymer Technology, 37(1), 2015, pp.262–274.

[4] P. Souda, L. Sreejith, *"Magnetic hydrogel for better adsorption of heavy metals from aqueous solutions"*, Journal of Environmental Chemical Engineering, 3(3), 2015, pp.1882-1891.

[5] S. Z. Pour, M. Ghaemy, *"Removal of dyes and heavy metal ions from water by magnetic hydrogel beads based on poly(vinyl alcohol)/carboxymethyl starch-g-poly(vinyl imidazole)"*, RSC Advances, 2015, 5, pp.64106-64118.

[6] M. H. Yang, K. S. Hwang, W. C. Park, W. K. Lee, *"Polyvinyl alcohol-borate hydrogel containing magnetic adsorbent for surface decontamination"*, Annals of Nuclear Energy, 2017, 109, pp.359–364.

[7] U. Kiraz, S. Teber, H.A. Peker, F.C. Sallan, G. Narin, E. Kılıç, "*Preparation and characterization magnetic hydrogel*", International Congress on Innovative solutions for sustainable development of textiles and leather industry, 25-26 May 2018, Oradea, Romania.

[8] W. Plazinski, W. Rudzinski, A. Plazinska, "*Theoretical models of sorption kinetics including a surface reaction mechanism: A review*", Adv Colloid Interface Sci., 2009, 152 (1–2), pp.2-13

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

FINISHING TECHNOLOGIES FOR NATURAL LEATHER USED IN MODERN GARMENTS

NICULESCU Olga[1], COARA Gheorghe[1]

[1] National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute, Ion Minulescu Street, no. 93, Sector 3, Bucharest, Romania, icpi@icpi.ro

Corresponding author: Niculescu Olga, E-mail: o_niculescu@yahoo.com

Abstract: *The paper presents modern finishing technologies using various auxiliaries in order to obtain semi-processed leather (nappa) for garments, with advanced esthetic and functional properties. Retanning auxiliaries based on acrylic polymers, tanning resins, synthetic tanning agents and fatliquoring and dyeing auxiliaries were used, providing leather with characteristics such as: drumming fastness, uniform dyeing, softness, low weight, dimensional stability, water vapour permeability. Finishing is done using disperse systems containing as auxiliaries: pigments, binders, natural and synthetic waxes, preservatives, plasticizers, thickeners, fillers, odorizers, penetrating agents, solvents. Essential oils, known for their particular scent and therapeutic qualities, are highly concentrated in biologically active compounds with different properties. These essential oils can be used to provide leather with fragrance. The composition of essential oils were analyzed by gas chromatography coupled with mass spectrometry - GC-MS. The framework dry finishing technology was developed for brown nappa sheep for clothing. The most powerful and persistent fragrance effect, determined by sensory test, is that of product containing a mixture of 60% essential oils. New shapes and lines were promoted in the design of leather garments to improve the quality of fashion design and modernize production of garments and leather goods. The developed technologies gives garment leather producers the possibility to diversify their product range and increasing quality, strengthening market confidence in the product.*

Key words: *sheepskins, essential oils, polyurethane binders, fragrance, quality, environmental protection.*

1. INTRODUCTION

Retanning auxiliaries based on acrylic polymers, tanning resins, synthetic tanning agents and fatliquoring and dyeing auxiliaries were used, providing leather with characteristics such as: drumming fastness, uniform dyeing, softness, low weight, dimensional stability, water vapour permeability.[1, 2]

Finishing, the last operation in natural leather processing determines, to a large extent, the appearance and value of finished product. Finishing is done using disperse systems containing as auxiliaries: pigments, binders, natural and synthetic waxes, preservatives, plasticizers, thickeners, fillers, odorizers, penetrating agents, solvents.[3]

Essential oils, known for their particular scent and therapeutic qualities, are highly concentrated in biologically active compounds with different properties.

These essential oils can be used to provide leather with fragrance.[4, 5]

2. EXPERIMENTAL

2.1. Materials

• The sheepskins nappa assortments, dyed brown (National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute Bucharest, Romania);

• Roda Casicolor Brown R (Triderma, Germania), viscous and homogenous fluid, dry substance – 38%, pH (10% solution) – 7, ash – 28%;

• Roda wax MONO (Triderma, Germany), wax emulsion for ground coat: dry substance – 36.87%, pH (10% solution) – 4.2, Ford cup viscosity Φ4 – 12, kinematic viscosity, cSt – 8.97, density – 0.957 g/cm^3;

• Roda-cryl 87 (Triderma, Germany), acrylic binder for ground coat, dry substance – 34.50%, pH (10% solution) – 6.0, Ford cup viscosity Φ4 – 14, density – 1.025 g/cm^3;

• Roda-pure 302 (Triderma, Germany) polyurethane binder for ground coat: dry substance – 30.87%, pH (10% solution) – 7.5, Ford cup viscosity Φ4 – 15, density – 1.076 g/cm^3;

• Roda pur 5011 (Triderma, Germania), dry substance – 40%, pH (10% solution) – 5.5, Ford cup viscosity Φ4 – 7, density – 1.053 g/cm^3;

• Lavender essential oil (Solaris Plant, Bucharest), containing 36.57% linalool, 35.60% linalyl acetate, 7.67% α-terpineol, camphor, carbitol, cineol, etc.;

• Orange essential oil (Solaris Plant, Bucharest), containing 94.7% limonene and small amounts of pinene, linalool and linalyl acetate;

• Ethanol (Chemical Company, Germany), density – 0.789 g/cm^3 at 20^{0}C, boiling point – 78^{0}C, melting point –114^{0}C, water solubility – in any proportion;

• Polyethylene glycol 600 (Merck, Germany), density – 1.13 g/cm^3 at 20^{0}C, ignition point – 270^{0}C, pH (10% solution) – 4-7; melting point – 17-22^{0}C, hygroscopic;

• Hexadecyl-trimethyl ammonium bromide (Merck, Germany), water solubility – 3g/L, pH (10% solution) – 5-7, melting point – 237-243^{0}C, hygroscopic;

• Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (Elton, Bucharest), melting point -15^{0}C, ignition point over 170^{0}C, density – 0.97 g/cm^3 at 40^{0}C, pH – 5-7, viscosity – 25 mPa x s.

2.2. Methods

Fragrance products were obtained at 30-35^{0}C in a glass flask, using a heating and homogenization installation (Velp) under mechanical stirring for 15-20 min. An ultrasound bath (Elmasonic S 15H) was also used, at 25^{0}C for 10 min.

2.2.1. Obtaining fragrance products based on essential oils

GC-MS analysis of orange essential oil shows that the limonene compound is predominant, in proportion of 94.7%.[6]

Lavender essential oil containing 36.57% linalool, 35.60% linalyl acetate, 7.67% α-terpineol, camphor, carbitol, cineol, etc.

Fragrance product preparations contain: 10-30% lavender essential oil, 10-30% orange essential oil, 20% ethyl alcohol, 10% lauryl alcohol ethoxylated with 7 moles of ethylene oxide, 9-10% polyethylene glycol 600, 1% hexadecyl-trimethyl ammonium bromide (cationic emulsifier) and deionized water.

The resulted products were marked P- LP-1(contain 30% lavender essential oil, 30% orange essential oil), P- LP-2 (contain 20% lavender essential oil, 20% orange essential oil) and P- LP-3 (contain 10% lavender essential oil, 10% orange essential oil).

2.2.1.Finishing technologies for sheepskins into nappa assortments using fragrance products

The framework dry finishing technology was developed for brown nappa sheep for clothing.

Finishing technologies for sheepskins into natural grain nappa assortments are shown in Table 1.

Table 1: *Framework technology for dry finishing of sheepskins into natural grain nappa assortments*

Operation	Composition of dispersion/Method of application
Applying dispersion I (basecoat)	40-60 g/L pigment paste (Roda Casicolor Brown R) 20-30 g/L wax emulsion (Roda wax MONO) 100 g/L acrylic binder (Roda-cryl 87) 150 g/L polyurethane binder (Roda-pure 302) 660-690 g/L water Application by spraying (2 passes of dispersion I)
Intermediate pressing	In hydraulic press using mirror or steam plate, parameters: - temperature – 50-60°C; - pressure – 50-100 bar
Applying dispersion I	By spraying (2-3 passes of dispersion I)
Applying final dressing (fixing)	Emulsion/dispersion with the following composition: 700 g/L polyurethane binder (Roda pur 5011) 300 g/L water Application by spraying (2 passes of final dressing)
Final pressing	In hydraulic press using mirror plate, parameters: - temperature – 70-80°C; - pressure – 50-100 bar.

The finished furs nappa samples were additionally treated with polyurethane final dressing in the composition of which the P-LP-1, P-LP-2 and P-LP-3 product was added in different proportions.

Some technological variants of treating sheepskins into Nappa assortments for clothing for samples PN1-PN9 are shown in Table 2.

Table 2: *Technological variants of treating sheepskins into nappa assortments*

Sample	***Final dressing composition***
PN1	500 g/L Roda pur 5011 and 500 g/L product P-LP-1
PN2	300 g/L Roda pur 5011 and 700 g/L product P-LP-1
PN3	1000 g/L product P-LP-1
PN4	500 g/L Roda pur 5011 and 500 g/L product P-LP-2
PN5	300 g/L Roda pur 5011 and 700 g/L product P-LP-2
PN6	1000 g/L product P-LP-2
PN7	500 g/L Roda pur 5011 and 500 g/L product P-LP-3
PN8	300 g/L Roda pur 5011 and 700 g/L product P-LP-3
PN9	1000 g/L product P-LP-3

3. RESULTS

3.1. Characterization of fragrance products by physical-chemical analysis

Products P-LP-1, P-LP-2 and P-LP-3 are homogenous yellowish white fluids with with 19-22% dry substance, pH – 5.2-6.2, density – 0.844-0.863 g/cm^3, total nitrogen – 0.39-0.57%.

3.2. Characterization of fragrant sheepskins nappa assortments

To monitor the fragrance effect and concentration of volatile perfume in the treated furs, samples PN1-PN9 in table 2 were tested using the sensory test.

The most fragrant leathers nappa are samples PN3, PN6 and PN9, treated with products as such. Of these, PN3, treated with product P-LP-1, has the most intense fragrance, and its effect is preserved for 15-20 days.

The fragrance effect of product P-LP-1, with 30% lavender essential oil and 30% orange essential oil, is stronger than that of products with lower amounts of oils, namely P-LP-2 (containing 20% lavender essential oil and 20% orange essential oil) and P-LP-3 (with 10% lavender essential oil and 10% orange essential oil).

New shapes and lines were promoted in the design of leather garments to improve the quality of fashion design and modernize production of garments and leather goods.

The developed technologies gives garment leather producers the possibility to diversify their product range and increasing quality, strengthening market confidence in the product.

4. CONCLUSION

- Products with fragrance properties are aqueous emulsions of lavender and orange essential oils mixtures in various ratios, ethyl alcohol and polyethylene glycol stabilized with ethoxylated lauryl alcohol, with homogeneous yellowish-white appearance.
- The most powerful and persistent fragrance effect, determined by sensory test, is that of product containing a mixture of 60% lavender and orange essential oils 1/1.
- Samples PN3, PN6 and PN9, treated with fragrance products as such, are the most fragrant, and of these, sample PN3, treated with P-LP-1 (product containing a mixture of 60% lavender and orange essential oils 1/1), the effect lasting for 15-20 days.
- The fragrance effect and persistence decrease when reducing the percentage of natural oils in the final dressing composition.

ACKNOWLEDGEMENTS

The present work was supported by the Ministry for Research and Innovation, project number 16 Nucleu / 2018, PN 18 23 01 04_SMART_PIEL (Materiale si tehnologii inteligente cu aplicatii in industria de pielarie, patrimoniu cultural si bioeconomie).

REFERENCES

[1] Deselnicu, M., Olteanu, S., Teodorescu, V., Istoria prelucrării pieilor pe teritoriul României, Ed. Tehnică, Bucureşti, 1984, pp. 12.

[2] Bacardit, A., Burgh, S., Armengol, J., Olle, L., Evaluation of a new environment friendly tanning process, J. Cleaner Prod., 2014, 65, pp. 568-573.

[3] Patent, Florescu, M., Marcu, C., Coara, G., Albu, L., Acsinte, D., Polymeric binder and its obtaining process, OSIM 122205/ 2009.

[4] Sirvaityte, J., Siugzdaite, J., Valeika, V., Application of commercial essential oils of Eucalyptus and Lavender as natural preservative for leather tanning industry, Rev. Chim. (Bucharest), 2011, 62(9), pp. 884-893.

[5] Farmacopeea Română, ediţia a X-a, Ed. Medicală, Bucureşti, 1998.

[6] David,V., Medvedovici, A., Metode de separare şi analiză cromatografică, ediţia a II-a, Ed. Universităţii din Bucureşti, 2008, pp. 148.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ALTERNATIVE LEATHER MANUFACTURING PROCESS - 2. ASSESSING THE LEATHER'S ECO-FRIENDLINESS

PRUNEANU Melinda, BUCIȘCANU Ingrid, MAIER Vasilica, BĂLĂU-MÎNDRU Iulia

"Gheorghe Asachi" Technical University of Iaşi, Faculty of Textiles, Leather and Industrial Management, Str. Prof. Dr. Doc. Dimitrie Mangeron, No. 29, 700500 Iaşi, Romania, E-Mail: decanat@tex.tuiasi.ro

Corresponding author: Ingrid Bucișcanu, E-mail: ibuciscanu@yahoo.com

Abstract: *It is the aim of this paper to assess the eco-friendliness of a bovine leather, obtained by an improved process that consists in pretanning with an oligomer resin, followed by low-offer chrome tannage. Namely, the leather tendency to release the tanning chemical auxiliaries was tested. The following analyses were performed to quantify the auxiliaries from aqueous leather extracts: total dissolved solids, organic and inorganic soluble matter, UV-VIS spectroscopy, HPLC chromatography. Experimental data indicated high release rates of oligomer and resorcin from the pre-tanned leather, which proves the reversibility of the pretanning process. The release rates of the same compounds after trivalent chrome tanning and retanning was about 4 times lower. This is due to the supplementary complexation effect of the oligomer resin and resorcin upon the trivalent chrome. Pretanning with oligomer resin and resorcin determined the decrease of chrome salt consumption by 50 ÷ 60 % as compared with the conventional chrome tanning technology, and advanced exhaustion of spent floats. Low-offer chrome tanning preceded by pretanning can contribute to the obtaining of eco-friendly leather, mainly due to lower Cr(III) content of finished leather. Consequently, the occurrence in leather of hexavalent chrome Cr(VI), which is one of the most restrictive indicators for leather eco-friendliness, is mitigated.*

Keywords: *leather tanning, clean technology, syntans, melamine-formaldehyde resins, wet-white*

1. INTRODUCTION

At present, about 80-85 % of the worldwide leather production is tanned with Cr(III) salts and, except some leather types with special applications, chrome basic sulfate cannot be replaced by salts of other metals if high quality products must be obtained. Regular chrome offer in conventional tanning processes is about 2% Cr_2O_3. In order to reduce chrome consumption in the tanning operation and chrome-tanned leather waste, mechanical operations such splitting and shaving must be performed as early as possible in the manufacturing process. Both effects can be achieved during the pretanning operation, performed with different chemical auxiliaries such as: Al, Zr, Ti or Mg basic salts, synthetic organics, silicates or combinations of them; modern leather manufacturing technologies demands that splitting and shaving are not performed on wet-blue leather, but on pre-tanned leather, which is categorized as wet-white leather [1-4]; thus, finding new pretanning agents is of interest for clean technologies with low chrome salts consumption.

Basically, the insertion of pretanning is beneficial to the manufacturing process, because it results in important saving of chrome tanning salts in the tanning operation and in chrome-free

leather wastes resulted from the shaving operation, which mitigates the environmental impact of the tanning industry.

It is the aim of this paper to assess the suitability of using an oligomeric resin as pretanning agent of a bovine leather obtained by an improved process, which consists in pretanning with an oligomeric benzenesulfonate melamine-formaldehyde resin (BSMF), followed by low-offer chrome tannage and conventional wet-end operations. Namely, the leather tendency to release the chemical auxiliaries used during pretanning, tanning and retanning in aqueous solution was tested.

2. EXPERIMENTAL

Dry-salted cattle hides not exceeding 12 kg, previously processed to reach the delimed pelt state, were used as raw material for the pretanning-tanning-wet finishing-crusting processing flow, as described in Table 1.

Table 1: *Alternative leather manufacturing process that includes pretanning*

Operation	Process description
Pretanning step with oligomer resin	
Input: delimed pelt from dry-salted cattle hides not exceeding 12 kg	
Pretanning with oligomer resin and resorcin	100 % float, 40 °C; stirring for 10 minutes + 5 % Densotan A (1:2); stirring for 10 minutes + 10 -15 % Oligomer resin; stirring for 120 minutes + 1.0 % Resorcinol; stirring for 60 minutes + 5 % salt; stirring for 15 minutes + 5 % Eskatan GLS; stirring for 30 minutes + 1-1.2 % formic acid (1:10); stirring for 20 minutes Control float pH = 3.5; float exhaustion
Washing	100 % float, 40 ºC; + 1 % Boron SE; stirring for 10 minutes; float exhaustion
Horse up after pretanning	Leathers are piled on the fleshing beam and covered with polyethylene foil, for 36 hours;
Setting out and sammying	On the setting-out and sammying machine
Splitting	On the splitting machine
Shaving	On the shaving machine
In-process product: Pretanned wet-white leather	
Tanning with low-offer basic chrome(III) sulfate	
Acid treatment	200 % float, at 25 ºC; + 8 % salt; + 10 % HCl solution stirring for 10 minutes
Tanning with basic chrome salt	In the same float at 25 ˚C; + 1 % Cr_2O_3, stirring for 4 hours; Basification with $NaHCO_3$ solution; + 5 % ESKATAN GLS, emulsion; Stirring for 60 minutes; Control float pH = 4.2; float exhaustion;
Horse up after chrome tanning	Leathers are piled on the fleshing beam and covered with polyethylene foil, for 36 hours;
Setting out and sammying	On the setting-out and sammying machine
In-process product: Wet-blue obtained by a combination tanning	
Wet finishing sub-process	
Washing	100 % float at 40 ºC; + 0.5 % BORRON SE; stirring for 10 minutes; float exhaustion

Neutralization	200 % float at, 40 ˚C; + 1.5 % $NaHCO_3$ (1:20); stirring for 3 hours; control; 200 % float at 40 ˚C; stirring for 15 minutes; float exhaustion.
Rinsing I	200 % float at 40 ˚C; stirring for 15 minutes; float exhaustion
Retanning	75 % float at 40 ˚C; + 4 % DENSOTAN A (1 : 2); stirring for 20 minutes; + 5 % mimoza extract; stirring for 60 minutes; + 3 % ESKATAN GLH; stirring for 30 minutes;
Dying and fatliquoring	In the same float: + 4 % LUGANIL Braun NR (1 : 2); + 4 % LIPODERM liquor PSE; + 2 % LIPODERM liquor SLW; stirring for 60 minutes + 1% formic acid solution 10 %;stirring for 20 minutes; float exhaustion.
Rinsing II	200 % float at 40 ˚C; stirring for 15 minutes; float exhaustion.
In-process product: dyed leather	
Leather crusting sub-process	
Setting out and sammying	On the setting out and sammying machine
Air Drying	In the tunnel dryer
Toogle Drying	In the toggle dryer;
Conditioning /Rewetting	On the water spray machine
Milling tumbling	In the milling drum;
Staking	On the staking machine;
Horse up	Piled on the beam for 5-6 h ;
Buffing on the flesh side	On the buffing machine;
Dedusting	On the dedusting machine;
Chemical grain correction	Spraying on the grain side with an aqueous solution of 1 g /L ammonia, 0.5 g / L BORRON SE and 6 g /L ethanol
Natural air drying	On the overhead air dry chain conveyor
Mechanical grain correction	On the hot plate machine
Intermediate product: crust leather ready for any dry finishing process.	

Leather samples were withdrawn at different moments of the manufacturing process, as given in Table 2. Aqueous extracts were prepared with a leather: water mass ratio of 1:20, under stirring for 6h. The following analyses were performed on the aqueous extracts of leather samples, in order to quantify the auxiliaries released from the in-process leather: solid matter content, UV-VIS spectroscopy, HPLC chromatography. Solid matter content, expressed as total dissolved solids, and organic and inorganic soluble matter, was determined gravimetrically. The UV-VIS spectra of the aqueous extracts were recorded on a Jasco 550 with the following characteristics: 1 mL quartz cuvette, wavelenght range 190÷600 nm, scan speed 200 nm/min,resolution 1 nm. A Zorbax SB-C18 (4,6 x150 mm) column, provided with a programmable Varian 9010 ternary pump, Waters 717plus autosampler and a Waters 486 UV-VIS detector, was used to record the extracts chromatograms; the HPLC system working conditions were as follows: MeOH solvent/water = 50/50 (v/v), solvent flow 0,5 mL/min, maximum absorbancy wavelenght = 254 nm.

The UV-VIS spectra were processed with a dedicated SpectraManager software and the chromatograms were processed with the OriginLab 7.5 software.

3. RESULTS AND DISCUSSION

The results of gravimetric determinations of solid matter released from leather samples are given in Table 2.

***Table 2**: The soluble solids content of aqueous leather extracts*

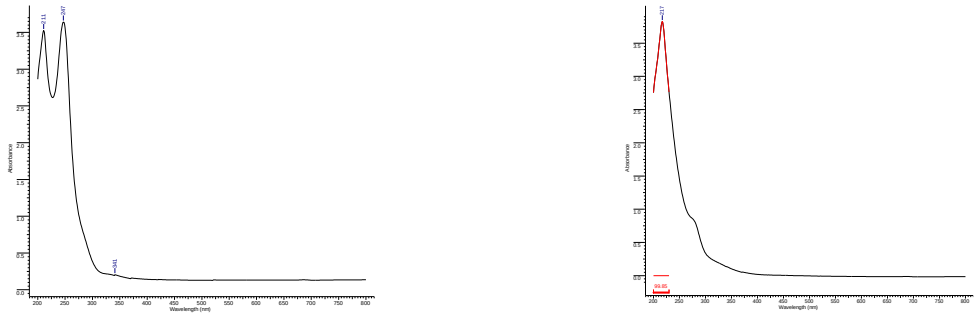
Leather sample (aqueous extract)	Sample label	Total soluble matter %	Maximum acceptable concentration MAC*	Inorganic soluble matter %	Organic soluble matter %
Pretanned with 10 % BSMF 1 % resorcin (wet-white)	BSMF10	1,44	max. 1,5 %	0,35	1,09
Pretanned with 15 % BSMF 1 % resorcin (wet-white)	BSMF15	2,38		0,8	1,58
Pretanned with 15 % BSMF, 1 % resorcin, tanned with 1 % Cr_2O_3, retanned with 5 % mimosa extract (wet-blue)	BSMF15T	0,77		0,5	0,27

**certifies the absence of adverse effects on users, assigned by TÜV Rheinland, Fresenius Institut, Prüf- und Forschungsinstitut Pirmasens e.V. (PFI),*

Experimental data indicate high release rates of oligomer and resorcin from the pre-tanned leather. This means that, when conventional chrome-tannage must be performed after organic pretanning and mechanical operations, the resin can be removed from the wet-white cross-section, and leather can be tanned with regular offer of Cr(III) basic salt.

Leather samples tanned with BSMF in the presence of resorcin have a pronounced tendency to release organic chemicals, which increases with the tanning oligomer initial offer. Instead, leather sample tanned according to the novel technology (BSMF15T) exhibit significantly lower release of solubles from its structure, which confirms the strong binding of the chemical auxiliaries to the collagen matrix.

The organic compounds released by the leather samples processed in accordance with the recipes given in Table 2 were identified on the UV-VIS spectra and HPLC chromatograms of the corresponding aqueous extracts.



a ***b***

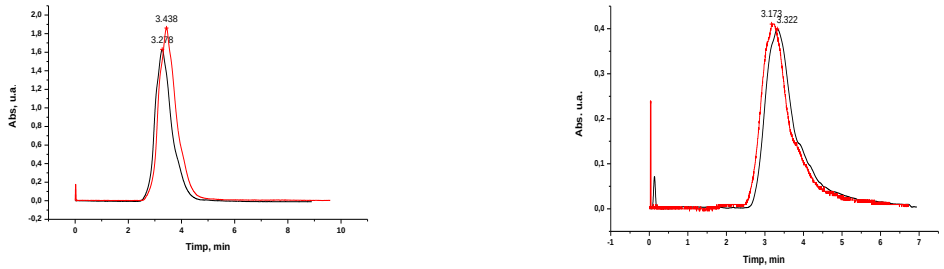
***Fig. 1**: UV-VIS spectra of leather aqueous extracts: **a)** Pretanning with 15% BSMF and 1% resorcin (BSMF15); **b)** Pretanning with 15% BSMF and 1% resorcin, tanning with 1% chrome(III) oxide, retanning with 5% mimosa (BSMF15T).*

The UV-VIS spectrum of the aqueous extract of the BSMF15 sample (Figure 1a) points out the release of two organic compounds, with maximum absorbance peaks at $\lambda = 211$ nm and $\lambda = 247$ nm. The first peak, at 211 nm is characteristic to the –C = O chromophore group of the carboxilic function of the formic acid. The second peak, at 247 nm, can be assigned to the chemical compound resulted from the reaction between the BSMF resin and resorcin, more precisely to the m-disubstituted benzen cycle reacted with the 1,3,5 triazine cycle.

The UV-VIS spectrum of the aqueous extract of the BSMF15T sample (Fig. 1b) indicates the presence of only one peak at λ = 217 nm [5-8], and the absence of the peak at 247 nm, which may indicate the absence of the reaction product between BMSF and resorcin in the tanned leather.

Two peaks are recorded on each of the HPLC chromatogram of aqueous extracts, corresponding to the two injection times (Fig. 3). The peak maximum corresponds to a certain retention time, which is the qualitative characteristic of the organic compounds found in the analyzed solutions. The peak hight (h) and area (A) account for the amount of the analyzed compound in the sample.

The HPLC chromatograms are consistent with the UV-VIS spectra and with the theoretically predictable composition of the aqueous extracts. Comparative chromatograms of the BSMF resin, resorcin and aqueous extracts of BSMF 15 and BSMF 15T samples are given in Fig. 4. The experimental retention times are as follows: resorcin, 4.53 min; BSMF resin, 2.81 min; aqueous extract of the BSMF15 sample, 3.26 min and aqueous extract of the BSMF15T sample, 3.31 min.



a ***b***

Fig. 3: *HPLC chromatograms of leather aqueous extracts:* ***(a)*** *Pretanning with 15% BSMF and 1% resorcin (BSMF15);* ***(b)*** *Pretanning with 15% BSMF and 1% resorcin, tanning with 1% chrome(III) oxide, retanning with 5% mimosa (BSMF15T);*

The values of retention time and maximum absorbancy indicate that leather pretanned with the BSMF oligomer in the presence of resorcin as cross-linking agent have the tendency to release the chemical auxiliaries entered into the collagen matrix cross-section, which proves the reversibility of the oligomer –collagen interaction.

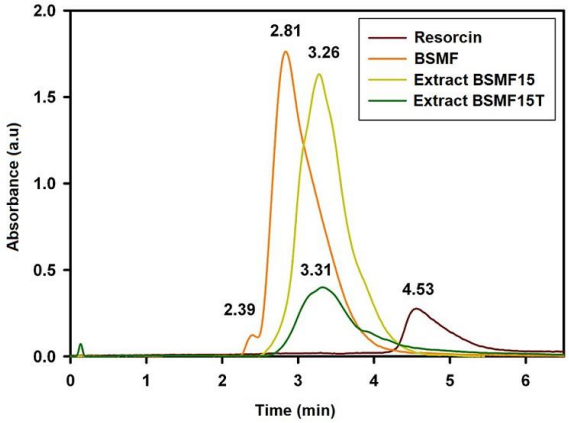


Fig. 4: *HPLC chromatograms of resorcin, BSMF, and aqueous extracts of tanned leather*

If pretanning is followed by conventional tanning and retanning, the amount of released organics is four-fold lower. The stronger binding of tanning agents to the collagen matrix is due to supplementary complexation effect that BSMF and resorcin exert on the chrome complex salt.

4. CONCLUSIONS

Experimental data indicate high release rates of oligomer and resorcin from the pre-tanned leather, which means that the pretanning process alone is a reversible process.

The oligomer resin and resorcin are extremely versatile complexing agents, and their use in the tanning process result in the reduction of chrome salts offer by 50-60% and an advanced chrome exhaustion in the tanning spent floats.

Pretanning with the oligomeric benzenesulfonate melamine-formaldehyde resin can be applied through different processes, depending on the desired leather type and degree of "eco-friendliness" requested to the final product.

Even if for most leather types chrome- tanning can not be replaced by any other alternative, pretanning allows a low-offer chrome tanning not exceeding 1% Cr_2O_3, which results in high exhaustion of spent floats and low chrome content of finished leather. At the same time, the appearance in leather cross-section of hexavalent chrome Cr(VI), which is one of the most restrictive indicators for leather eco-friendliness, is considerably reduced.

The pretanning operation complicates the overall manufacturing process, but this disadvantage is counterbalanced by technological and environmental benefits.

REFERENCES

[1] Seggiani M., Puccini M., Vitolo S., Chiappe C., Pomelli C. S., Catiello D., "*Eco-friendly titanium tanning for the manufacture of bovine upper leather: pilot scal studies"*, Clean Techn. Policy, 16, 2014, pp. 1795-1803.

[2] Roșu D., Crudu M., Roșu L., Crudu I., et.al. "*New Eco-efficient products used in leather industry"* Annals of the University of Oradea Fascile of Textiles, Leatherwork, vol.XVII, (1), 2016, Oradea, Romania, pp. 195-198.

[3] **** *Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins* Industrial Emissions Directive 2010/75/EU, Integrated Pollution Prevention and Control http://eippcb.jrc.ec.europa.eu/reference/BREF/TAN_Adopted552013.pdf

[4] Sathiyamoorthy M., Selvi V., Mekonnen D., Habtamu S., "*Preparation of Eco-Friendly Leather by Process Modifications to Make Pollution Free Tanneries"*, Journal of Engineering, Computers & Applied Sciences (JEC&AS), Vol. 2 (5), 2013, pp.17-22,

[5] Albu, M.G., Ghica, M.V., Giurginca, M., Trandafir, V., Popa, L. şi Cotruţ, C., „*Spectral characteristics and antioxidant properties of tannic acid immobilized in drug delivery systems"*, Rev. Chim. (Bucuresti), 2009, vol.60, pp. 666-672.

[6] Anderson R., Bendell D., GroundWater P. „*Organic Spectroscopic Analysis"*, Publisher The Royal Society of Chemistry, 2004, pp.1- 27.

[7] Giurgincă M., Badea N., Miu L., Meghea A. *„Spectral Technics for Identifying Tanning Agents in the Heritage Leather Items",*Revista de Chimie, vol. **58** (9), 2007, pp. 923-928.

[8] Vijay Kumar et.al. *„Isolation of Phytoconstituents from Mimosa pudica leaves"*, Journal of Pharmacy Research, vol. 3 (7), 2010, pp.1697-1699.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CHARACTERISTICS OF COMPOUND MATERIALS FOR THE PROTECTIVE FOOTWEAR

SECAN Cristina

University of Oradea, Faculty of Energy Engineering, Department of Textiles-Leather and Industrial Management, B.St.Delavrancea str., No. 4, 410087, Oradea, Romania, E-Mail: cris_secan@yahoo.com

Corresponding author: Secan Cristina, E-mail:cris_secan@yahoo.com

Abstract: *This paper presents a study on certain types of textile materials for working shoes destined for footwear upper. Thus, determinations will be made regarding the structure of the raw material and its nature, polyamide and other polyester yarns will be identified with chemical reagents. Subsequently, determinations will be made regarding the physico-mechanical properties of the materials for this type of footwear. The abrasion resistance will be determined by mass loss of the specimens subjected to friction. The air permeability of the composite materials will be determined on the basis of the pressure difference, and the water permeability is determined by the "artificial rain" method. It is worth noting that the footwear must have certain functions, also taking into account its purpose, such as protection against chemical agents, atmospheric agents, and mechanical actions. At the same time, the footwear must provide a certain microclimate for the foot to ensure its comfort during wear. In order to have a good maintenance value, leather substitutes should have functional indices close to the real leather. The quality and functionality of the protective footwear products is given by the characteristics and properties of the materials used in making them.*

Key words: *material, composite, microclimate, footwear, permeability, abrasion.*

1. INTRODUCTION

Textile materials are used more and more for the manufacture of footwear and leather goods, along with leather and artificial leather.
Thus, a wide range of composite textiles, synthetic yarns respectively, laminated with linen or diagonal linen fabrics, multilayered leather substitutes are used in the production of protective footwear.

Materials used in the manufacture of leather products must have certain characteristics which ensure both performance during use and their wear as well as during the manufacturing process. Thus, these materials must have physical characteristics, mechanical characteristics, and have a good performance towards physical-chemical agents [1].

Physical characteristics refer to geometric characteristics: length, width, area, thickness, mass, density, and transfer characteristics are those related to sanogenic indicators and refer to: water, vapor and air permeability, insulation capacity.

The mechanical characteristics refer to the ability of the materials to deform under the action of the stresses, but also to the recovery of the deformation after the ceasing of the forces. These

include: tensile strength, tear strength, adhesivity on textile support, color resistance, resistance to atmospheric agents. The value of these characteristics depends on the nature of the support, in this case different fabrics are used to provide tensile strength, knits for increased flexibility, non-woven, polyurethane foams.

If textiles are used to make the upper assembly, the elongation or strength characteristics are clearly differentiated on the direction of the warp compared to the weft direction, due to the different characteristics of the warp and weft yarns respectively.

Among the physical and mechanical characteristics, which are of particular importance for the textile materials that are part of the components of the upper assembly, are mentioned: impermeability, tear resistance, abrasion resistance.

The paper presents the results of the research regarding the identification of the raw material and the physical - mechanical properties of composite textile materials used for the uppers of the protective footwear.

2. EXPERIMENTAL PART

The materials used in the experiments were taken over from SAFETY firm, which were used for certain parts of footwear upper components.

The structural analysis of the tested materials consisted in determining the thickness, mass, density and density of the yarns of the fabric.

The thickness of the materials was determined with a Louis Schopper textile micrometer with a measurement pressure rated on the mobile top disc. Reading was done with an accuracy of 0.005 mm.

The mass of composite material in g/m^2 was determined by weighing on an electronic scale of some specimens with well-known area (dimensions 5 cm/5 cm).

The technological density of yarns in fabric, expressed in yarns/10 cm, was determined by counting. The identification of yarn systems (warp, weft) was made on the basis of the difference in width criterion, according to which the warp system is more often used. This type of identification is not very certain, but it is the only way to apply it in this case.

The density of the yarns length from the fabric was determined by weighing a length of 10 cm of yarns. To eliminate the creases due to weaving, the yarn blocked in the torsiometer clips was pretensioned with a force dependent on the nature of the raw material and the yarns fineness.

Identification the raw material was done by determining the solubility of the fibers in various reagents and comparing it with the known solubility of the different fiber classes.

In the case of composite materials tested, the following characteristics were determined: resistance to abrasion, air permeability and water permeability.

The abrasion resistance was calculated by the mass loss of the specimens subjected to friction with a polyamide monofilament fabric. The pressure was made on the WEARTESTER with a press force of 1500 cN for 210 min.

The mass loss was calculated at intervals of 30 minutes according to the following equation [2], [3]:

$$p = \frac{M_0 - M}{M_0} \cdot 100 \quad (1)$$

where:

p - mass loss of the sample ;
M_0 - initial mass of the sample;
M - mass of worn sample;

k - ratio between the area actually worn and the sample surface (0.485).

The air permeability was determined on the METRIMPEX apparatus at a pressure difference of 200 Pa and a section area of the air intake of 20 cm^2.

The air permeability at the set pressure difference (Δp) is given by[4,5]:

$$P_a = \frac{q}{A} \cdot 16 \quad \text{(mm/s)} \qquad \textbf{(2)}$$

where: q - airflow in dm^3/min or l/min;

A - the area of the absorption exit section in cm^2;

167 – conversion factor from $dm^3/min.cm^2$ to mm/s

P_a – air permeability in mm/s.

The water permeability was determined on the METRIMPEX apparatus by the "artificial rain" method. The sample, inclined at 45° angle, was sprayed for 30 minutes with a flow rate of 750 cm^3/min.

The water permeability is measured by the water absorption coefficient, which is calculated with the relation[6,7]:

$$C_s = \frac{m_u - m}{m} \cdot 100 \ [\%] \qquad \textbf{(3)}$$

where:

m_u - the mass of a square with the 10 cm side of the test material after the rain, in g;

m - the mass of a square with the 10 cm side of the tested material in conditioned status, in g..

3. RESULTS AN DISCUSSIONS

The structural analysis of tested fabrics comprises a series of characteristics, presented in Table 1.

***Table** 1 Structural analysis of composite materials*

The feature analyzed		**Variant**	
		V_1 (polyurethane foam support)	**V_2** (nonwoven material support)
Thickness of composite material, [mm]		3.01	1.58
Mass of composite material, [g/m^2]		525	580.4
The yarn density in the fabric , [yarns/10 cm]	Warp	105	100
	Weft	87	87
The length density of the yarns in the fabric, [tex]	Warp	1. 157.8 (black) 2. 148,6 (beige)	153.6 (grey)
	Weft	139.8 (khaki)	153.4 (grey)
Link		Cloth	Cloth

Obs. Because of the adhesive adherent to the yarns, their density of real length is smaller.

The behavior of fibers on reagents in order to identify the raw material is shown in Table 2

Table 2. *Identification of raw material*

		Raw material colour	Reagents					
			Phenol 70 %	Sulfuric acid 70 %	Dimethylformamide	Nitro-benzene	Xylene	Toluene
Variant	V_1	Black	S_c	I	S_c*	S_c	I	I
		Beige	I	I	S_c*	S_c	I	I
		Khaki	S_r	S_r				
	V_2	Grey	I	I	S_c	S_c	I	I
		White	I	I	S_c*	S_c	I	I

S_c - soluble while boiling
S_r – soluble at room temperature
S_c*- partially soluble while boiling forming small melt balls
I - insoluble

By analyzing the behavior of the fibers in the reagents it can be stated that: the khaki yarn is made of polyamide;

- the black yarn is polyester;
- for beige and grey yarns and for white yarns in nonwoven material, its nature can not be clearly stated. If it were polypropylene, it should be soluble when boiling in xylene and toluene. Taking into account the behavior in nitrobenzene and dimethylformamide, it could be assumed that these yarns are of polyester, but this supposition is contradicted by phenol (insoluble) behavior. Therefore, because of the contradictory behavior in solvents, the nature of these yarns can not be established with certainty. One possible explanation would be that because of the age the solvents' quality has deteriorated.

Obs. *At the burning test, it behaves similarly to polyester yarns.*

The abrasion resistance, as measured by the mass loss of test specimens subjected to friction, is shown in Table 3.

Table 3. *Determining the mass loss*

Feature	Variant	Stress time			
		30 min	60 min	90 min	120 min
Mass loss, [%]	V_1	0	0	0,01	0.103
	V_2	0.014	0.407	0.734	1.331
Feature	**Variant**	**Stress time**			
		150 min	**180 min**	**210 min**	
Mass loss, [%]	V1	0.409	0.605	0.945	
	V2	1.824	2.336	2.837	

Regarding the abrasion resistance of the two samples, there is an increase in mass loss over time, and if we compare them, we can say that the samples from polyurethane foam materials are more resistant to abrasion because they have a lower weight loss in time, the value being 0.945% at a friction time of 210 minutes versus the non-woven material samples. This can be seen more suggestively in Figure 1.

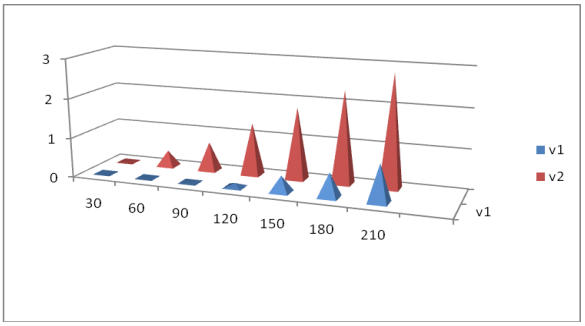


Figure no. 1 *Variation of mass loss over time*

So this material having a polyurethane foam layer can be used successfully to make uppers for protective footwear, being more resistant.

The values obtained for the air permeability of the composite materials tested are shown in Table 4.

Table 4. *Air permeability*

Feature	**Variant**	**The sense of air passage through the composite material**	
		Fabric – Layer	**Layer - Fabric**
Air permeability, [mm/s]	V_1 - polyurethane foam layer	2127.99	361.89
	V_2 - non-woven material layer	284.23	506.01

In terms of air permeability, it is observed that the passage of air from the fabric to the layer is higher for the polyurethane layer material, reaching a value of 2127.99 mm/sec, while the passage of air from the layer to the fabric has a value 361.89 mm/sec. This difference is due to the compactness of the layer that comes in direct contact with the air, but also to the structure and chemical composition, respectively to the nature of the composite.

In the non-woven fabric, the passage of air from the layer to the fabric is higher than in the case of the polyurethane foam material. So we will opt for the second material because it has better thermal insulation capacity, providing optimum comfort to the person wearing the protective footwear product made of such a type of material.

The water permeability by determining the absorption coefficient of the composite materials tested is shown in Table 5.

Table 5. *Absorption coefficient*

Feature	**Variant**	
	V_1 - polyurethane foam layer	**V_2 - non-woven material layer**
Absorption coefficient, [%]	38.17	30.18

In contact with water, higher values of the water absorption coefficient for the polyurethane foam material are observed.

It should also be noted that water has not passed through any of the composite materials tested.

4. CONCLUSIONS

The quality and functionality of the protective footwear products is given by the characteristics and properties of the materials used in making them.

As a result of the experimental research of the composite materials used for the protective footwear, the following conclusions can be drawn:

- The structural analysis of the two tested materials reveals different thicknesses, the material with a polyurethane foam layer having a higher thickness, but weighs less;
- The materials have the same type of link, namely cloth;
- The material with a polyurethane foam layer has a higher abrasion resistance than the non-woven layer;
- The non-woven material has a better thermal insulation capacity, providing optimal comfort to the person wearing a protective footwear product made of such a material;
- The two tested materials do not let through the water, the water absorption coefficient for the polyurethane foam material is higher.

The method of calculating the results obtained will be made in close connection with the production, so that the products obtained using these materials can be tested under both manufacturing and operating conditions.

5. REFERENCES

[1]. Malureanu G., Cociu V., Bazele tehnologiei produselor din piele si inlocuitori, Rotaprint I.P.Iasi, 1993

[2]. Mitu Stan , Confortul si functiile produselor vestimentare, Editura Gh.Asachi, Iasi 1993

[3]. Malureanu G., Aspecte privind sanogeneza încălţămintei, 50 de ani de Invatamânt superior în domeniul confecţiilor din piele, Iasi , 1999

[4]. Malurean G. Mihai A., Bazele proiectării încălămintei, Editura Performantica, Iasi, 2003

[5]. Mihai A., Harnagea F**,** Mãlureanu G,*The influence of the upper's materials properties on the footwear hygienic comfort*, International Scientific conference Unitech ' 04 Gabrovo, Proceedings, vol.II, Technologies in textile production, ISBN 954-683-304-5, Bulgaria 18-19 November 2004, 301-304

[6]. Iovan –Dragomir Alina, Confortul piciorului, Ed.Performantic, Iaşi , 2012, ISBN978-973-730-922 -8.

[7]. Kilic E., Puig R.,Fullana-i-Palmer P., Composites from leather industry Buffing dust: A review, Annals of the Oradea University,"Fascicle of Textile - Leatherwork", The International scientific conference, "Innovative solutions for sustainable development of textiles industry", vol XVIII, Ed.Universităţii din Oradea, ISSN 1843-813X, 2017.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PREPARATION AND CHARACTERIZATION MAGNETIC HYDROGEL

KİRAZ Uğur[1], TEBER Sena[1], PEKER Hakan[1], SALLAN Furkan Cahit[1], NARİN Güler[2], KILIÇ Eylem[1]

[1] Usak University University, Faculty of Engineering, Department of Material Science and Nanotechnology Engineering, 64200, Usak, Turkey, E-Mail: eylem.kilic@usak.edu.tr
[2] Usak University University, Faculty of Engineering, Department of Chemical Engineering, 64200, Usak, Turkey, guler.narin@usak.edu.tr

Corresponding author: Kılıç, Eylem, E-mail: eylem.kilic@usak.edu.tr

Abstract: *Every year more than 100,000 kinds of commercially available dyestuff are produced. Most of industrial dyes have synthetic origin, which are applied in many industries such as textiles, rubber, paper, plastics, leather, petrochemicals etc. The textile industry is one of the major consumers of dyestuff and the effluent from textile industries carries a large number of dyes and other additives which are added as auxiliary chemicals. During the dyeing process some of dyestuff does not bind and approximately 10-15 % of them remains in the wastewater effluents. The release of synthetic dyes to the environment cause serious environmental problems and detrimental effects to human health. Therefore development of an effective treatment method for removing dyes from wastewater is of great significance. In this study poly(vinyl) alcohol hydrogels containing different amounts of magnetic particles were prepared and characterized for dye adsorption from wastewater. The magnetic particles synthesized by co-precipitation methos were dispersed in aqueous poly(vinyl) alcohol solutions. The solutions were then physically crosslinked by the freezing-thawing method. The hydrogels prepared were characterized for their drying, swelling and gelation properties. It was found that the hydrogels has high water absorption capacity (equilibrium degree of swelling: 200–214% and equilibrium water content: 66–68%) and high crosslinking degree (95%) almost independent from their magnetic particle content. They gained magnetic property after addition of the magnetic particles in the polymer matrix.*

Key words: *poly(vinyl) alcohol, swelling behaviour, freeze-thaw, magnetic hydrogel*

1. INTRODUCTION

Magnetic hydrogels are a type of functional hydrogel with magnetic properties, which enables recovery of the composite in a magnetic field following its application. Due to their relatively facile recovery they are used in removal of numerous pollutants such as heavy metals [1], fluoride, [2] and more recently dyes [3]. Most of industrial dyes have synthetic origin, which are toxic, carcinogenic, and teratogenic, they are widely used in industries such as textile and leather. Therefore development of an effective treatment method in removing dyes from wastewater is of great importance [4].

The aim of this work was to prepare and characterize composite poly(vinyl) alcohol magnetic hydrogels containing different amounts of magnetic particles (2.1, 4.0, 6.2, and 8.1 wt % of dry films) for dye removal applications.

2. EXPERIMENTAL

2.1 Materials

For the synthesis of magnetic particles $FeSO_4.7H_2O$ (CAS. No: 7782-63-0), $FeCl_3$ (CAS No: 7705-08-0) and NaOH (CAS No:1310-73-2). Polyvinyl alcohol (PVA) (CAS No: 9002-89-5, Density: 0.4-0.6 g/cm^3, %87.8 purity) was used in order to prepare magnetic hydrogels.

2.2 Preparation of magnetic particles (MP) and magnetic hydrogels

The co-precipitation method was chosen as a method for synthesizing of the magnetic particles. 4.6 grams of $FeCl_3$ and 3.4 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 400 mL deionized water. The temperature was increased to 70 ºC and solution was stirred with a speed of 1200 rpm to form a homogeneous solution. Then 5 M ammonia solution (100 mL) was added to the solution drop-by-drop and stirred at 70 ºC for 24 hours, with a final pH of 13. The color of the solution changed from light brown to black after mixing implying the formation of Fe_3O_4. Precipitated Fe_3O_4 particles were washed by surplus amount of deionized water repeatedly until pH 7 was achieved. The final products were dried in a static oven at 70 ºC for 48 h, and the Fe_3O_4 magnetic particles were finally obtained (Fig. 1a).

Aqueous solutions of PVA were prepared by dissolving 2 g of PVA powder in 20 mL deionized water at 90 ºC in a water bath under magnetic stirring. Different amounts of the synthesized magnetic particles (MP) (0.05, 0.10, 0.15 and 0.20 g) were added to the PVA solutions corresponding to 2.1, 4.0, 6.2 and 8.1 wt% MP in the dry films, respectively. Thereafter, the solutions were continuously stirred at 90 ºC for about 15 minutes and were cast in separate polyethylene petri dishes. The solutions were crosslinked by the freezing-thawing method by instantaneous freezing at -20 ºC for 16 h and then thawing at room temperature for 8 h. After the three freezing-thawing cycles, circular specimens with 27 mm in diameter were cut off the films using a cork borer. The films were dried in a static oven at 37 ºC until constant mass. The PVA film without MP was prepared and tested as control. The compositions of the films prepared are given in Table 1. They gained magnetic property after addition of the magnetic particles in the polymer matrix (Fig. 1, b1–b4).

Table 1: *Compositions of magnetic hydrogel films*

Films	MP amount added to PVA solutions (g/20 mL solution)	MP content of dry films (wt %)
0	0	0
1	0.05	2.1
2	0.10	4.0
3	0.15	6.2
4	0.20	8.1

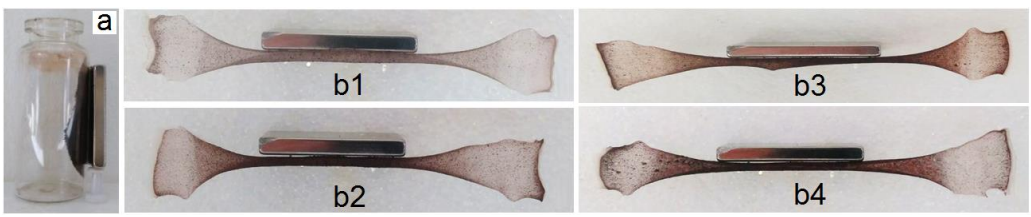


Fig. 1: *Photos of the magnetic particles (a) and magnetic hydrogels (b1: Film 1, b2: Film 2, b3: Film 3, b4: Film 4) under magnetic field.*

2.2 Characterization of magnetic hydrogels

The hydrogels with different compositions were characterized for their drying, swelling and gelation properties. Drying kinetics was investigated by measuring mass loss at 40 ºC until constant mass. Swelling kinetics experiments were conducted using 50 mL deionized water at 25 ºC, in a thermostated water bath. The mass of the films during drying and swelling were recorded as a function of time. Percent equilibrium degree of swelling (*EDS*) and equilibrium water content (*EWC*) of the films were calculated as,

$$EDS(\%) = (m_f - m_i) \times 100 / m_i \quad \textbf{(1)}$$

$$EWC(\%) = (m_f - m_i) \times 100 / m_f \quad \textbf{(2)}$$

where m_i and m_f are the initial (dry) and final masses of the films, respectively. The swelling tests were performed on three specimens for each film and the average *EDS* and *EWC* values were reported. Dissolution test was carried out in order to examine the stability of hydrogels upon swelling and fractional dissolution of uncrosslinked PVA. Following the swelling tests, the discs were dried at 40 ºC in a static oven until constant mass. Percent gelation degree was calculated as:

$$\text{Gelation degree}(\%) = m_f' / m_i \times 100 \quad \textbf{(3)}$$

where m_f' is the mass of the film after the soluble part was removed and m_i is the initial (dry) mass the film.

3. RESULTS AND DISCUSSION

The change in the mass of the films with time during drying process at 40 ºC is shown in Fig. 2. The mass loss has almost completed within the first 6 hours. The presence of MPs in the film did not affect diffusion kinetics of water through the film. Fig. 3 presents the swelling kinetics of films. The mass of all films increased rapidly within the first 4 h and then stabilized over the next 17 h period.

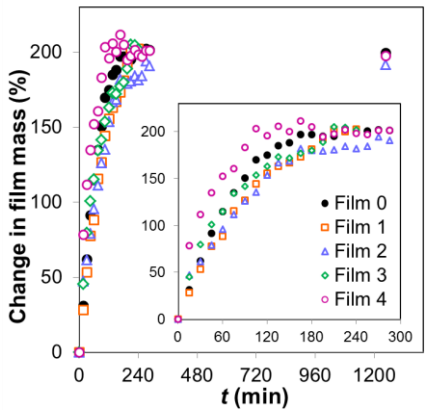


Fig. 2: *Film mass change with time during drying at 40 ºC*

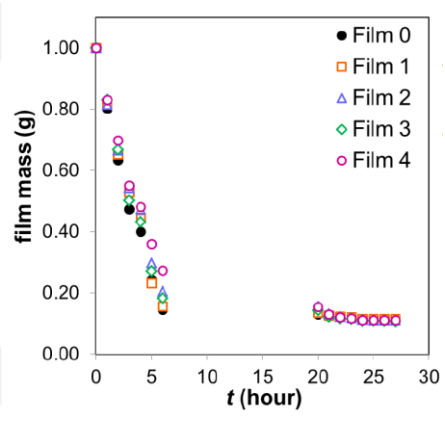
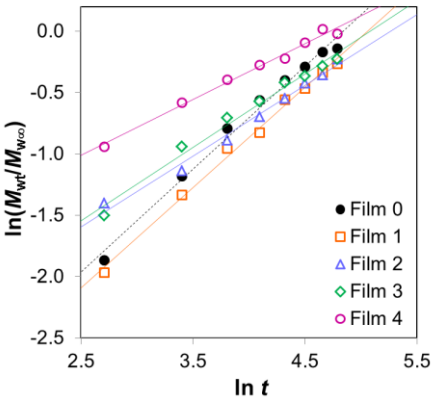


Fig. 3: *Swelling kinetics of the hydrogels*

Kinetics of the water absorption by the hydrogels can be expressed as:

$$M_{wt}/M_{w\infty} = kt^n \quad \textbf{(4)}$$

where $M_{w\infty}$ and M_{wt} represent the amount of water in the film at time t and at equilibrium, respectively, k is a constant characteristic of the system, and n is an exponent which represents transport modes inside the film and provides information about the transport mechanism. A value of $n \leq 0.5$ indicates a Fickian diffusion mechanism (the rate of diffusion is much lower than the rate of relaxation), a value of $0.5 \leq n \leq 1$ indicates that diffusion is anomalous or Fickian and $n = 1$ implies case II (relaxation-controlled transport, diffusion is very fast contrary to the rate of relaxation). The constants n and k were calculated from the slope and intercept of the $\ln(M_{wt}/M_{w\infty})$ versus $\ln t$ curves were given in Fig. 4



Films	*r²*	*slope (n)*	*intercept (lnk)*	*k*
0	0.989	0.839	-4.055	0.017
1	0.994	0.818	-4.135	0.016
2	0.987	0.577	-3.034	0.048
3	0.985	0.598	-3.039	0.048
4	0.989	0.455	-2.146	0.117

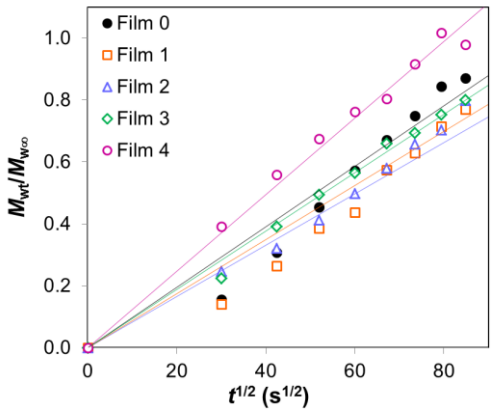
Fig. 4: *Diffusion kinetics of water in films (first 120 min of immersion)*

The calculated n value for Film 4, which is smaller than 0.5 indicated that the diffusion of water in this film is governed by a Fickian diffusion mechanism. The n values for the other films are between 0.5 and 1 indicating that diffusion is anomalous or Fickian. The diffusion coefficients for water in the swollen films were calculated by the following equation.

$$\frac{M_{wt}}{M_{w\infty}} = 4\sqrt{\frac{Dt}{\pi l^2}} \quad \textbf{(5)}$$

where l is the thickness of the film measured by a micrometer and D is the diffusion coefficient of the water molecules from the film.

From the $M_{wt}/M_{w\infty}$ versus $t^{1/2}$ plots shown in the calculated diffusion coefficients and the regression coefficients (r^2) are given in Fig. 5. The diffusivity of water molecules in the films were in the range of $3.5–20.9\times10^{-5}$ cm²/s. The presence of magnetic particles did not change the swelling kinetics of the films remarkably.



Films	*MP content of dry films (wt %)*	r^2	D (cm^2/s)
0	0	0.966	2.09×10^{-4}
1	2.1	0.962	5.43×10^{-5}
2	4.0	0.987	3.51×10^{-5}
3	6.2	0.994	9.47×10^{-5}
4	8.1	0.990	8.09×10^{-5}

Fig. 5: *$M_{wt}/M_{w\infty}$ vs $t^{1/2}$ plots for diffusion of water in films (first 120 min of immersion)*

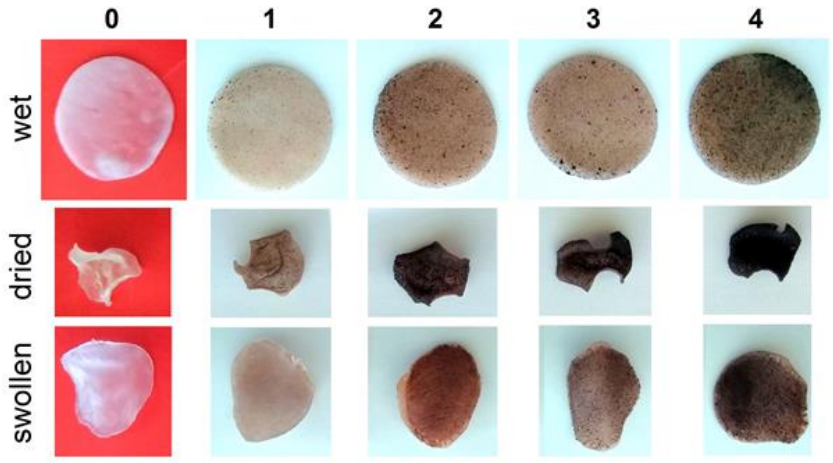


Fig. 6*: Wet, dried and swollen magnetic PVA hydrogel samples with increasing magnetic particle (MP) content (0: Film 0, 1: Film 1, 2: Film 2, 3: Film 3, and 4: Film 4)*

The volume of the films increased appreciably during the swelling test without disintegration as shown in Fig. 6. The pure PVA film has excellent transparency, while the films have become more and more opaque by the addition of MPs in increasing amounts. The transparent nature of the pure PVA film indicates the homogeneous network structure. The opacity of the blend films might be attributed to the increased crystallinity and microphase separation, which occurs in the early stage of the gelation process [5]. Fig. 7 shows dependence of the *EDS* and *EWC* of the films on their MPs content. The *EDS* values were in the range of 200–214 % of the dry mass. The *EWC* values were in the range of 66–68 %. Neither *EDS* nor *EWC* of the films were affected by the amount of MPs added.

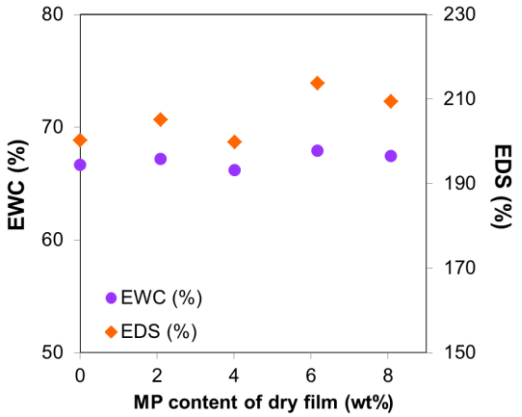


Fig. 7: *Effect of MP content of the film on EDS and EWC*

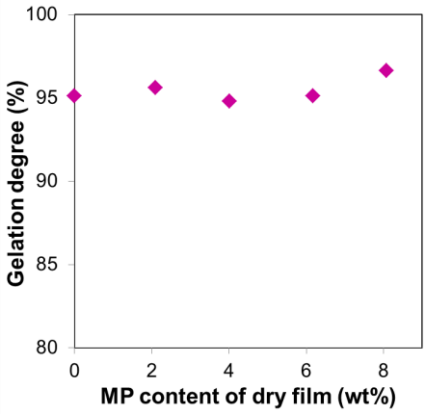


Fig. 8: *Effect of MP content on gelation degree*

5. CONCLUSIONS

It was found that the hydrogels have high water absorption capacity (equilibrium degree of swelling: 200–214% and equilibrium water content: 66–68%) and high crosslinking degree (95%) almost independent from their magnetic particle content. They gained magnetic property after addition of the magnetic particles in the polymer matrix.

REFERENCES

[1] G. A. Mahmoud, "*Adsorption of copper (II), lead (II), and cadmium (II) ions from aqueous solution by using hydrogel with magnetic properties*", Monatsh. Chem., 2013, 144, pp.1097–1106.

[2] S. Dong, Y. Wang, "*Characterization and adsorption properties of a lanthanum-loaded magnetic cationic hydrogel composite for fluoride removal*", Water Res., 2016, 88, pp.852–860.

[3] M. Pooresmaeil, Y. Mansoori, M. Mirzaeinejad, A. Khodayari, "*Efficient removal of methylene blue by novel magnetic hydrogel nanocomposites of poly(acrylic acid)"* Advances in Polymer Technology, 2016, 37 (1), pp.1-13.

[4] E. Varzaru, I. Dumitrescu, C.E. Mitran, G.O. Iordache, *"Investigation Of Different Reducing Agents Of Azo Dyes From Textile Materials"* Annals of The University of Oradea Fascicle of Textiles, Leatherwork, 2017, 1(21), pp.125-130.

[5] J.O. Kim, J.K. Park, J.H. Kim, S.G. Jin, C.S. Yong, D.X. Li, J.Y. Choi, J.S. Woo, B.K. Yoo, W.S. Lyoo, J.A. Kim, H.G. Choi, "*Development of polyvinyl alcohol-sodium alginate gel-matrix-based wound dressing system containing nitrofurazone"* Int J Pharm, 2008, 359, pp.79–86.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

MOTIVATION OF MANUFACTURING PERSONNEL IN THE FIELD OF BUSINESS

CHICU Svetlana[1], BERNAZ Luminița[2], MALCOCI Marina[3]

[1, 2, 3] University Technical of Moldova, Faculty of Textile and Printing, Department, Postal address MD 2045, S. Rădăuțan str. 4, degree block number 11, Chisinau, Republic of Moldova, E-Mail: mmalcoci2005@yahoo.com

Corresponding author: Malcoci, Marina, E-mail: mmalcoci2005@yahoo.com

Abstract: *In the Republic of Moldova, the analyzed footwear enterprise is known as a brand that produces and sells footwear for the whole family, with an experience of more than 70 years of activity. Over the years, this has been noted by the quality of the footwear and the variety of models for all ages. Analyzing the evolution of the company's staff between 2016-2017, there is a decrease in the number of employees. In 2017 there are 129 fewer people than in 2016. Reducing the number of employees is a consequence of the reduction in production volume.In order not to use the forced redundancy procedure, which involves additional personnel costs (redundancy and time-outs), the company redirected part of the workers to other employers and most of them retired were convinced to resign. Only a small number of people left the job on their own initiative, the main reason being the unsatisfactory salary. In the study, in order to evaluate employees' satisfaction with the existing motivation system, the questioning of employees was made. The questionnaire consists of 14 items, being closed questions with multiple responses that allow the respondent to choose from a predefined list the variants that best define their preferences. The survey was attended by 35 employees, out of 135 directly prductive.*

Key words: *employer, worker, questionnaire, evolution, incentive.*

1. INTRODUCTION

The success, performance and competitiveness of any organization depends to a large extent on the content and quality of human resource management, as, as many specialists have pointed out, the competitive advantage of an organization resides in its people [1].

Personnel is the indispensable resource of any production enterprise. Every tenth or even hundreds of people are directly involved in each product. Without the contribution of people, the production process can not exist [2].

Motivation is one of the most important issues of any organization, as the relationship between the organization and the employees is governed by the reasons why employees feel involved in their work. The consequence of this is the need for the management of the organization to be able to translate the organization's goals into the employees and to relate them to their personal goals, as only by doing so can the organization become effective and achieve its objectives [3].

2. GENERAL INFORMATION ABOUT MOTIVATION

2.1 Motivate staff within the organization

Work motivation involves employee behavior characterized by interest, orientation and persistence in the performance of tasks. This behavior does not depend only on the individual or the context in which they work but is an interaction between the personality of the individual and the working environment.

The path to efficient human resource management lies in understanding their motivation. Only by knowing what determines the individual to carry out activities, what motivates his actions is possible the design of an efficient system of methods and forms of human resources management [4].

It is quite difficult to motivate employees. In an organization, the motivation of staff must take into account an ensemble of variables, some internal, other external ones, some related to the intrinsic aspect of the personality of the individual, others to the extrinsic, sensitive to the characteristics of the organizational environment [5].

2.2. Types of motivation

It is well known that most people do not come to work just to get their salary at the end of the month. In addition to the financial aspect, people are looking for a job the possibility of developing proficiently, the recognition of the work done by the colleagues and the superiors, the belonging to the staff and working atmosphere. Money needs a lifetime, but for action, proper motivation is needed [6].

Staff motivation is of two categories:

Intrinsic motivation that is given by internal factors that influence individuals in having a particular behavior. These factors refer to responsibility, freedom of action, the ability to develop and use skills, interesting work and the opportunity of promotion. Intrinsic motivation refers to the quality of work, which will have a deeper effect in the long run.

Extrinsic motivation - refers to what is done to people to motivate them. This includes rewards, such as salary increases, promotion, bonuses, and punishments such as disciplinary action, criticism, or even salary cuts. Extrinsic motivation can have a strong but long-lasting effect [7].

Personnel motivation strategies within organizations are centered on two major issues: financial and non-financial motivation.

The first direction is mirrored in the financial structure of a company by means of salaries, bonuses, bonuses, bonuses, commissions, vouchers (meal, gift, crest, holiday), more rarely diiviende. Money can help some people not become overwhelmed, but it does not necessarily help them become more motivated [8].

Human resources specialists, as well as studies in the field, have shown that non-financial motivations are more effective than a bonus on salary when a company aims to build a long-term relationship with its own employees. Non-financial modes of recognition and reward can be the solution, especially when budgets for additional rewards are small or almost non-existent in times of economic crisis.

In addition to an appropriate salary, employees need safety, which can be provided by job security, social and health insurance, pension funds, need for group membership, which can be offered through a special work environment, enrollments free courses, sports halls.

3. ANALYSIS OF MOTIVATION IN THE FOOTWEAR COMPANY

3.1. Analysis of the existing situation within the enterprise

In the Republic of Moldova, the analyzed footwear enterprise is known as a brand that produces and sells footwear for the whole family, with an experience of more than 70 years of activity. Over the years, this has been noted by the quality of the footwear and the variety of models for all ages.

The evolution in time of the number of employees in the company analyzed lately is presented in Table 1.

Table 1: *Evolution of the number of employees over time*

	12.01.2016	**12.01.2017**
Scriptic number (total)	487	358
Including: Workers	196	135
Administration	51	38
Auxiliary staff	72	56
Maternity leave	168	129

Analyzing the evolution of the company's personnel between 2016-2017 (Table 1) there is a decrease in the number of employees. In 2017 there are 129 fewer people than in 2016. The decrease in the number of employees is a consequence of the decrease in production volume. In order not to use the forced redundancy procedure, which involves additional personnel costs (redundancy and time-outs), the company redirected part of the workers to other employers and most of them retired were convinced to resign. Only a small number of people left the job on their own initiative, the main reason being the unsatisfactory salary.

The human resources assurance business is analyzed as follows: for each year, the number of persons required by specialties, professions and the costs of preparing skilled workers are included in the business plan. The recruitment of people is carried out from the territory of Chisinau municipality and from suburbs through: internet advertisements, newspapers and recommendations. People who go for employment are subject to an initial selection interview. The selection interview is carried out before the applicant completes the employment forms in order to see if he has the chance to be elected in the available job. New staff arriving at the enterprise are met and informed by the staff of the service personnel about: the business activity; technology and finite production; getting acquainted with production departments; with the enterprise regulation; quality requirements; with the enterprise's team. With the people who agreed to work, the individual work contract ends.

Having as basic activity the production of goods, it means the existence of two categories of staff and two categories of relationships in the organization: personnel directly involved in the production of the basic product; personnel who contribute indirectly to the realization of the basic product, through design, quality control, staffing, commercial complex.

Depending on the role of the basic activity in the production process, the personnel is divided into the categories: workers and specialists.

3.2. Analysis of motivation within the enterprise

In the study, in order to evaluate employees' satisfaction with the existing motivation system, the questioning of employees was made. The questionnaire aims to highlight the motivational factors, which act on the behavior of the employees. The questionnaire is made up of 14 items, which are closed questions with multiple responses that allow the respondent to choose

from a predefined list the variants that best define their preferences. The survey was attended by 35 employees, out of 135 directly productive.

Table 2 summarizes the results of the questionnaire.

Table 2: *Generalized table of questionnaire results*

The question		Employee Response	
		number	%
1	**What is the importance that you give to financial incentives ?**		
	a. small	**0**	**0**
	b. average	**0**	**0**
	c. big	**9**	**25,71**
	d. is the main incentive	**26**	**74,29**
2	**What do you think would make you work better, perform better?**		
	a. a prize / bonus	**7**	**20**
	b. a move to a more interesting job	**2**	**5,71**
	c. praise the boss	**2**	**5,71**
	d. a higher salary on the same job	**24**	**68,57**
	e. the boss's criticism	**0**	**0**
3	**What would you do to voluntarily perform additional tasks:**		
	a. the pleasure of working on something interesting	**2**	**5,71**
	b. what they gain from doing so	**33**	**94,29**
4	**I think it is more important:**		
	a. to know that I did a good job	**7**	**20**
	b. to confirm my boss that I did a good job	**28**	**80**
5	**I am tempted to make extra effort if my work:**		
	a. is well paid	**35**	**100**
	b. is favorably appreciated by other colleagues	**0**	**0**
6	**Are you happy with your direct boss communication?**		
	a. Yes	**5**	**14,29**
	b. sometimes	**20**	**57,14**
	c. not	**10**	**28,57**
7	**Are you satisfied with communicating with colleagues?**		
	a. Yes	**7**	**20**
	b. sometimes	**21**	**60**
	c. not	**7**	**20**
8	**Are you satisfied with how you get the necessary information at work?**		
	a. Yes	**4**	**11,43**
	b. sometimes	**22**	**62,86**
	c. not	**9**	**25,71**
9	**Are you satisfied with the working conditions ?**		
	a. Yes	**17**	**48,57**
	b. not really	**16**	**45,71**
	c. not	**13**	**37,14**
10	**Are you satisfied with the current salary?**		
	a. Yes	**2**	**5,71**
	b. somewhat	**18**	**51,43**
	c. not	**15**	**42,86**
11	**How do you assess how you are paid for your work?**		

	a. I am paid correctly	**2**	**5,71**
	b. I think I should get more money	**26**	**74,29**
	c. I am paid for my results	**7**	**20**
12	**Things THAT WANT to be present in the company, and now they are NOT:**		
	a. a set of very clear rules	**0**	**0**
	b. awarding special merits	**0**	**0**
	c. respect for employees by the leaders	**33**	**94,29**
	d. the celebration of the birthday of the employees	**35**	**100**
	e. respect among colleagues	**30**	**85,71**
	f. human communication	**26**	**74,29**
13	You would work harder if:		
	a. you will be appreciated publicly	**2**	**5,71**
	b. would be a more enjoyable atmosphere in the company	**18**	**51,43**
	c. and the other colleagues would be more interested	**1**	**2,86**
	d. ensuring the safety of the day	**14**	**40**
14	**To what extent are you dissatisfied with the current work?**		
	a. very dissatisfied	**4**	**11,43**
	b. somewhat unhappy	**12**	**34,29**
	c. in the middle	**19**	**54,29**
	d. somewhat pleased	**0**	**0**
	e. very pleased	**0**	**0**

After analyzing the results of the questionnaires on the importance of the financial incentives of the employees within the enterprise, it was found that for the majority of employees, 74,29%, financial incentives are a priority. This is because the expectations of workers are limited to meeting physiological needs. For most people working in the enterprise, wages are the only source of life. It can be seen that the highest share in the results is recorded by a higher salary in the same job, in the proportion of 68,57%. A bonus, a premium is another motivation for 20% of employees. It is noticed that the boss's criticism is nothing for the employees. These results are consistent with Maslow's theory of needs, that needs security, safety, work safety conditions, job stability, are required to be met before social needs, esteem and personal achievement.

Again, additional gain is the most motivating reason for most of the company's employees. About 6% of the angels work out of pleasure. They are those who are enthusiastic and wish to continue a continuous professional development in the future. It is noted that for 80% of the interviewed subjects, the boss's confirmation that he has done a good job is of greater importance. From the results, we see that 20% of employees do not need the supervisor's boss because they are responsible for tasks, usually they are part of the 50-year age group. All employees want to be well paid. This means that salary and prizes are the greatest motivation for workers.

According to the results, 57,14% are sometimes satisfied with the communication with the boss. A fairly high percentage of employees (28,57%) are not satisfied and only 14,29% of them are satisfied with communication with superiors. These results demonstrate a lack of communication between hierarchical levels, which are most often caused by poor information transmission by superiors and the ability to receive the message by subordinates who only have general studies. The respondents considered that they were only satisfied with communicating with their colleagues at a rate of 60%. But in equal percentage is satisfaction and dissatisfaction with communication with colleagues. These results are due to the diversity of workers, who have principles, values of life and come from different cultural backgrounds.

Most of the workers consider that the company sometimes provides 62,86% job-related information, while 25,71% is not satisfied at all with the information received. What again demonstrates that the transmission and reception of information is deficient. The results show that only 17,14% of respondents are satisfied with the conditions they are currently working on, 45,71% of respondents consider working conditions satisfactory and 37,14% of employees consider the conditions to be unsatisfactory. These results show that the organization fails to provide satisfactory working conditions (working arrangements, organizational level of the process, job safety, hygiene conditions, psychological atmosphere), so that there is no discomfort for the employees and the process is not affected production.

It can be seen that only 5,71% of the interviewed subjects are satisfied with the salary they receive at the moment. Hence, only those who work with pleasure are satisfied with salary. Only 51,43% are somewhat satisfied, and 48,86% of employees appreciate the salary system as unsatisfactory. The responses of the employees differ, it can be seen that only 5,71% of the respondents think they are paid correctly are the same workers who answered the previous questions that they work with pleasure and are satisfied with the salary. And most respondents – 74,29% think they should get more money, and 20% of employees think they are paid according to their results. The wage system for workers is in agreement, so salary is directly proportional to the productivity of each.It is noted that all 100% of respondents want to celebrate birthdays, 94,29% respect for employees, 95% college respect 85,71% and human communication 74, 29%.

As with the previous questions on communication in the organization, and the answers given once again prove that the circulation of information between specialists and workers is flawed. As a result of the questioning of the workers, it was found that the employees would work more if it was a more pleasant atmosphere within the company and there would be the safety of tomorrow. And these results confirm that no worker is satisfied with the job. While 54,29% are satisfied on average, 11,43% are very dissatisfied. Major job discomfort is a consequence of low wages.

4. CONCLUSIONS

The financial reward is the main motivating factor within the footwear enterprise under review. Money, in the minds of employees, is a way in which it assures its material needs, because it is the reward for the work done, is a factor of its professional fulfillment, as well as proof of the employer's appreciation for the work he / she enters into the organization.

REFERENCES

[1] B. BACANU, "*Management stretegic"*, Editura Teora, București, 1997.

[2] L. BUGAIAN, *"Antreprenoriat: Inițierea afacerii"*, Tipografia A.Ș.M., Chișinău, 2010.

[3] ***"*Noile tendinte si strategii de motivare a angajatilor"*, [Online]. Available: http://www.hranatate.ro/noile-tendinte-si-strategii-de-motivare-a-angajatilor.

[4] L. Bîrz, "*Motivarea personalului. O problemă esențială a unei biblioteci"*, [Online]. Available: https://hcccdi.files.wordpress.com/2013/01/carte-lucretia-birz.pdf

[5] G. PÂNIȘOARĂ, I. O. PÂNIȘOARĂ *"Motivarea eficientă. Ghid practic"*, Editura Polirom, București, 1998.

[6] A. A. PURCAREA, D. CONSTANTINESCU, D. SERBAN, ș. a. *"Managementul resurselor umane"*, Editura BREN, București, 2000.

[7] M. AMSTRONG, ″Managementul resurselor umane″, Editura Codecs, București, 2003.

[8] G. PÂNIȘOARĂ, I. O. PÂNIȘOARĂ *"Motivarea eficientă. Ghid practic"*, Editura Polirom, București, 2005.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

STUDY OF THE INTEGRATED QUALITY-RISK MANAGEMENT FOR INDUSTRIAL COMPANIES

GHERGHEL Sabina [1], INDRIE Liliana[2]

[1,2] University of Oradea, Faculty of Energy Engineering and Industrial Management, Department of Textiles, Leather and Industrial Management, B.St. Delavrancea 4, Oradea, Romania, sgherghel@uoradea.ro, lindrie@uoradea.ro

Corresponding author: Gherghel, Sabina, E-mail: sgherghel@uoradea.ro

***Abstract**: The quality of products is the final expression of the quality of production processes, given the technical, economic, psycho-sensory, etc. performances of the products. Industrial quality refers to the conformity of the product with the normative technical documents (standards, technical data sheets, etc.). Continuous improvement is the gradual improvement of the quality of products and services, productivity and competitiveness, with the participation of all the staff of the company. This way of improving quality has registered a major development in Japan where it is known as Kaizen. Quality risk management is a systematic process of assessing, controlling, communicating, and reviewing risks regarding the quality of products / services throughout their lives.*
This paper briefly describes the factors that influence the quality of industrial products, as well as the indicators for assessing the quality of the products. It insists on the methods and techniques for continuous improvement of quality, especially by appreciating the Kaizen strategy and the stages of designing the integrated quality-risk management system for industrial companies. The last part of the paper presents a model for quality risk management and a predictive risk analysis in quality for planning future corrective actions and necessary measures to prevent their occurrence, as well as concepts and classification criteria for failure analysis and effects.

***Key words:** product quality, industrial quality, productivity, competitiveness, risk management*

1. INTRODUCTION. GENERAL CONSIDERATIONS ON THE QUALITY OF INDUSTRIAL PRODUCTS

The quality of the products is the final expression of the quality of the production processes, given the technical, economic, psycho-sensory, etc. performance of the products. Industrial quality refers to the conformity of the product with the normative technical documents (standards, technical data sheets, etc.). In order for a product to meet the customer's requirements, it must have certain qualities that can be divided into several categories as shown in Figure 1:

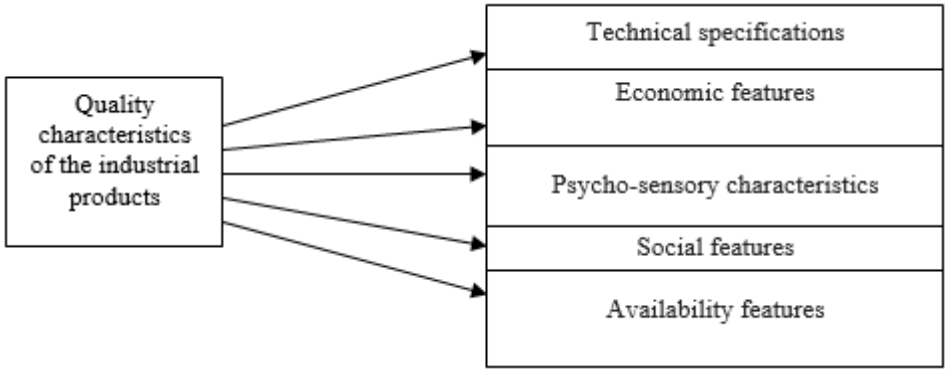


Fig. 1: *Quality characteristics of the industrial products*

1.2. Factors that influence the quality of the industrial products

The quality of the industrial products depends on many factors whose influence is due to the conditions in which the production process takes place. These factors are classified according to the criteria given in Figure 2:

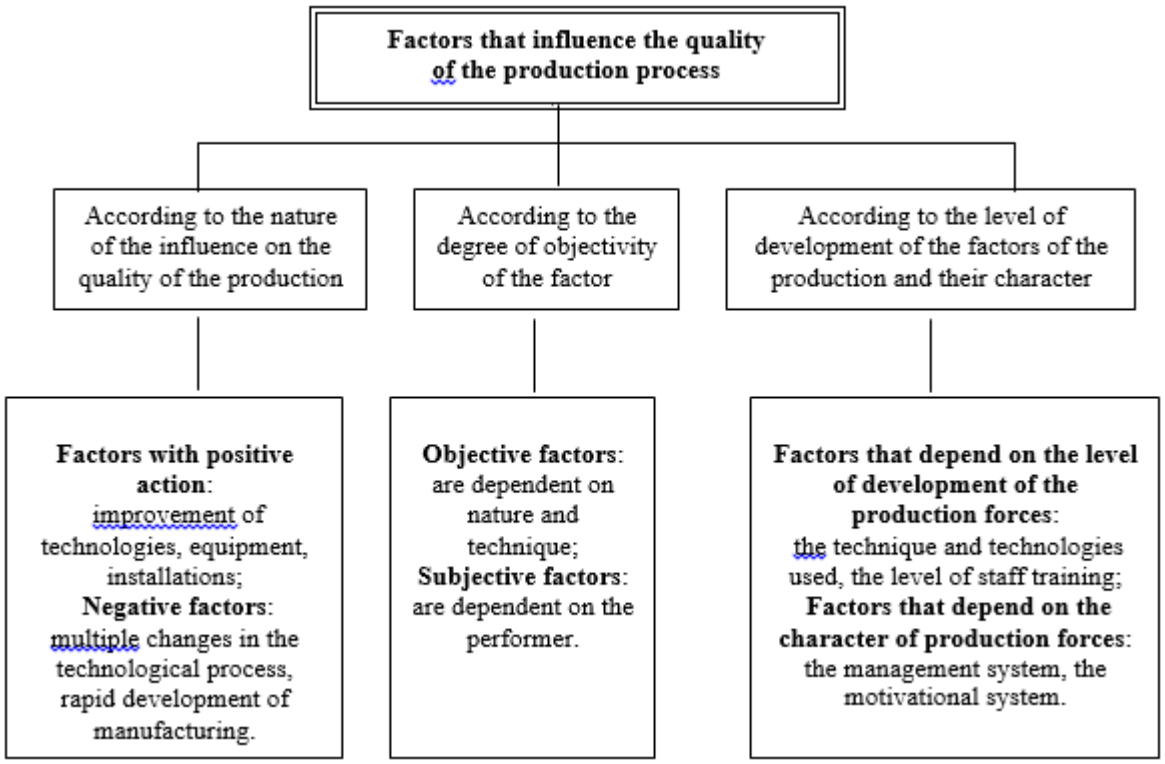


Fig. 2: *Factors that influence the quality of the production process*

2. INDICATORS FOR ASSESSING THE QUALITY OF INDUSTRIAL PRODUCTS

For the quality assessment we can use a system of indicators of which the most important are:
a) partial product quality indicators;
b) quality class indicators;
c) indicators of rejections;
d) indicators of customer complaints.

a) Partial product quality indicators reflect a range of measurable product characteristics, the content of which refers to an attribute, trait or property that meets certain requirements.

b) Class quality indicators are divided into two categories:
1. Indicators that are used by companies making a homogeneous production;
2. Indicators that are used by companies making heterogeneous production.

c) Scrap indicators

The value of rebutted production is determined according to the relationship:

$$R_V = \sum_{i=1}^{n} q_{rdi} x c_{rdi} + \sum_{i=1}^{n} q_{rri} x c_{rri} \quad \textbf{(1)}$$

Where: i – type of product;
q_{rd} – the amount of definitive scrap;
c_{rd} – the unit cost of a definitive rejection;
q_{rr} – the amount of recoverable waste;
c_{rr} -- the unit cost of recovering a recoverable scrap.

Percentage of rebutted production:

The calculation formula is as follows:

$$P_{pr} = \frac{R_v}{\sum_{i=1}^{n} q_i x c_i} x100 \quad \textbf{(2)}$$

Where: R_v – the value of the rebutted production;

$\sum_{i=1}^{n} q_i x c_i$ - the value of production expressed in costs.

The value losses registered by the company in the resumption of production are determined as follows:

$$Pr = Rv - Srec \quad \textbf{(3)}$$

Where: R_v – the value of the rebutted production;

Srec – the amounts recovered by the company by the use of the scrap, the sums withheld from the guilty persons, as well as the indemnities received from the suppliers who delivered the inappropriate materials that generated the appearance of these scrap.

The percentage of losses of the rebutted production is calculated according to the following formula:

$$P_r\% = \frac{\Pr}{\sum_{i=1}^{n} q_i x c_i} x100 \quad \textbf{(4)}$$

Where: Pr - the value losses registered by the company in the resumption of production;

$\sum_{i=1}^{n} q_i x c_i$ - the value of production expressed in costs.

d) Clients' complaints indicators.

These indicators reflect non-quality and refer to:

- The amount of products refused at reception or claimed during the warranty period and their value; - The quantity and value of the products refused or claimed in the total production;
- Expenditure on remediation of the products refused or claimed;
- Number of repair requests per 1000 pieces shipped.

3. CONTINUOUS IMPROVEMENT OF THE QUALITY. METHODS AND TECHNIQUES

Continuous improvement is the gradual improvement of the quality of products and services, productivity and competitiveness, with the participation of all the staff of the company. This way of improving quality has registered a major development in Japan, where it is known as Kaizen. [3]. Kaizen is different from the methods for improving the quality of the European and American managers, which emphasize innovation; the superiority of the Japanese concept results from the fact that for the implementation of the "small steps" strategy, the necessary resources are insignificant, while the innovation-based strategies require very large investments, the change being radical compared to the initial situation. Both strategies are shown in Figures 3 and 4:

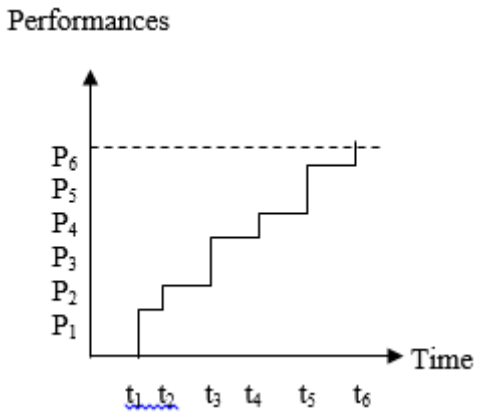


Fig. 3: *Improving quality through Kaizen strategy ("small step" strategy)*

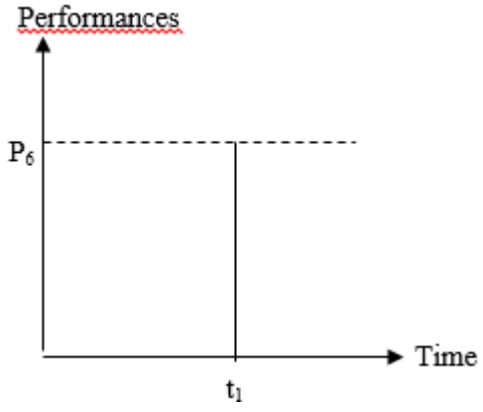


Fig. 4: *Improving quality through innovation ("big step" strategy)*

There are several issues that make a difference between the Kaizen strategy and the quality improvement strategy through innovation, as shown in Table 1:

***Table 1**: The main elements of differentiating the Kaizen strategy from the innovation strategy*

CRITERIA	KAIZEN STRATEGY	INOVATION STRATEGY
Complexity of change	Low	High, radical
Frequency of change	High	Low
Delimitation over time	Continuous	In jumps
Degree of risk	Low	High
Participants	Every employee of the company	Chosen employees for innovating
Motto	Maintenance and improvement	Discarding the previous situation and rebuilding
Technologies used	Conventional know-how and the existing level of the technique	Important technological change, new solutions
Effort	Small investment, strong mobilization	Important investment, low mobilization
The main success factor	Human factor	Technical factor
Effect	Slow economic growth	Rapid economic growth

4. RISK MANAGEMENT IN QUALITY. THE PHASES OF THE QUALITY RISK MANAGEMENT PROCESS.

Quality risk management is a systematic process of assessing, controlling, communicating, and reviewing risks regarding the quality of products / services throughout their lives. A model for quality risk management is presented in Figure 5, but other models may also be used, the emphasis on each component being different from case to case [4], [5].

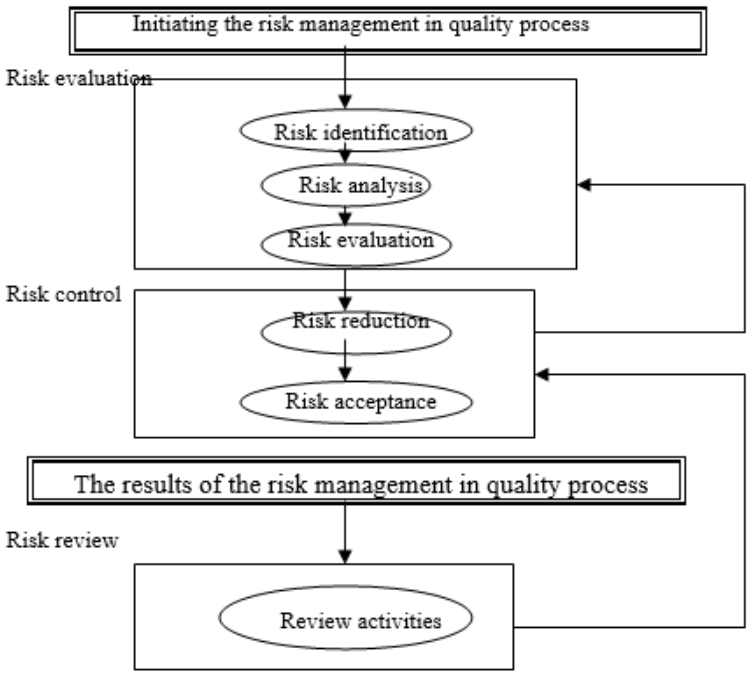


***Fig. 5:** Stages of risk management process in quality*

4.1. Estimative risk analysis in quality

The analysis of failure modes and their effects is a method of analyzing the probability of failure of a product, process or technological system in order to plan the corrective actions and the measures that are necessary to prevent their occurrence [6], [7].

The implementation steps are as follows:

- planning and preparation,
- risk analysis,
- evaluation,
- minimizing risk. [8]

5. CONCLUSIONS

A quality-risk integrated management will simplify the existing management systems within a company by increasing the benefits of each system, will facilitate the optimizing of the resource consumption, and it will also reduce the costs of maintaining more management systems.

It is imperative that in the industrial companies (and not only) the emphasis to be put on the awareness that an integrated quality-risk management will contribute to maximizing the real potential of the organizations, enabling them to integrate as quickly as possible in the business environment.

REFERENCES

[1] Morariu, C. O.*"Sistemul de management al calităţii"*, Editura Universităţii Transilvania, Braşov, 2006, ISBN (10)973-635-738-4,(13)978-973-635-738-1

[2].Olaru, M. şi colectiv *"Tehnici şi instrumente utilizate în managementul calităţii"* Editura Economica Bucuresti, , 2000, ISBN 973-590-256-7

[3]. Masaaki, Imai. "Apply Kaizen successfully. The structure defines the flexibility of a company. Kaizen Forum Magazine" Global Edition 06/2006. Switzerland, Kaizen Institute, quoted 9th of sept 2008, http://www.kaizen.com

[4]. Gheorghiu, A., Orfescu, D. S., Păunescu I., "Analiza riscurilor în activitatea întreprinderii si strategii de prevenire ",Editura ASE, Bucureşti, 2006

[5]. Garvey, Paul R., "Analytical Methods for Risk Management: A Systems Engineering Perspective".Taylor & Francis Group,USA, 2009,ISBN 9781584886372

[6]. . Doherty, Neil A, "Integrated Risk Management: Techniques and Strategies for Reducing Risk ",McGraw – Hill, New York, USA, 2000, ISBN 0-07-135861-7

[7]. Oprean, C., Kifor, C. V., Suciu, O., "Managementul integrat al calitatii. ",Editura Universitatii Lucian Blaga din Sibiu, Sibiu, 2005, ISBN 973-739-034-2

[8]. Stamou, T., "Integrated Management Systems: Theory and Practice",University of East England, 2003

The editors take no responsibility of the results, opinions and conclusion expressed in the published papers.