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Aspects regarding the experimental researches of Romanian mohair properties

CARMEN GHIȚULEASA
ANA-MARIA MOCIOIU

LILIOARA SURDU
AUREL CONSTANTIN

REZUMAT – ABSTRACT

Aspecte privind cercetările experimentale ale proprietăților mohairului românesc

„Reîntoarcerea la natură" este o tendință în creştere în industria textilă. De-a lungul timpului, fibrele artificiale au cunoscut evoluții spectaculoase, chiar fascinante, în încercarea de a imita natura, în toate aspectele ei specifice. În ciuda extinderii producției şi prelucrării fibrelor artificiale cu caracteristici extrem de diversificate şi sofisticate, proprietățile specifice ale fibrelor naturale şi, în special, cele ale părurilor animale nu au putut fi egalate. Utilizarea acestor materii prime prețioase, a aşa-ziselor fibre nobile sau păruri animale de lux, a depăşit bariera produselor din categoria „lux", devenind, în ultimii ani, o caracteristică a pieței de produse textile. În România, caprele Angora au fost aduse sub formă de donații, pentru a revigora fermele de animale din țară. Institutul Național de Cercetare-Dezvoltare pentru Textile şi Pielărie a inițiat – în colaborare cu Ferm Prod SRL, din județul Brăila, o zonă favorabilă din punctul de vedere al condițiilor de mediu şi al climei, un proiect de aclimatizare în România a unui nucleu de capre Angora. Lucrarea prezintă aspecte privitoare la procesul de aclimatizare, creştere şi înmulțire a animalelor, precum şi un studiu comparativ al principalelor caracteristici ale fibrelor de mohair românesc Angora.

Cuvinte-cheie: mohair românesc, aclimatizare, caracteristici, fibre

Aspects regarding the experimental researches of Romanian mohair properties

"Returning to Nature" is a growing tendency in the textile industry. Chemical fibers had known spectacular, even fascinating developments over time, trying to imitate nature in all its specific aspects. Despite this expansion of the production and processing of chemical fibers with extremely diversified and sophisticated characteristics, the specific properties of natural fibers and especially those of animal hairs could not be equalized. The use of these precious raw materials, the so-called noble fibers or "luxury hair fibers" overcame the barriers of "luxury" products, becoming a characteristic of the textile product market in the last years. In Romania, Angora goats were brought under the form of donations, in order to reinvigorate Romanian livestock farms. The National Research and Development Institute for Textiles and Leather Bucharest initiated, in collaboration with the Ferm Prod ltd. company from Braila county (area favorable in terms of environmental conditions and climate), an acclimatization project in Romania of a group of Angora goats. The paper presents aspects regarding the acclimatization process of animals, their breeding and multiplication and the comparative study of the main characteristics of Romanian Angora mohair fibers.

Key-words: Romanian mohair, acclimatization, characteristics, fibers

The tendencies of fashion towards clothes having special comfort characteristics have determined, in the last period, the manufacturers to focus their attention towards a greater usage of natural animal fibres. Usually known under the generic title of noble animal fibres, they present specific characteristics: soft, fluffy, handle, bulky, superior thermal isolation, breathable characteristic, air and humidity permeability, that give to the products containing such fibres an increased degree of comfort in wearing; possibility of adjusting to different environmental temperatures, maintaining he thermal equilibrium of the body.

The market researches indicate that the society's evolution has determined, and still does, a certain change of the consumers' perspective. Their requests and exigencies go beyond the level of quality textile products, reaching a superior one: natural fiber products, with a high added value, that bring "services" to the consumer, such as: comfort, easy care, functionality, "anti" properties: anti-soiling, anti-felting, anti-moths, odor control.

Globally, the major concerns of the consumer goods textiles' manufacturers meet these requests and refer to:

– the use to the full extent of natural textile fibers;
– the increase of the added value of the products;
– achieving quality products that combine the engineering factors with the aesthetic and economic ones;
– achieving quality products that combine the engineering factors with the aesthetic and economic ones.

The paper presents aspects regarding the study of the complex structural properties of Romanian Angora mohair, as compared to those corresponding to wool fibres, through:

– electronic microscopy
– thermo gravimetrical analysis;
– birefringence analysis.

There are also examined the physical-mechanical and physical-chemical properties of mohair fibers and their evolution during the acclimatization of goats. Further, there are presented aspects regarding the manufacturing of the Romanian mohair fibres for obtaining yarns and woven fabrics containing mohair, wool fibres and/or wool type chemical fibres, with superior aesthetic and comfort characteristics and high added value.

SOME ASPECTS REGARDING THE ACCLIMATIZATION PROCESS OF THE ANGORA GOATS

After the acclimatization process initiation, it was noted that the animals have adapted easily to the new living conditions and the acclimatization process is completed, the quantity of mohair is 4–6 kg fiber per animal and the goats that give birth to two kids are in percentage of 50–60%. Nevertheless, because of the inbreeding process, we noticed that he percentage of healthy kids at calving, the body weight and the quantity of fiber per animal, as well as the animal size were decreased.

Due to this situation, the specialists from Ferm-Prod made tests for cross-breeding, 20 females were crossbreed with males of normal breed. It was noticed that some kids kept the mother genetic character, fact noticed by the fleece aspect, specific to Angora; other kids have mainly their father character and the Angora specific aspect was lost.

In order to restore the specific characteristics of the breed, in 2011 there were purchased 5 Angora males from France and this study presents aspects regarding the properties of mohair fibres obtained in 2012.

CONTRIBUTIONS TO THE STUDY OF THE PHYSICAL-MECHANICAL CHARACTERISTICS OF THE ROMANIAN MOHAIR FIBRES

Regarding to the main physical-mechanical characteristics for Romanian mohair fibers (2003, 2010, 2012), compared with Romanian wool fibers, the following aspects there are highlighted:

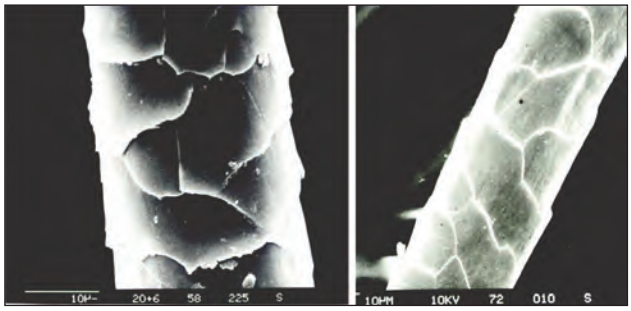
- Mean diameter is found around 30 mm, for the fibers coming from adult goats, value comparable with the one corresponding to the semi-fine wools, sort 29P (21), no modifications are noticed as far as samples in the 2010 production are concerned, as compared to the 2003 production and the goatling obtained in 2011 have a diameter between 22–27 mm;
- Mean length of the mohair fibers in the 2010 production shows a higher value (130 mm), in comparison with fibers in the 2003 production (100.2 mm) and the average fibers length for the goatling from 2011, is between 112–115 mm, which indicates a good behavior, from the point of view of this parameter;
- Staple fibers content has high values in case of mohair against wool, as this is generally a characteristic specific to goats (Angora, Cashmere) and camellids (camels, alpaca), being formed out of the fibers layer next to the animals skin (cca. 14% of total fleece);
- A reduction of the breaking resistance is determined for the 2010 production fibers, as compared to the 2003 production fibers, phenomenon that can be interpreted as an effect of the acclimatization process and of animal consanguinization and for the fibers from 2011, the values are between 14–18 cN, values appropriate for young goatlings;
- Friction coefficient values (static and dynamic, fiber/fiber and fiber/metal) prove a sensible increase in case of 2012 and 2010 production fibers, against the 2003 ones, process that can be explained by possible changes of the scales, which, due to acclimatization, thickened and became more prominent, the plasma treatment of the fibers determines an around 10% increase of these values, both for fiber/fiber and fiber/metal friction coefficients;
- Number of wrinkles for the mohair fibers is 0.7 wrinkles/cm, with 86% lower against the one corresponding to wool fibers (5.3 wrinkles/cm), this aspect is preserved for all samples mohair fibers analyzed and is due to differences existing at the level of cuticle cells, these aspects have to be considered when designing the fibrous blends and, further, when managing the technological processing stages;
- Luster is influenced by the cuticle cells characteristics, which determine an increase of the even reflecting component to the decrease of the diffuse reflecting one, thus leading to a more intense luster gained, as compared to wool, whiteness degree determined by the Elrepho method amounts to 37.90 for the mohair, which highlights a white color with a soft yellowish tint favoring the fibers luster. These aspects are well observed in samples from 2012, after crossbreeding with Angora male goats.

It can also be observed that the variation coefficient of all characteristics is high; this is a specific characteristic of animal hairs. Also the number of crimps is low, compared with wool fibers; the friction coefficients, fiber/fiber and fiber/metal also have low values. These aspects determine the lowest adherence of the mohair fibers.

CONTRIBUTIONS TO THE STUDY OF STRUCTURAL PROPERTIES OF THE ROMANIAN MOHAIR FIBRES

The mohair (keratin fibre) is characterized from the morphological point of view by the existence of three distinctive cellular layers: cortical layer, cuticle layer and medulla. Medulla is specific for coarse fibres, with diameter over 35–38 mm.

For emphasizing the longitudinal aspect of the fibres, there are effected electronic microscopy analyses (Stereoscan 250), in the laboratories of our institute: fibres – production 2003, 2010 and 2012.



a ***b***

Fig. 1. The aspect of the longitudinal surface [2]:
a – for the wool fibres; ***b*** – for the 2003 mohair fibres

Figure 1 highlights the fibres longitudinal surface for mohair fibres – 2003, as compared with wool fibres. It can observe the existence of some fine denticulate cuticle cells, with sharp peaks and with smaller thickness (scale height) in comparison with wool fibre scales.

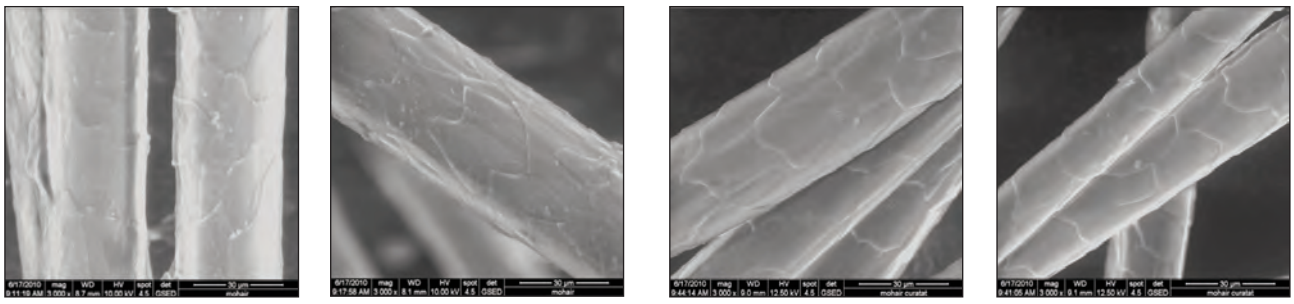
Figures 2 *a, b* present the fibres longitudinal surface for mohair fibres – 2010, raw and washed (SEM QUANTA 200, GSED).

The specific surface scale appearance is one of the factors that determine the high natural luster degree and the improved tinctorial properties of mohair fibers. The analyses of electronic microscopy undertaken in the specialized laboratories in the institute have emphasized for the mohair fibres a cortical structure formed of orthocells and para heterotype cells (cells of transition from ortho to para).

The undertaken researches have emphasized a close connection between the cortical structure and crimping of the fibres. The mohair fibres have a reduced number of crimps (0.7 crimps/cm) and a monotype distribution (ortho-cortical cell and of transition ortho → para).

Figure 4 presents the aspect of the cross-section for the mohair fibres. For the emphasizing of the cortical structure a coloration specific to the para-cortical cells (silver nitrate 2.5%) has been performed.

In the section one can observe that there are not clear differences of color inside the cortex as it is in the case of fine wools, that prove the character of ortho-paracortical transition of the cells. The lack of the para cells, strongly reticulated, generates a labile



a ***b***

Fig. 2. The aspect of the longitudinal surface [1, 2]:
a – for 2010 raw mohair fibres; ***b*** – for 2010 washed mohair fibres

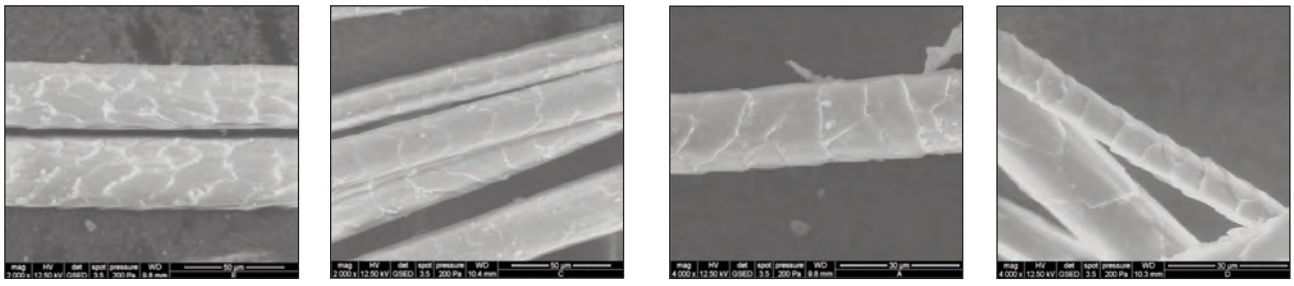
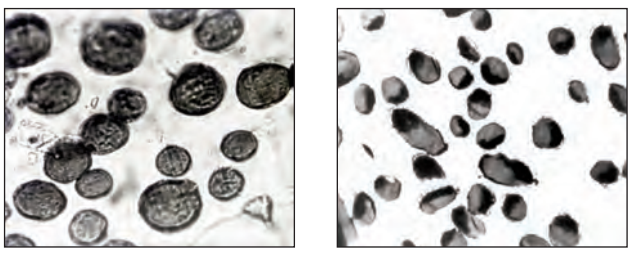


Fig. 3. The aspect of the longitudinal surface for the 2012 raw mohair fibres

One can observe that the longitudinal surface aspect of the mohair fibres is more uniform as compared with wool fibres. There are not significant differences between analyzed fibres (2010 as compared with 2003).

Figures 3 present different aspects of the fibres longitudinal surface for raw mohair fibres – 2012 (SEM QUANTA 200, GSED). One can observe the impurities, sebum and fat adherent of the raw fibres.

It highlights specific aspect of cuticular cells: scales oblong, flattened, that covers a large area fiber body, causing the drift between fibers.



a ***b***

Fig. 4. The aspect of the cross-section [1, 2, 4]:
a – for mohair fibres; ***b*** – for wool fibres

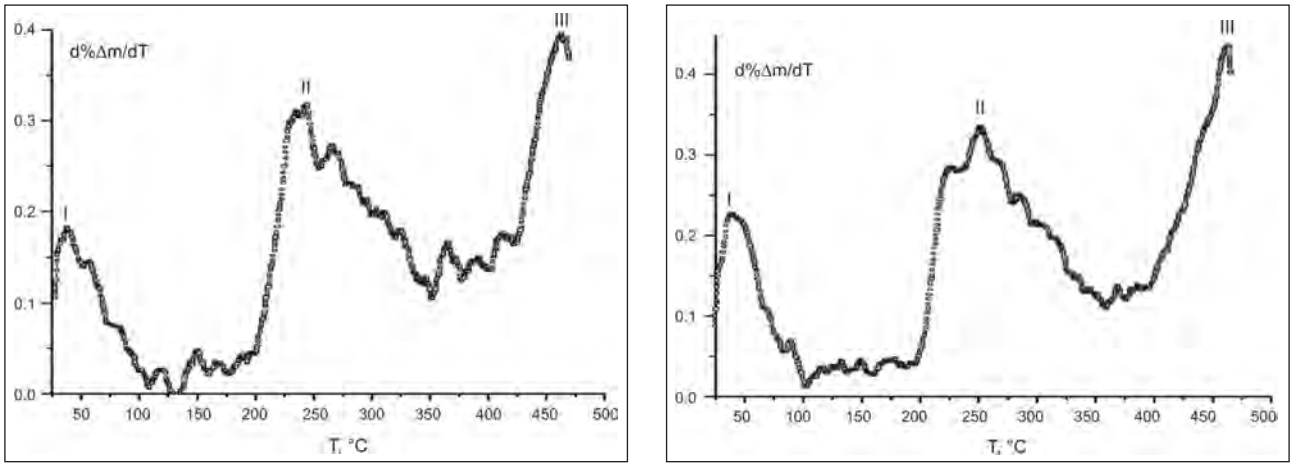


Fig. 5. DTG curves [3, 5, 6]:
a – for wool fibres; ***b*** – for mohair fibres

character and an increased reactivity of fibres towards the chemical agents.

The thick mohair fibers with a diameter exceeding 38–40 μm are characterized by the presence of the medullar channel, situated at the center of the cross-section;

The presence of the medullar channel roots back in the insufficient keratinization of the fiber and represents, at the same time, a result of the lower inclusion of sulphur-containing amino-acids (cysteine).

THERMOGRAVIMETRICAL ANALYSES

Thermogravimetrical analyses for 2003 mohair fibres

Work method

DTG results of the mohair and wool fibres samples (2003), were recorded by MOM 1500 D Budapest (fig. 5). The initial temperature was T_o = 26ºC.

The analyses of figure 5 and the data presented in the table 1 emphasize the following aspects:

- The rising of the temperature up to 125ºC determines a process of eliminating water by evaporation, corresponding to a mass loss of 10.7% for mohair fibres by about 23% higher than the adequate value of the wool fibres, which is 8.7%. During this interval, the average temperature of heat absorption adequate to the maximum speed of eliminating humidity (first peak endothermic) has values between 50–80ºC. The higher value of mohair fibres mass loss due to humidity elimination can be in relation with the higher water content of these fibres and with the structural differences specific to the process of ortho-keratinisation, emphasized by analyses of electronic microscopy and X-rays diffraction;
- After the humidity elimination, the thermal degradation of the fibres occurs in two stages: decomposition and thermo-oxidation;
- The more the temperature rises, the more the percentage mass decreases, both for mohair and for wool and the fibres decomposition occurs. It is emphasized that when temperature is about 200–228ºC, when the value of mass loss is 13.2–15%, a super-contraction of fibres associated with a shortening of the molecular chain occurs.

Table 1

THE VARIATION OF PERCENTAGE MASS LOSS, DEPENDING ON TEMPERATURE, FOR 2003 MOHAIR FIBRES AND WOOL FIBRES [3, 5, 6]

Temperature, °C	**Mass loss, % Δm**		**Ratio, % Δm mohair/wool, %**
	Mohair	***Wool***	
125	10.7	8,7	123
292.5	13.2	10.5	125.7
363.5	48.8	42	116.1
466	72.2	66.5	109

The second endothermic peak appears at the temperature of 260–275ºC and occurs at the level of heterotype para-cortical cells, with a higher cysteine content:

- Starting with this temperature, the fibres samples decompose quickly. During the decomposition process, the mohair loses 9–25% mass more than wool does, with close values of temperature. Thus, at temperature of 360ºC the mass loss has the value of 48.8% for mohair and 42% for wool;
- The second stage of the fibre degradation starts with a temperature of 400ºC, when the fibres thermo-oxidation occurs and the value of mass loss of 72.2% for mohair and of 66.5% for wool;
- At 500ºC the thermal decomposition is complete.

Thermogravimetrical analyses for 2010 mohair fibres

Work method

Equipment used for 2010 mohair fibres was STA 6000 – PerkinElmer. Mass samples was about 5 mg. Temperature range was between 25–70ºC.

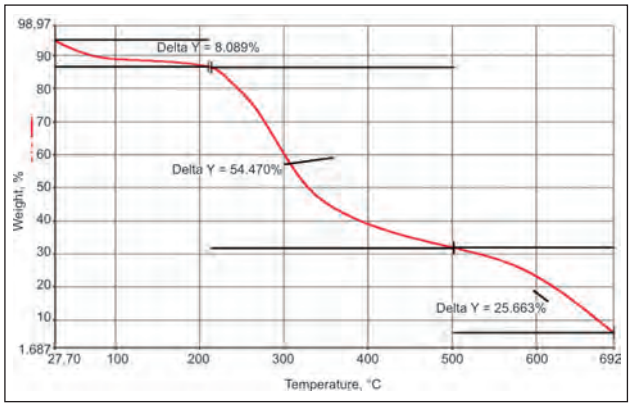


Fig. 6. STA thermogram for 2010 mohair fibres [3]

It can be observed that the biggest mass loss (thermo degradation of the fibres) occurs for 225–500ºC. The analyses of figure 6 and the data presented in the table 2 emphasizes that there are no differences between the temperature behavior of the 2003 and 2010 mohair fibres. The wool and mohair fibers different behavior under the temperature action is caused by the ortho-keratinization process specific to mohair that generates a more labile or instable structure, which is bulkier and richer in the water content.

Thermogravimetrical analyses for 2012 mohair fibres

Equipment used for 2012 mohair fibres was STA 6000 – PerkinElmer. Mass samples was about 5 mg. Temperature range was between 30–800ºC (fig. 7 and table 3).

From thermal analysis for 2012 mohair fibres following aspects were highlighted:

- The rising of the temperature up to 100ºC determines a process of eliminating water by evaporation, corresponding to a mass loss of 5.934%;
- After the humidity elimination, the thermal degradation of the fibres occurs in two stages – decomposition and thermo-oxidation. With increasing temperature the percentage weight decreases for mohair fibers because occurs fibres decomposition. It is emphasized that when temperature is about 250ºC, mass loss is 39.765%, a supercontraction of fibres associated with a shortening of the molecular chain occurs. The second endothermic process appears about 380ºC and occurs at the level of heterotype para-cortical cells, with higher cysteine content. During the decomposition process, the mohair fiber loses 24.10% mass;
- At 500ºC the thermal decomposition is complete.

Table 2

THE VARIATION OF PERCENTAGE MASS LOSS, DEPENDING ON TEMPERATURE FOR 2010 MOHAIR FIBRES [3]	
Temperature, °C	**Mass loss,** % Δm
27 – 225	8,089
225 – 500	54,47
500 – 692	25,67
> 700	11,78

Table 3

THE VARIATION OF PERCENTAGE MASS LOSS, DEPENDING ON TEMPERATURE FOR 2012 MOHAIR FIBRES [3]	
Temperature, °C	**Mass loss,** % Δm
32 – 100	5.934
100 – 340	39.765
340 – 500	16.361
500 – 800	22.403
> 800	15.537

CONCLUSIONS

On the global level, the use of “rare” animal fibers, also known under the name of “noble, precious, special fibers” has increased considerably in the recent years.

Taking into account the global trends in the field, the acclimatization of a nucleus of Angora goats in Romania, the setting up of a new autochthonous base of valuable raw material and the evaluation of the possibilities of efficient processing of these fibers, represent an alternative for the Romanian zootechnical

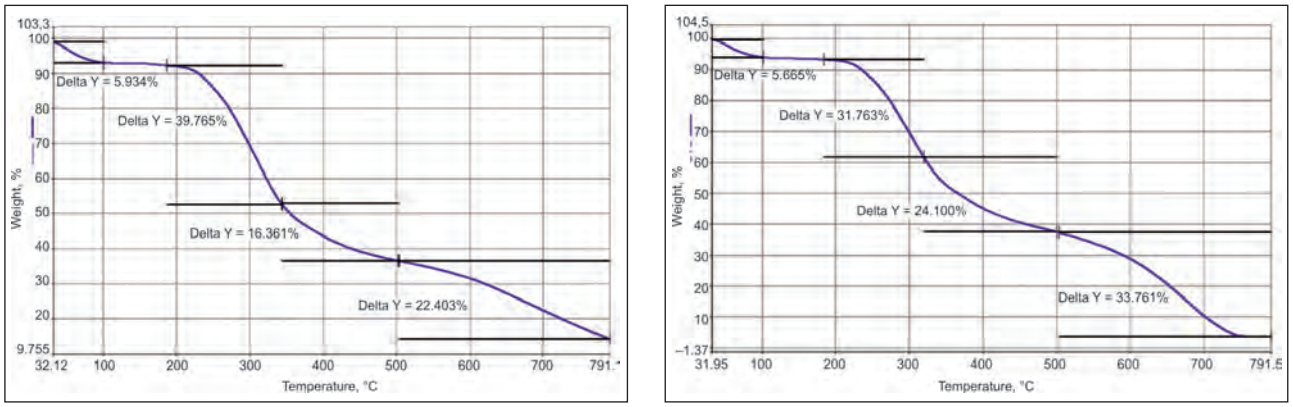


Fig. 7. STA thermogram for 2012 mohair fibers

sector and a challenge for the scientific research and textile industry of our country.
The issues presented demonstrate the importance given to mohair fiber production and processing in Romania and motivate the continuation and extension of the researches on highlighting opportunities for the efficient capitalization of this valuable raw material.
Research will continue for developing the range of products containing mohair fibers.
Mohair can become a valuable source of raw material for the textile industry in Romania.

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DOCUMENTARE

Noi tehnologii

TEHNOLOGIE CU ENZIME ŞI LASER PENTRU VOPSIREA ŞI REALIZAREA TIPARELOR

Un proiect de cercetare dezvoltat de către ***Universitatea Loughborough*** şi ***Universitatea Monfort***, din Marea Britanie, studiază posibilitățile de utilizare a unor noi tehnologii pe bază de enzime şi laser şi de combinații ale acestora în vopsirea şi conceperea modelelor textile.
Cu toate că laserul şi enzimele au fost folosite şi anterior în industria textilă, aplicațiile şi potențialul de utilizare a acestora ca instrument de proiectare creativ sunt încă insuficient explorate, ceea ce face ca ele să constituie subiectul actualului proiect de cercetare.
În proiect, este studiată tehnologia pe bază de enzime, precum şi efectele sale în realizarea culorii şi proiectarea modelelor 3D. Tehnicile utilizate şi efectele obținute pot fi îmbunătățite prin utilizarea laserului, atât în procesul de pretratare enzimatică, cât şi în cel de tratare enzimatică ulterioară.
Cercetarea poate avea rezultate remarcabile în creşterea sustenabilității sectorului de textile şi îmbrăcăminte. De obicei, în vopsirea tradițională şi în tehnicile de albire, imprimare şi finisare sunt utilizate substanțe chimice. Aceste procese necesită mari cantități de apă şi un consum ridicat de energie. Din ele rezultă o cantitate mare de efluenți. Utilizarea tehnologiei bazate pe enzime şi laser oferă perspectiva unor reduceri substanțiale ale cantităților utilizate de substanțe chimice, apă şi energie, precum şi a efluenților produşi.
O finanțare de peste 200 000 de lire sterline a fost primită pentru acest proiect din partea Consiliului de Arte şi Ştiințe Umaniste. De asemenea, Speedo, Camira Fabrics şi Teresa Green Design sprijină proiectul prin furnizarea țesăturilor, prototiparea şi evaluarea conceptelor. Cercetarea este programată pentru finalizare în 2015.

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Comparison of the evenness, faults and hairiness of compact and conventional spun ring yarns

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REZUMAT – ABSTRACT

Studiu comparativ privind uniformitatea, defectele şi pilozitatea firelor filate cu inele, compacte şi clasice

Lucrarea prezintă o analiză comparativă a uniformității optice, a defectelor optice ale firelor – subțieri, îngroşări şi nopeuri, şi a pilozității firelor filate cu inele, prin tehnologii compacte şi clasice. În acest studiu, s-au folosit, ca materii prime, bumbacul cardat, bumbacul pieptănat, fibrele modale, poliesterul şi semitorturile din tencel şi viscoză. Firele filate cu inele, prin metode compacte şi clasice, au fost produse cu trei valori diferite ale gradului de finețe şi cu trei niveluri de torsiune. Pentru a compara proprietățile fizice ale firelor cardate compacte cu cele ale firelor pieptănate clasice, în procesul de filare s-a folosit, ca materie primă, bumbacul. Rezultatele au aratat că firele compacte au o uniformitate optică mai mică, mai puține defecte optice şi o pilozitate mai redusă decât firele clasice, filate cu inele. În plus, firele cardate compacte prezintă o uniformitate mult mai mare, mai multe subțieri şi îngroşări, un număr mai mare de nopeuri şi o pilozitate mai mică decât firele pieptănate clasice.

Cuvinte-cheie: filare mecanică compactă, filare clasică cu inele, bumbac, modal, tencel, poliester, viscoză, aparat de testare CTT

Comparison of the evenness, faults and hairiness of compact and conventional spun ring yarns

This paper is a comparative study of the optical evenness, optical yarn faults (thin place, thick place and neps) and hairiness properties of compact and conventional spun yarns. Carded cotton, combed cotton, modal, polyester, tencel and viscose rovings were used as raw material in the study. Compact and conventional spun ring yarns were produced at three yarn counts having three twist levels. In order to compare the physical properties of compact spun carded and conventional spun combed cotton yarns one type of cotton raw material was used in the spinning. Results showed that compact yarns have less optical evenness, optical faults and hairiness than conventional spun ring yarns. In addition to this, compact spun carded yarns have significantly higher evenness, thin places, thick places, neps values and less hairiness than conventional spun combed yarns.

Key-words: mechanical compact spinning, conventional ring spinning, cotton, modal, tencel, polyester, viscose, CTT test machine

Compact spinning is a modified ring spinning system that converts the yarn structure, which is considered as perfect for the near future, almost ideal. The ideal structure was accomplished by the elimination of the spinning triangle. Spinning triangle is the most critical part of the ring spinning system due to the critical weak spot of the ring spinning process. In this zone, the fibre assembly contains no twist. The edge fibres play out from this zone, and make little or no contribution to the yarn tenacity. Furthermore, the edge fibres lead to the familiar problem of yarn hairiness [1].

In compact spinning, “spinning triangle” is eliminated and almost all fibres are incorporated into the yarn structure under the same tension. This results in increased tenacity, as more fibres contribute to the yarn tenacity. This leads to significant advantages such as increasing yarn tenacity, yarn abrasion resistance and reducing yarn hairiness [2–4].

There are different compact spinning systems on the market from different manufacturers. The main difference is the condensing system. Mostly pneumatic compacting system is used via the perforated drums or lattice aprons over the openings of the suction slots. Following the air flow, the fibres move sideways and they are consequently condensed. Today, this method is widely used in compact yarn production. However the adaptation of this system to conventional ring spinning machine is very complex and expensive. In addition to this, the energy consumption is very high in spinning process. Mechanical compact spinning is an important alternative for compact yarn production. The system is cheaper and less complicated than pneumatic yarn compacting systems. In addition to this, there is not any energy consumption in the spinning process [5].

Mechanical compact spinning system which is used in the production of compact yarns of the study is the design of Rotorcraft Company. In RoCoS compact spinning, the compact yarn is produced by adding positive nip at the end of the drafting unit. The condenser is held against the bottom front drafting roller by means of a magnet. The operation is bringing the fibres closer and eliminating the spinning triangle [6, 7].

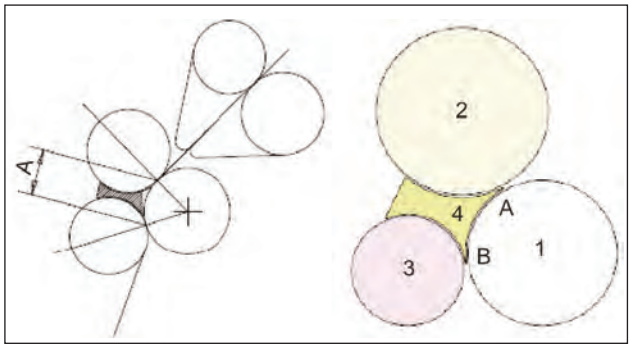

Fig. 1. RoCoS mechanical compact spinning principle: *1* – the front bottom roller; *2* – the front top roller; *3* – delivery roller; *4* – magnetic compactor; *A* – *B* – the condensing zone

The view of the RoCoS mechanical compact spinning principle is given in figure 1.

According to previous researches, mechanical compact spinning significantly improves the yarn tensile properties and reduce its hairiness [8, 9]. Until now there are many studies about the comparison of the conventional ring and compact yarns properties [10–15]. However there are very few studies regarding to the comparison of optical evenness and optical faults of conventional ring and compact spun yarns [16].

EXPERIMENTAL PART

Yarn samples production

In the experimental part of the study 100% carded cotton, 100% combed cotton, 100% modal, 100% polyester, 100% tencel and 100% viscose rovings were collected from several spinning mills. The carded and combed cotton fiber properties measured with HVI test were given in table 1. The other properties of the raw materials used in the study were given in table 2.

The linear densities of the compact and conventional ring yarns were 29.5/1 tex (Ne 20/1), 19.6/1 tex (Ne 30/1) and 14.7/1 tex (Ne 40/1). For each yarn count, twist multipliers were chosen as: α_{tex} 103 (α_e 3.4), α_{tex} 115 (α_e 3.8) and α_{tex} 127 (α_e 4.2). During compact and conventional spinning, the same rovings and the same spindles were used in order to eliminate any possible effect of roving and spindle on yarn quality properties. The experimental plan and the set parameters of compact and spinning systems were given in table 3.

After proper conditioning (65% relative humidity, 20ºC), all yarn samples were tested with CTT (Constan Tension Transport) test machine from Lawson-Hemphill Inc., USA. With this test machine, it is pos-

Table 1

CARDED AND COMBED COTTON FIBER PROPERTIES

Measured fibre properties	Carded cotton	Combed cotton
Fibre fineness, micronaire	4.30	4.35
Fibre strength, gf/tex	37.00	39.02
2.5% span length, mm	28.43	29.57
Uniformity, %	85.40	86.62
Short fibre percentage, %	6.83	5.75
Elongation at break, %	4.40	4.82
Roving linear density, Ne	1.04	1.04
Roving twist, twist/m	45	45

Table 2

MODAL, POLYESTER, TENCEL AND VISCOSE STAPLE FIBER PROPERTIES

Raw material type	Roving linear density	Roving twist, twist/m	Fiber length, mm	Fiber fineness, dtex
Modal	Ne 1.03	28	38	1.3
Polyester	Ne 1.03	25.6	40	1.3
Tencel	Ne 1.03	28	38	1.4
Viscose	Ne 0.99	32	35.4	1.58

Table 3

EXPERIMENTAL PLAN AND YARN SPINNING SET PARAMETERS

Technological/machine parameters	Yarn linear density								
	29.5/1 tex			19.6/1 tex			14.7/1 tex		
Ring yarn type	conventional and compact			conventional and compact			conventional and compact		
Twist coefficient, α_{tex}	103	115	127	103	115	127	103	115	127
Twists, twist/m	602	667	735	735	818	902	838	947	1 044
Spindle speed, rpm	10 000			10 000			10 000		
Ring type	Orbit			Orbit			Orbit		
Ring diameter, mm	42			42			42		
Traveller type, ISO no	80			45			35.5		
Design and finishing treatment	SFB 2 Pm dr Saphir			SFB 2 Pm dr Saphir			SFB 2 Pm dr Saphir		
Cradle spacer thickness, mm	3.75			3.25			2.75		

Table 4

THE *F* AND SIGNIFICANCE VALUES OF ANALYSIS

Compared pairs	Yarn property	Raw material type											
		Carded		*Combed*		*Modal*		*Polyester*		*Tencel*		*Viscose*	
		F	*Sig.*	*F*	*Sig.*	*F*	*Sig.*	*F*	*Sig.*	*F*	*Sig.*	*F*	*Sig.*
Yarn linear density	Evenness	4.66	0.032*	4.81	0.029*	35.89	0.000*	9.79	0.003*	4.23	0.043*	69.33	0.000*
	Thin place (–25%)	25.67	0.000*	16.85	0.000*	12.46	0.001*	17.37	0.000*	22.07	0.000*	15.37	0.000*
	Thick place +25%	6.92	0.010*	87.01	0.000*	13.62	0.001*	11.29	0.002*	19.70	0.000*	3.81	0.052
	Thick place +50%	30.94	0.000*	17.89	0.000*	3.35	0.070	4.53	0.034*	13.82	0.001*	3.06	0.084
	Neps (+200%)	8.77	0.004*	5.63	0.019*	2.43	0.130	4.68	0.031*	0.97	0.405	1.87	0.196
	1 mm hairs	5.30	0.022*	1.66	0.229	19.24	0.000*	12.42	0.001*	4.25	0.040*	73.23	0.000*
	2 mm hairs	1.74	0.216	0.03	0.967	0.17	0.846	1.79	0.208	1.22	0.328	14.44	0.001*
	3 mm hairs	1.56	0.248	1.58	0.246	1.53	0.255	1.14	0.351	0.22	0.805	0.65	0.538
Twist multiplier	Evenness	6.21	0.014*	1.90	0.192	9.60	0.004*	1.15	0.349	7.71	0.008*	2.94	0.091
	Thin place (–25%)	1.36	0.293	1.37	0.289	1.27	0.316	2.49	0.124	2.49	0.124	2.00	0.178
	Thick place +25%	9.11	0.004*	21.90	0.000*	0.32	0.727	0.76	0.486	17.88	0.000*	5.04	0.026*
	Thick place +50%	8.43	0.005*	3.30	0.072	3.17	0.078	0.33	0.720	9.18	0.004*	2.19	0.154
	Neps (+200%)	0.26	0.773	0.51	0.608	0.60	0.560	0.15	0.858	0.07	0.928	1.07	0.374
	1 mm hairs	4.65	0.032*	1.22	0.329	3.41	0.067	0.92	0.423	9.71	0.003*	0.42	0.663
	2 mm hairs	0.51	0.608	0.65	0.537	5.03	0.026*	0.23	0.792	7.18	0.009*	0.07	0.926
	3 mm hairs	0.40	0.674	0.18	0.830	0.08	0.922	0.28	0.756	3.36	0.069	0.52	0.606
Spinning system	Evenness	175.04	0.000*	96.0	0.000*	281.02	0.000*	7.95	0.015*	4.64	0.054	61.50	0.000*
	Thin place (–25%)	7.48	0.018*	7.57	0.018*	3.20	0.099	1.10	0.314	1.73	0.213	0.13	0.723
	Thick place +25%	57.79	0.000*	312.91	0.000*	31.67	0.000*	3.80	0.075	11.70	0.005*	12.79	0.004*
	Thick place +50%	39.79	0.000*	59.41	0.000*	24.30	0.000*	4.52	0.055	14.02	0.003*	7.65	0.017*
	Neps (+200%)	4.70	0.051	1.18	0.298	1.39	0.261	4.68	0.051	2.70	0.126	2.86	0.116
	1 mm hairs	214.08	0.000*	91.87	0.000*	167.62	0.000*	4.97	0.046*	0.00	0.986	40.87	0.000*
	2 mm hairs	194.37	0.000*	114.79	0.000*	93.19	0.000*	16.86	0.001*	4.07	0.066	15.87	0.002*
	3 mm hairs	2.86	0.116	6.62	0.024*	4.97	0.046*	1.14	0.306	2.55	0.136	4.70	0.051

sible to measure yarn profile, evenness, entanglement count, yarn appearance grade and hairiness index [17]. During the yarn tests, first of all the diameter values of the yarns were measured and according to the reference diameter the number of thin place, thick place and neps are calculated. It is possible to express the evenness value of yarns with determining the yarn diameter and the surface structure of yarns. The optical evenness of the yarns is expressed by the coefficient variation of the yarn diameter. With this instrument it is also possible to measure the number of 1, 2 and 3 mm hairs length classes. The experimental plan and yarn spinning set parameters is given in table 3.

The results obtained from the laboratory testing of yarn samples were statistically evaluated with Factorial ANOVA method by using SPSS statistical pocket program with the 0.05 significance level. We compared the quality properties of compact and conventional spun yarns. We observed the main effect of yarn linear density, twist multiple and spinning system on yarn quality.

RESULTS AND DISCUSSIONS

Table 4 represents the statistical results of the main effect of spinning system, yarn linear density and twist multiplier. Based on analysis results the following conclusions can be drawn:

Optical yarn evenness and faults – thin place, thick place and neps

The effect of yarn linear density, twist multiplier and spinning system on optical yarn evenness and faults are given in table 4.

The effect of yarn linear density on both yarn evenness and imperfection is statistically significant for

almost all raw materials observed in the study. As the yarn become coarser, evenness increase on the other hand the number of thin place, thick place and neps decrease. This can be explained by the number of the fibers in yarn cross-section. Due to few fiber amounts in fine yarns, the coefficient variation of the yarn diameter is smaller. On the other hand, slight increase in the number of fiber causes optical yarn faults in fine yarns.

For carded, modal and tencel yarns the effect of twist multiplier is statistically significant, as the twist multiplier increase evenness decrease. Except modal and polyester yarns, the effect of yarn twist on the number of thick places (+25%) is statistically significant. In addition to this, the effect of yarn twist is only significant on carded and tencel yarns thick place (+50%). As the yarn twist multiplier increase, the number of thick places decreases. We could not find any significant effect of twist multiplier on both thin place (–25%) and neps (+200) properties.

Except tencel yarns, all other compact yarns have less evenness than conventional ring yarns. Carded and combed compact yarns have less thin place than conventional ring yarns. On the other hand; for modal, polyester, tencel and viscose yarns there is not any significant difference between the thin place values of compact and conventional spun ring yarns.

Except polyester yarns, all other compact yarns spun observed in this study have lower thick places (+25% and +50%) than conventional spun ring yarns. For all yarns observed in the study, we could not find any significant difference between neps (+200) properties of compact and conventional spun yarns.

Yarn hairiness – the number of 1 mm, 2 mm and 3 mm hair lengths

The effect of yarn linear density, twist multiplier and spinning system on the number of 1 mm, 2 mm and 3 mm hair lengths are given in table 4.

Except combed yarns, the effect of yarn linear density on the number of 1 mm hair length is statistically significant. For only viscose yarns the effect of yarn linear density on the number of 2 mm hair length is statistically significant. As the yarn become coarser, the number of the fibres in the yarn cross-section and thus yarn hairiness increase. For all yarns observed in the study, we could not find any significant effect of yarn linear density on the number of 3 mm hair lengths.

For carded and tencel yarns, the effect of twist multiplier on the number of 1 mm hair length is statistically significant. For modal and tencel yarns, the effect of twist multiplier on the number of 2 mm hair length is statistically significant. As the yarn twist multiplier increase, yarn hairiness decrease.

Except tencel yarns, the number of 1 mm and 2 mm hair lengths of compact yarns is less then conventional spun ring yarns. In addition, for combed and modal yarns the number of 3 mm hair lengths of compact yarns is less then conventional spun ring yarns.

CONCLUSIONS

- For almost all raw materials observed in the study, the optical evenness and optical faults of compact spun yarns are significantly lower than conventional spun yarns.
- Due to elimination of spinning triangle in compact yarn spinning system, the fly decrease and more fibre contribute yarn structure. For this reason compact yarns have less hairiness than conventional ring yarns.
- Compact spun carded yarns have significantly higher evenness, thin places, thick places and neps values than conventional spun combed yarns due to less control of short fibres in compact spinning. On the other hand, due to elimination of spinning triangle compact spun carded yarns have lower hairiness.
- The improvements of mechanical compact spinning on yarn quality properties depend on the raw material used in the spinning. The best results are obtained in the compact spinning of cotton. It appears that the advantages of the compact spinning system are more noticeable when raw material contains short fibers.

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DOCUMENTARE

Materii prime

FIRE FILAMENTARE CU EFECT DE AUTOCURĂȚARE

Institutul de Chimie Textilă şi Fibre Chimice (*ITCF*), în colaborare cu ***Institutul pentru Tehnologie şi Inginerie a Textilelor*** (*ITV*) – ambele cu sediul în Denkendorf – Germania, şi cu compania ***TWD Fibres GmbH,*** au dezvoltat un fir filamentar superhidrofob, cu efect de autocurățare permanentă.
Inovația a avut ca sursă de inspirație frunza de lotus, care are o suprafață aspră şi impermeabilă, de pe care ploaia curăță murdăria şi microorganismele şi le îndepărtează prin rostogolire. Până în prezent, acest efect a fost obținut doar temporar, prin procese de rafinare externă, de exemplu prin aplicarea unor tratamente chimice ulterioare.
Noile fire TWD posedă un efect permanent de autocurățare, care este conferit printr-un proces special de filare. Se preconizează ca firele filamentare din poliester să fie disponibile în culoarea alb natur, vopsite în bobine sau în masă, în diverse game de finețe a firului, pentru a acoperi un spectru larg al cerințelor pieței de textile tehnice.
În ceea ce priveşte structura țesăturii, noul material TWD posedă caracteristici semnificativ mai bune, decât variantele disponibile până în prezent, evidențiate prin testul de abraziune Martindale, teste de curățare în condiții artificiale nefavorabile, conform DIN EN ISO 105-B04 şi DIN EN ISO 6330, metoda 7a, teste de spălare.

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Knitted fabrics with variable geometry and controllable functionality with fixing purpose for dressings or compression bandages

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REZUMAT – ABSTRACT

Structuri tricotate cu geometrie variabilă şi funcţionalitate controlabilă pentru bandaje de fixare şi compresie

Cercetările descrise în cadrul acestei lucrări se referă la proiectarea şi realizarea de tricoturi pentru bandaje de fixare şi compresie sau pentru pansamente. Tricoturile proiectate şi analizate au fost realizate din fire Nm 50/1 – obținute dintr-un amestec de 50% PES/50% bumbac, şi din fire cu finețea de 78 den, din 24 de filamente, cu torsiune Z – din poliamidă PA 6 texturată, cu elasticitate ridicată. Din aceste fire s-au obținut 4 tipuri de structuri, fiecare structură având câte trei valori ale desimii, pentru a putea regla elasticitatea. Firele de poliamidă PA6 au fost utilizate pentru a controla nivelul de presiune a tricoturilor asupra diferitelor zone ale corpului, în funcție de destinația acestora. Procesul de proiectare a tricoturilor a fost optimizat cu ajutorul modelării matematice. De asemenea, a fost analizat comportamentul acestor tricouri în diferite zone ale corpului, folosind simularea 3D.

Cuvinte-cheie: tricoturi, simulare 3D, structură, modelare matematică

Knitted fabrics with variable geometry and controllable functionality with fixing purpose for dressings or compression bandages

The researches described in this paper refer to the design and implementation of knitted fabrics for the fixing bandages dressings or compression. The knitted fabrics designed and analyzed were obtained using yarns 50% PES/50% cotton count Nm 50/1 and textured yarns with high elasticity of polyamide PA 6 with length density 78/24/Z den. With these yarns obtained 4 types of structures, each structure having densities by 3 steps to adjust the elasticity. The yarn of polyamide PA6 was used because it is possible to control pressure level on different areas of the body, depending on the product's destination. The design of knitted fabrics was optimized using the mathematical modeling. Also, their behavior on different areas of the body was analyzed, using the 3D simulations.

Key-words: knitted fabrics, 3D simulations, structure, mathematical modeling

The nature of raw materials used in the knitted fabrics was chosen as to obtain knitted fabrics with controllable heat degree, knowing that body temperature varies on different areas of the body. The cotton, polyamide or polyester yarns have different coefficients of thermal conductivity. Elastomer yarns, alone, could not offer the necessary properties required from knitted fabrics, reason why they were knitted with 50% cotton blend/50% PES yarns (table 1). This ensemble of yarns, ensure knitting products the corresponding properties obtained regarding of appearance, touch and their functionality. The knitted fabrics were obtained using linear knitting machine Stoll, electronically controlled. The experimental variants are analyzed from point of view of biaxial extensibility and compression capacity. The mathematical models established allowed using for optimization of some certain properties of the knitted fabric optimization regarding without making actual experimentations [1].

The pressure level of these knitted fabrics on different areas of the human body was evaluated using 3D simulation of the different body parts and of the pressure applied by the fabrics, using color codes for the values of compression [2]. The medical knitted fabrics producing with different structures and forms, with suitable destination (fixing bandages officials or compression bandages, medical belts, complex configurations adapted to body morphology, medicinal socks etc.) can be classification like in figure 1.

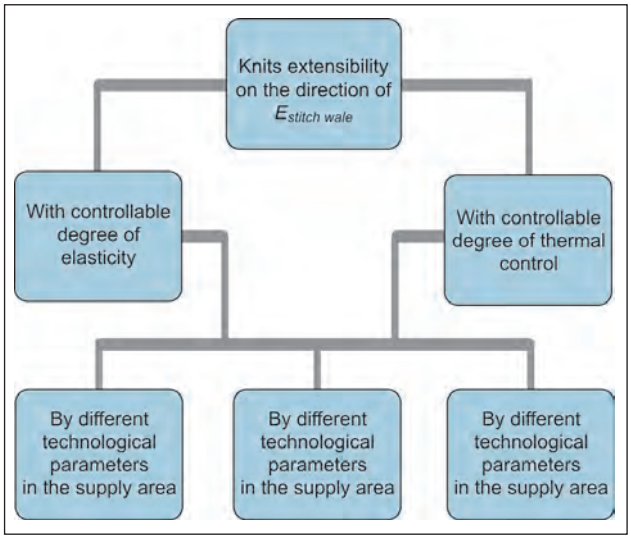


Fig. 1. The classification of compression knitted fabrics

Table 1

THE KNITTED STRUCTURES		
Knitted sample	**Knitted structures**	**The characteristics of knitted**
V_1	Jersey with fleece yarns	Jersey – 1 yarn 50% cotton/ 50% PES Fleece yarn – 1 polyamide 6 yarn
V_2	Plated jersey 2:1	2 cotton/polyester yarns; 1 polyamide 6 yarn
V_3	Jersey	2 cotton/polyester yarns
V_4	Plated jersey 1:1	1 cotton/polyester yarn; 1 polyamide 6 yarn

The compression knitted fabrics can be produced on one hand by using yarns with certain properties and on the other hand, by using a variety of weft or warp knitted structures, without or with patterns (especially tuck or transferred patterns) with or without additional yarns (including weft yarn) with specific properties, and with the introduction of elastic yarns in table1.

EXPERIMETAL PART

The determination of parameters knitted structure

For variants of knitted analyzed were determined the following structure parameters: D_o horizontal density [*s*/50 mm], D_v vertical density [*r*/50 mm], thickness [mm] and the mass unit area *M* [g/m^2]. Average values of determinations are presented in table 2.
The determination of knitted fabrics extensibility was made to appreciate the compression degree on different parts of body. The extensibility degree of the knitted fabrics was determined with Extensometer device for textile FRYMA (BS 4292/1968). The average values of extensibility stitch wale and extensibility row were presented in histogram from figure 2.
From the study of histogram from figure 2 established that the knitted fabrics extensibility on both directions varies in very expand limits of 35% to 101% (V_4B). These variations are owed from row material nature as long as the knitted fabrics structure parameters. Therefore the V_4B variant accomplishes large extensibility properties in both directions.

RESULTS AND DISCUSSIONS

The mathematical modeling of extensibility in function of knitted fabrics of the structure parameters

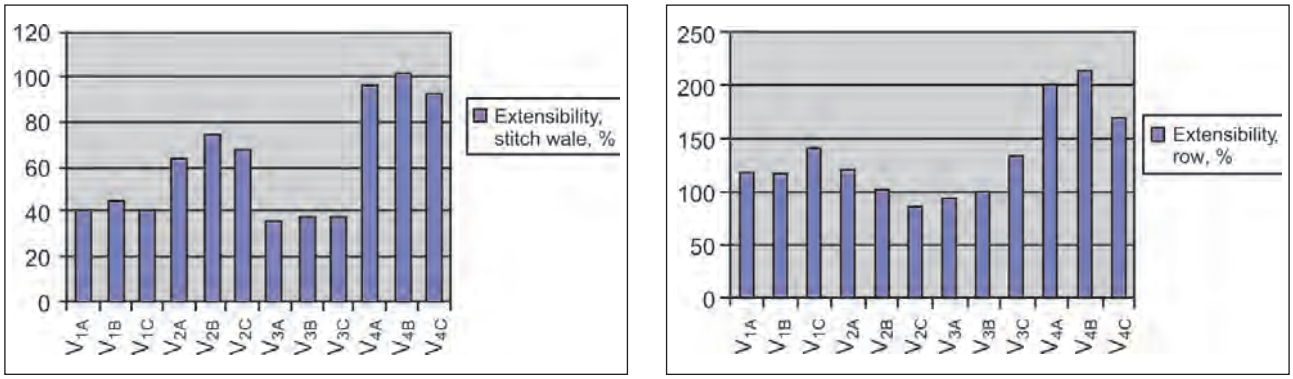
The mathematical modeling of knitted fabrics extensibility, function of the structure parameters was realized by processing experimental data obtained and presented before. By using the MATLAB software library has considered as input of the experimental data the average densities D_{om} horizontal, the vertically densities D_{vm}, the extensibility for horizontal E_{row} and vertical $E_{stitch\ wale}$ directions and the mass per unit surface *M* [g/m^2] and thickness [mm].

The mathematical modeling of knits extensibility on the direction of row E_{row}, in function of average horizontal density D_{om} and thickness:
$E_{row} = f(D_{om}, thickness)$

Using interpolation [3] obtained the 2 degree polynomial in two variables – equation (1) – where *x* and *y*

Table 2

THE CHARACTERISTICS OF KNITTED FABRICS						
Variants	**D_o,** s/50 mm	**D_v,** r/50mm	**Extensibility,** *stitch wale*, **%**	**Extensibility,** *row*, **%**	**Thickness,** mm	**Mass unit of surface,** *M*, g/m^2
V_1						
V_{1A}	54	56	40	120	1.53	243.7
V_{1B}	52	46	45	118	1.42	231.2
V_{1C}	53	48	40	140	1.55	225
V_2						
V_{2A}	39	63	63	122	1.33	243.7
V_{2B}	40	70	75	102	1.36	275
V_{2C}	43	75	67	85	1.37	287.5
V_3						
V_{3A}	40	57	35	94	1.12	131.2
V_{3B}	42	50	38	100	1.24	162.5
V_{3C}	43	44	37	135	1.28	143.7
V_4						
V_{4A}	44	62	96	201	1.24	125
V_{4B}	45	72	101	214	1.27	143.7
V_{4C}	46	76	92	170	1.47	162.5



a *b*

Fig. 2. The histograms of stitch wale and row extensibility

Table 3

THE CALCULATED AND MEASURED VALUES, E_{row}		
Variants knitted fabrics	**E_{row} calculated**	**E_{row} measured**
V_{1A}	119.41	120
V_{1B}	151.25	118
V_{1C}	118.37	140
V_{2A}	87.78	122
V_{2B}	103.35	102
V_{2C}	141.90	85
V_{3A}	113.01	94
V_{3B}	135.77	100

* E_{row} is knits extensibility on the row direction

are experimentally determined values for the D_{om} and the thickness. The result is the function of extensibility on horizontal direction, E_{row}.

$$E_{row} = f(x, y) = -2447 + 119.8 \cdot x - 314.1 \cdot y - \\ - 0.9847 \cdot x^2 - 18.04 \cdot x \cdot y + 401.4 \cdot y^2 \quad (1)$$

Using interpolation [6] there were obtained the 2 degree polynomial in two variables – equation (1) – where x and y are experimentally determined values for the D_{om} and the thickness. The result is the function of extensibility on horizontal direction, E_{row}. There is a huge degree of mathematical model approximation from equation (1) resulted from comparing the calculated values of model and those measured experimentally in table 3.

The representation of the model is given in figure 3. On 3D surface, the color blue shows the minimal extensibility area, and the color red marks the high extensibility.

The marked points on the 3D surface are the E_{row} values. The mathematical model and graphical representation enabled intuitive appreciation of the values parameters of structure D_{om} and thickness, with

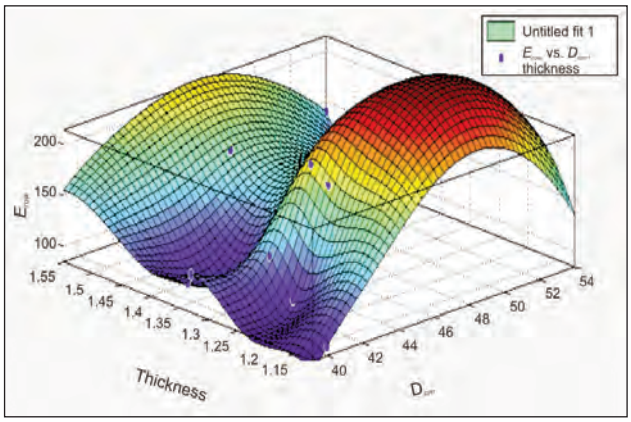


Fig. 3. $E_{row} = f(D_{om}$, thickness)

which it can design a knitted fabric with E_{row} desired elasticity.

The mathematical modeling of knits extensibility on the direction of $E_{stitch\ wale}$ and average density on vertical direction D_{vm} and thickness: $E_{stitch\ wale} = f(D_{vm}$, thickness)

Regarding the analysis of the dependence between elasticity onto the $E_{stitch\ wale}$ and average density on vertical direction D_{vm} and thickness: $E_{stitch\ wale} = f(D_{vm}$, thickness) it possible appreciate the same nonlinear dependence, reason for that with the experimental data presented in table 2 was obtained the mathematical model from equation (2) in which x is the thickness and y is vertical density D_{vm}.

$$E_{stitch\ wale} = f(x, y) = 60.86 - 3.929 \cdot \\ \cdot \sin(2.428 \cdot 3.14 \cdot x \cdot y) + 0.521 \cdot \exp(-(0.6559 \cdot y)^2) \quad (2)$$

Table 4, containing the calculated and measured values of $E_{stitch\ wale}$ elasticity, shows a lower approximation of the mathematical model to this phenomenon. The observation is supported by the comparison between measured and calculated values like the 3D graphic of the mathematical model in figure 4.

The points marked on the chart for elasticity are placed at the bottom. To obtain an increase of knitted

Table 4

THE APPROXIMATED AND MEASURED VALUES FOR $E_{stich\ wale}$		
Knitted fabrics variants	**$E_{stich\ wale}$ approximated**	**$E_{stich\ wale}$ measured**
V_{1A}	61.770	40
V_{1B}	56.936	45
V_{1C}	56.982	40
V_{2A}	64.605	63
V_{2B}	61.210	75
V_{2C}	60.669	67
V_{3A}	57.200	35
V_{3B}	56.962	38
V_{3C}	57.514	37
V_{4A}	57.025	96
V_{4B}	62.029	101
V_{4C}	62.290	92

* $E_{stitch\ wale}$ is knits extensibility on the wale direction

fabrics elasticity on the row direction E_{row} it is recommended that the thickness values be small and vertical density values D_{vm} be high.

Simulation in virtual environment the behavior of knitted fabrics

Knitted fabrics variants made and investigated experimentally are destined for bandages with fixing or compression function with the role of dressings in body areas such as knees, arm, neck, and waist. For these areas of human body were performed, using Lectra software, simulations of the behavior [4] of four different knitted structures in table 2. The virtual

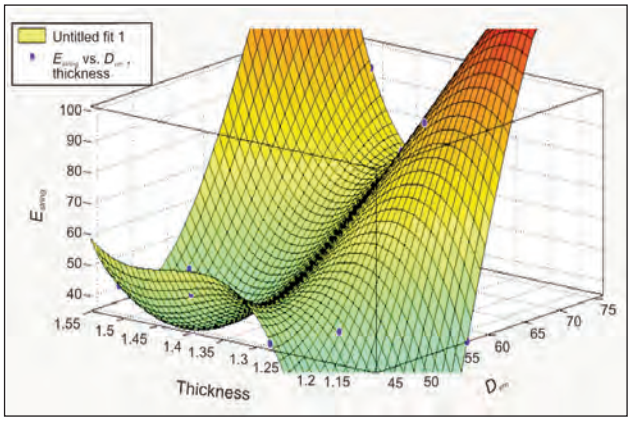


Fig. 4. $E_{stitch\ wale} = f(D_{vm}$, thikness)

visualization of tensions values that occur in areas of application on virtual models, depending on the elasticity of knit and parameters of the structure is evidenced by the color variation which corresponds to a numeric value.

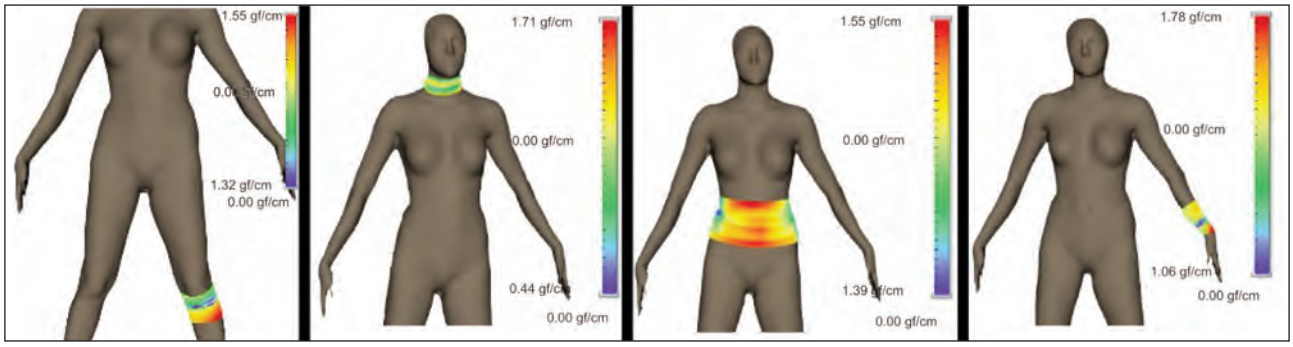
For knitted variant V_4B (plated jersey 1:1, 1 yarn cotton/polyester; 1 yarn polyamide 6) was obtained the widest range of variation (1.57 to 1.0 gf/cm) for the degree of compression on the knee. From table 5 it sees that this value corresponds to the area in red. Minimum values for compression are located in the colored blue. The simulations [5] of the knitted fabric compression are presented in figure 5 for knee area, neck area, waist area and for arm area.

CONCLUSIONS

According to the values on table 2 and graphical representation of figure 2, extensibility in the row direction [%] is greater than on the vertical direction [%] for all analyzed knitted fabric knitted variant V_4 (plated

Table 5

THE RANGE OF KNITTED FABRICS COMPRESSION [gf/cm] FOR THE KNEE, NECK, WAIST AND ARM				
Knitted fabrics variants	**The range knitted fabrics compression in the knee area,** gf/cm	**The range knitted fabrics compression in the neck area,** gf/cm	**The range knitted fabrics compression in the waist area,** gf/cm	**The range knitted fabrics compression in the arm area,** gf/cm
V_{1A}	1.35 - 1.57	0.44 - 1.71	1.39 - 1.55	1.06 - 1.78
V_{1B}	1.32 - 1.58	0.61 - 1.73	1.37 - 1.55	1.30 - 1.74
V_{1C}	1.33 - 1.57	0.64 - 1.73	1.40 - 1.55	1.21 - 1.74
V_{2A}	1.06 - 1.57	0.40 - 1.70	1.36 - 1.55	1.05 - 1.73
V_{2B}	1.32 - 1.58	1.05 - 1.77	1.33 - 1.55	0.84 - 1.73
V_{2C}	1.29 - 1.57	0.45 - 1.72	1.32 - 1.55	0.78 - 1.70
V_{3A}	1.29 - 1.57	0.64 - 1.70	1.40 - 1.55	1.04 - 1.69
V_{3B}	0.81 - 1.57	0.4 - 1.73	1.40 - 1.55	1.22 - 1.69
V_{3C}	1.35 - 1.57	0.65 - 1.73	1.41 - 1.55	1.04 - 1.72
V_{4A}	1.03 - 1.56	0.32 - 1.54	1.38 - 1.56	1.06 - 1.73
V_{4B}	1.00 - 1.57	0.26 - 1.73	1.37 - 1.55	0.91 - 1.78
V_{4C}	1.24 - 1.58	1.00 - 1.77	1.38 - 1.55	0.99 - 1.69



a ***b*** ***c*** ***d***

Fig. 5. ***a*** – knitted fabrics compression in the knee area; ***b*** – knitted fabrics compression in the neck area; ***c*** – knitted fabrics compression in the waist area; ***d*** – knitted fabrics compression in the arm area

jersey 1:1; 1 yarn cotton/polyester; 1 yarn polyamide 6) for all 3 levels of density *A, B, C,* has the highest values of extensibility for both directions variants. This finding is explained by the fact that densities on vertical direction of analyzed knitted fabrics are higher than horizontally density. In same time knitted fabric variant V_4 have and the smallest mass per unit surface M [g/m^2]. Also V_4B variant has the highest elasticity on row direction while V_2C variant has the lowest value for the same feature. The most important parameter is the elasticity whose values are reflected in the values of other parameters of the structure. For example knitted V_3 variant has the lowest values for thickness, due to homogeneous structure and the raw material and therefore extensibility is the lowest of all options.

The mathematical models obtained can be used for optimization of some knitted fabric properties. In this way the knitted structure can be created without actual experimentations.

If the knitted fabrics analyzed are used for bandages on the knee area, the optimal examination value is 1.73 gf/cm, that belong to V_4B knit variant.

If the analyzed fabrics are used for bandages on the waist area, after virtual simulation of their behavior [6], the interest interval is 1.37 – 1.55 gf/cm. The best waist compression is obtained by using V_4B knit variant.

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Comfort properties of multilayer textile materials for clothing

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REZUMAT – ABSTRACT

Caracteristici de confort ale materialelor textile multistratificate destinate confecțiilor

Studiile de cercetare recente arată faptul că cea mai importantă caracteristică a îmbrăcămintei solicitată de consumatori o reprezintă confortul. În lucrare este prezentat un studiu al cărui obiectiv îl reprezintă evidențierea posibilităților de determinare a parametrilor de confort ai materialelor textile multistratificate destinate confecțiilor, prin metode de laborator. Cercetarea se bazează pe rezultalele testelor efectuate în laboratoarele I.N.C.D.T.P., dotate cu echipamente moderne, de ultimă generație. Parametrii de confort al materialelor textile multistratificate, determinați în laborator, sunt: compoziția fibroasă, masa pe unitatea de suprafață, grosimea materialului, rezistența termică, porozitatea, structura multistrat, conductivitatea termică, permeabilitatea la aer şi rezistența la vaporii de apă. Determinarea comportamentului diferitelor materiale textile în ce priveşte confortul termofiziologic reprezintă un element important în selectarea materialelor multistratificate, folosite pentru diferite aplicații, dar şi un ghid de referință pentru dezvoltarea de inovații în sectorul de confecții.

Cuvinte-cheie: textile, proprietăți de confort, materiale multistratificate

Comfort properties of multi-layer textile materials for clothing

Recent researches show that the wear comfort is the most important property of clothing requested by the consumer. This paper presents a study having as objective to highlight the possibilities to determine through laboratory methods the comfort characteristics of multilayer textile assemblies for clothing. The research studies are based on the test results obtained in INCDTP laboratories, endowed with modern equipment. The comfort parameters of multilayer textile materials that were measured in laboratory conditions: fibre composition, mass per unit area, thickness, thermal resistance, porosity, multilayer structure, thermal conductivity, air permeability and vapour resistance. Determining the behaviour of different textile materials, in terms of thermo-physiological comfort, will serve as an important tool in the selection of multilayered materials for various applications, as well as a reference guide for innovations in the clothing sector.

Key-words: textiles, comfort properties, multi-layer fabrics

Consumers require for clothing comfort the following properties of textile-composite materials:

– lightweight;
– optimal thermal and humidity transport capability;
– controlled air-permeable textile layers;
– convenient design for a good freedom of movement;
– no skin irritation (interaction between fabric surface structure and the skin of user, often expressed as feelings of softness, smoothness, prickliness etc.).

In order to evaluate clothing comfort, it has to be considered that this type of research needs the inclusion of several domains, such as physics, physiology, neuro-physiology and comfort-physiology. The prediction of comfort properties can be achieved only by integrating all of the above.

Hence, the complex issue of clothing comfort has two approaches:

– subjective – reflection of all the sensations perceived by the user;
– objective – comfort being interpreted based on physical states and described by adequate physical measurements and principles.

This study gives an overall view of the objective comfort approach.

The objective comfort evaluation is based on a multitude of experimental methods, which can be classified as follows:

– tests in wearing with special dummies;
– laboratory tests made on textile materials.

These experimental methods can deliver information about the modality in which textile materials and especially clothing structures influence the physiologic responses of the human body and subjective responses, depending on the physical state of the subject and the environmental climatic conditions.

This study focuses on the thermo-physiological properties of the clothing materials. They relate to how well the fabric dissipates metabolic heat and evaporated sweat from the skin into the environment [1].

Several researchers have tried to establish a relationship between comfort and clothing [6–8]. Particularly, attention was given to the effect of fiber type, fabric structure, fabric layering and fabric finish, on the water vapor and liquid water transport rates of the fabrics [10].
The aim of this study was to gain better understanding of the interactions between fabric physical properties and the thermo-physiological and sensorial comfort properties. Multilayered structures were preferred since special yarns with hydrophobic and hydrophilic characters can be used to achieve optimum water vapor permeability and water absorbency features [1–11].

EXPERIMENTAL PART

The experiments were carried out in INCDTP laboratories, on textile materials (multilayered) with various fibrous compositions, using modern equipment to determine textile material physical properties which contribute to the physiological comfort.
The following tests were carried out for the multilayer fabrics: fabric mass, fabric thickness, air permeability, water permeability, thermal conductivity and thermal resistance.
The standard test procedure SR EN 12127/2003 was followed for determining the fabric mass and Karl Schroder instrument was used for the measurement of fabric thickness according to SR EN ISO 5084/2001.
The thermoregulatory model of human skin (Skin Model), according to SR EN 31 092 (ISO 11 092):1997 was used to assess processes of heat and moisture management of the textile with the Sweating hotplate 10,5 measurement technology instrument. The thermal conductivity was measured with Heat flow meter thermal conductivity instrument model Quickline – 16, Anter corporation instrument.
The air permeability of the fabrics was measured on a FX 3300 Air Permeability Tester by TEXTEST AG at a test pressure of 100 Pa and on a test area of 20 cm^2, according to EN ISO 9237.
Tests were carried out in a standard conditioning and testing atmosphere according to SR EN ISO 139: 2005, at a temperature of (20 ± 2)°C and a relative humidity of (65,0 ± 4)%. The samples tested are knitted fabrics and woven fabrics made of one, two and three textile material layers with various fibrous compositions.

RESULTS AND DISCUSSIONS

The experiments were carried out on textile materials (monolayer and multilayer for clothing) with various fibrous compositions, the results being shown in table 1.

Air permeability tests

The air exchange between the clothing and the environment has a great influence in ensuring the comfort, the well-being in wearing. By air exchange, the water vapor transport (when slow diffusion processes are losing a part of their importance) and heat transfer can increase.
Through the clothing, three air change modalities are possible, which have different causes and influence factors:
– air exchange due to wind influence;
– air exchange due to body movement;
– air exchange due to density differences.
When clothing is made of textile materials having good air permeability and the body is in motion, air is practically "pumped" through the clothing structure layers. The more air permeable a clothing product is, the more powerful the wind will be felt (air streams) towards the body. If the clothing has reduced or very tight air permeability, the air is "pushed" when the body is moving in various directions, yet being maintained in the same "layer". Therefore, it is important that between clothing layers should be a reciprocal air exchange, which could intensify water vapor transport and heat exchanges. Also, in the case of the air impermeable clothing an air exchange with the environment by certain disclosures can be ensured, these areas allowing the ventilation process from outside [9–11].
Air permeability was affected by fabric density, too. The results were also supported by statistical analysis, which showed that air permeability was influenced by course density and fiber type in top and bottom layers.
The results show that the air permeability of the sample *3* (multilayer fabric: woven fabric 100% PES, thermo-insulating aramide layer, viscose layer) was higher than the sample *7* (multilayer fabric: woven fabric, thermo- insulating textile material, viscose lining FR). The sample *3* is the most comfortable sample for clothing having the biggest value for air permeability, therefore permitting a good transfer of humidity through the fabric structures.
The samples *2, 4, 5, 6, 8, 9* consisting of two or three layers present air resistance, in line with the smallest value for thermal conductivity.

Thermal conductivity tests

Human body takes over the heat from the environment and produces heat at the same time. When the metabolic processes work under minimum conditions, there is a balance between heat produced by the body and heat transferred to the environment. Heat produced by the body is according to physiological reactions, and the heat yielded depends on the physical factors of the environment. Clothing should ensure the heat exchange between body and environment.
Thermal conductivity, λ, is the property of a textile material to conduct heat. Heat transfer across materials of high thermal conductivity occurs at a higher rate than across materials of low thermal conductivity. The average values of thermal conductivity for the tested multilayer fabrics are presented in figure 1.
Thermal conductivity coefficient, λ, indicates the ability of material to allow heat flow. It varies from material to material. It has a strong correlation with the

Table 1

EXPERIMENTAL RESULTS FOR COMFORT TESTS							
Sample no.	**Fabric description**	**Air permeability,** mm/s.	**Thermal conductivity,** W/mK	**Thermal resistance,** $m^2 \cdot K/W$	**Average mass,** g/m^2	**Thickeness,** mm	**Resistance to water vapour,** m^2Pa/W
1	Multilayer fabric consisting of: – woven layer 100% PES; – nonwoven layer 100% PES; – knitlayer 100% PA	20.1	0.04485	0.51616	516	23.15	160.299
2	Laminated fabric consisting of: – woven layer 100% PES; – membrane PTFE	Air-resistant	0.00085	0.66470	325	0.565	16.354
3	Multilayer fabric consisting of: – woven fabric 100% PES; – thermoinsulating aramidic layer; – viscose layer	59.68	0.02395	0.11430	591	2.7375	13.314
4	Three-layer laminate fabric consisting of 3 woven of 100% PES	Air-resistant	0.00085	0.48235	182	0.41	8.892
5	Polyester laminate fabric, two layers of 100% PES, double film (PUR)	Air-resistant	0.00075	0.41333	148	0.31	6.288
6	Fabric laminate with two layers: 100% PES + PTFE membrane	Air-resistant	0.00065	0.38077	145	0.2475	6.187
7	Multilayer fabric consisting of: – woven fabric; – thermoinsulating textile; – viscose lining FR	14.48	0.03995	0.25282	593	10.1	41.197
8	Fabric laminated with PTFE membrane	Air-resistant	0.00065	0.5120	327	0.64	7.392
9	Fabric laminate 100% PES with two layers	Air-resistant	0.00075	0.47692	146	0.31	3.279
10	Fabric laminate with three layers: – 100% PES; – PUR membrane; – PA knit	1.022	0.075	0.75667	210	0.5675	7.396

chemical and physical structure of the material. Metals have the highest thermal conductivity. Polymers have low thermal conductivity as compared to metals. Thermal conductivity of polymers is ranging from 0.2 to 0.4 W/mK in solid form. Nevertheless, there is a significant variation in thermal conductivity if these polymers are used to produce a yarn and then a fabric. Thermal conductivity of steady air by 20ºC is 0,026 W/mK. Thermal conductivity of water is 0.6 W/mK, which is 25 times more than textile materials. That is why the water presence in textile materials is not desirable for the wearers [10].

The three layers fabrics, samples *1, 3, 7* which have a considerable thickness, compared to other samples, offer a good heat exchange of the wearer with the environment. The sample *10* (fabric laminate with three layers) has the higher thermal conductivity of the samples, so the heat of the body is very well transferred in the environment.

Thermal resistance

Thermal resistance results directly from the combination of transfers of radiant, conductive and convective heat and its values depend on the contribution of each of them to the total heat transfer. Although it is an intrinsic property of the textile material, the value resulted from measuring can vary according to testing conditions, due to interactions of parameters, as for example the transfer of radiant heat with the environment. Thermal resistance represents the temperature difference between the two sides of the material, distributed by unit area to the heat flow in gradient direction.

The thermal resistance, R_{ct}, expressed into Kelvin square meters/Watt is a quantity specific to textile materials or composites, which determines the dry heat flow by a given surface when a time stable temperature gradient is applied.

The higher is the thermal resistance, R_{ct}, the lower is the heat transferred. It depends upon the thickness and thermal conductivity of the material (equation 1):

$$R_{ct} = \frac{h}{\lambda} \quad [m^2K/W] \qquad (1)$$

where:

λ is thermal conductivity;

h – thickness of the material;

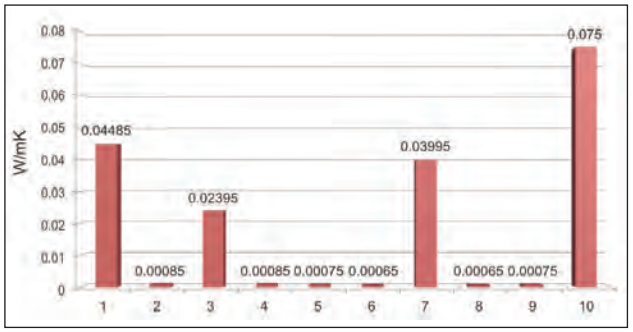

Fig. 1. Thermal conductivity for the multilayer fabrics

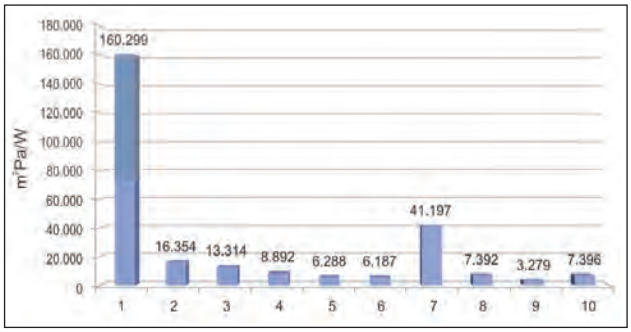

Fig. 3. Resistance to water vapor for the multilayer fabrics

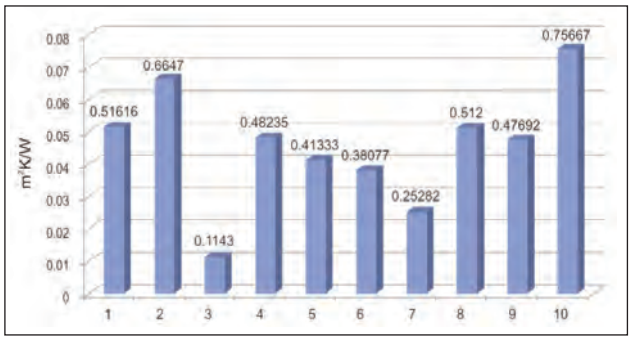

Fig. 2. Thermal resistance for the multilayer fabrics

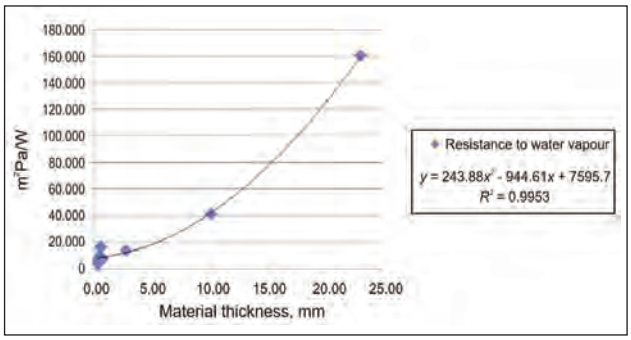

Fig. 4. Correlation between resistance to water vapor and material thickness

The average of the thermal resistance for the tested multilayer fabrics are presented in figure 2.

The highest thermal resistance values were obtained for the fabric sample *10* (laminate fabric, with three layers) and so this one ensures the best thermal isolation for the body.

Resistance to water vapor

The resistance to water vapor, R_{et}, characterizes the breathability of clothing (fig. 3). Breathable garments evacuate the perspiration away from the skin and from the garments. When too much humidity has accumulated in the clothing, condensation occurs and the skin feels clammy. The temperature is also important then in cold atmospheric circumstances one risks to cool down too quickly. Otherwise in warm circumstances, the rhythm of the heart will increase and after some time there is a risk of high stress.

The higher the R_{et} value, the higher the resistance of the fabric, the less vapor passes through in these particular lab conditions (static, temperature 20ºC). It is claimed (Document no. FTTS-FA-005, Specified requirements of water-vapor permeable and liquid-water impermeable textiles, Committee for Conformity Assessment of Accreditation and Certification on Functional and Technical Textiles) that for 6 < water-vapor resistance, R_{et} < 13 the breathability of a clothing is Very Good 13 < water-vapor resistance, R_{et} < 27 the breathability of a clothing is good.

The resistance to water vapor was measured by the Sweating hotplate 10,5 measurement technology instrument according to SR EN 31092 (ISO 11092): 1997.

Except for the values for the samples *1, 2,* and 7, all the other tested samples indicate very good materials for breathability. This comfort parameter shows a nonlinear dependence with the material thickness (fig. 4).

The tested values for R_{et} could be represented by a regression equation in the form of a quadratic polynome (equation 2):

$$R_{et} = ax^2 + bx + c \qquad (2)$$

where:

R_{et} is resistance to water vapor, m²Pa/W;

x – material thickness, mm;

a = 243.88; b = 944.61; c = 7595.7.

In order to see the correspondence of this formula with the originally tested, it was calculated the statistical term R^2. If R-squared is near 1.0 it means a better predictability of another term. In our case, R^2 is 0.9953 so there is a very strong correlation between the resistance to water vapor of the textile material and the material thickness.

CONCLUSIONS

The impact of heat arising from climate change on human health is predicted to be profound. It is important therefore to be prepared with various preventive measures for such impact on society. So, the objective of this paper was to investigate clothing materials that could improve the human thermal comfort.

This paper presents a quantitative study of thermo-physiological comfort properties carried out on different multilayer fabric structures. For this purpose ten samples were tested and the fabrics description was presented in table 1.

A variety of properties that contribute to the cumulative perception of the comfort of these fabrics were measured. Results showed that the fabric sample *3* (multilayer fabric consisting of woven + thermo insulating aramidic material + viscose lining) had greater moisture absorption capacity and the value for air permeability was higher, which is an advantage in the perception of comfort sensations associated with feeling of skin wetness. Inclusion of viscose yarns into the fabric structure improved the moisture absorption, as well. For thermo-physiological comfort, particularly in summer or hot climates multilayer fabrics for clothing should absorb sweat easily and evaporate it rapidly. Samples *1, 3, 7, 10* assure higher heat transfer. Fabric tightness affected water absorption, water wicking, air permeability and heat transfer.

In conclusion, the analysis of measured material properties associated with fabric comfort provided comprehensive and informative data for assessing comfort properties of multilayer fabrics. However, in order to scientifically assess and compare the comfort properties of these fabrics controlled wear trials should be conducted.

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Cellulase enzyme application for the cotton based woven fabrics Part II. The determining of necessity and cellulase enzyme application sequence in the finishing process*

ONUR BALCI UĞUR GENÇER

REZUMAT – ABSTRACT

Aplicarea enzimelor celulozolitice pe țesăturile din bumbac

Partea a II-a. Stabilirea necesității şi succesiunii etapelor de aplicare a enzimelor celulozolitice în procesul de finisare

În cea de-a doua parte a lucrării a fost studiată necesitatea aplicării enzimelor celulozolitice pe țesăturile din bumbac. În acest scop au fost analizate rigiditatea la încovoiere, tuşeul, diferențele de culoare CIELab şi rezistența vopsirilor. În funcție de rezultatele acestor măsurători, s-a stabilit necesitatea şi succesiunea etapelor de tratare cu celulază acidă. S-a constatat că aplicarea tratamentului enzimatic, înainte şi după vopsire, influențează, în special, tuşeul şi valorile CIELab ale celor două mostre de țesătură. În plus, pentru a determina valoarea de semnificație a factorilor, s-au utilizat rezultatele tuturor încercărilor folosind testul ANOVA.

Cuvinte-cheie: ANOVA, rigiditate la încovoiere, biolustruire, enzime celulozolitice, CIELab, rezistență, tuşeu

Cellulase enzyme application for the cotton based woven fabrics

Part II. The determining of necessity and cellulase enzyme application sequence in the finishing process*

In the second part of the study, the necessity of the cellulase enzyme application for cotton based woven fabrics was investigated. For this purpose, the bending rigidity, handle properties, CIELab changes and fastness were tested, and depending on the results of these tests, it was decided about the necessity and sequence of the acid cellulase treatments. We found out that the sequence, before or after dyeing, of application of cellulase enzyme treatment especially affected the handle properties and CIELab values of both woven samples. In addition, the whole test results were analyzed with one way ANOVA test in order to determine the significantly effective factors.

Key-words: ANOVA, bending rigidity, bio polishing, cellulase enzyme, CIELab, fastness, handle

The handle properties are the most important performance criteria for the fabric used for the men or women apparels in conjunction with color and fastness properties. In order to develop the handle properties of the woven fabrics, several application as some chemical and mechanical processes can be applied to the fabrics, and the singeing and cellulase enzyme applications are known among the most important ones.

In the first part of experimental study, we investigated the effect of cellulase enzyme treatments on the mechanical performances of two kinds of woven fabric processed by singeing.

In the second part, we tried to find responses to the questions whether the application of the cellulase enzymes to the cotton based woven fabrics made from the ring spun yarns was necessary together with singeing process. According to the these results, we also researched the sequence of the cellulase enzyme treatment in order to obtain the best handle results from fabrics without causing any decrease on the color, fastness and other physical performances.

EXPERIMENTAL PART

In this part, we applied bending rigidity (handle properties), color measurement (CIELab values) and different color fastness tests to the fabrics in order to determine the necessity and sequence of the cellulase application. In addition, we applied one way ANOVA (analyze of variance) in order to check the effect of the process parameters on the results statistically. The results were evaluated at 5% ($\alpha = 0.05$) significance level by Design-Expert Trial version [1].

Investigation methods

CIELab measurement

The colorimetric measurements were carried out using a DataColor SF 600 Plus spectrophotometer interfaced to a PC. The measurements were taken with the specular component of the light included (SCI) and the UV component excluded, using illuminant D_{65} and 10° standard observer. The samples were folded to ensure opacity and an average of three readings was calculated. We recorded *L*, a*,*

* Part II. Part I was published in *Industria Textilă*, 2013, vol. 64, issue 1, p. 20

b, C, h* values of all samples. In addition, CIE "Δ" values between the samples obtained from P_I (reference samples) and samples processed with enzymes (P_{II} and P_{III}) were calculated according to CIELab formulation by software.

Color fastness

In the study, the several fastness performances as color fastness to the washing, color fastness to water, color fastness to perspiration, color fastness to artificial light and color fastness to light of textiles wetted with artificial perspiration were measured according to EN ISO 105-CO6, EN ISO 105-E01, EN ISO 105-E04, EN ISO 105-B02, EN ISO 105-B07, respectively. We recorded only "fading result (color change on the samples)" of the samples as fastness results [2–6].

Bending length and rigidity (Handle)

The bending rigidity and length of the samples were measured according to ASTM D 1388-96, and these results were used to comment about the handle properties of the samples [7].

As it is known from the literature, the cellulase enzyme treatment contributes the handle properties of the cotton based knitted or weaved fabrics [8–13]. The bending behavior of the fabric and yarn play an important role in the handling properties and the end-use performance of textiles. So, many authors have been studying the handle of the fabric or even yarn by the measurements of the mechanical properties, especially for the bending properties (bending length and rigidity) [14–17]. According to the Sülar and Okur [14], there were good correlations between bending rigidity-length and handle properties, and they established empirical models having high R^2 values.

The bending length is measured from the equipment and bending rigidity is calculated according to the formulas shown below in equations (1) – (3).

$$G_{wa} = 0{,}1 \cdot W \cdot C^3 \quad [\text{mg·cm}] \quad (1)$$

$$G_{we} = 0{,}1 \cdot W \cdot C^3 \quad [\text{mg·cm}] \quad (2)$$

where:

W [g/m^2] and C [cm] are the mass per unit area and, respectively, bending length values of the samples;

G_{wa} and G_{we} – the bending rigidity values of the warp and, respectively, weft directions of the fabric

$$G_F = \sqrt{G_{wa}\, G_{we}} \quad [\text{mg·cm}] \quad (3)$$

where:

G_F is the total bending rigidity of the fabric.

The rigid fabrics bend slower than soft ones. In addition, rigid fabrics have bigger bending length than soft ones.

RESULTS AND DISCUSSIONS

Handle properties

The results of the bending length (cm), bending rigidity of the warp and the weft directions (mg·cm) and total bending rigidity of the F_1 and F_2 samples [mg·cm] can be seen in figures 1, 2 and 3. There were determined the handle properties of the samples according to the results of the bending length and rigidity.

According to the results shown in figure 1, for both F_1 and F_2, the bending length was measured approximately similar for all samples. However, there is little differences between them, and it can be important while commenting the rigidity results. Therefore, we can say that the biggest and the least bending length was measured for the samples processed by P_{II} and P_I applications, respectively for both samples.

In terms of the bending rigidity (fig. 3), for sample F_2, it was found out that the samples manufactured without any enzymatic application (P_I) showed bigger resistance against bending force than samples produced by enzymatic processes (P_{II} and P_{III}), and this state could be the proof of the good bending tendency of the samples obtained from enzymatic P_{II} and P_{III} processes compare to the others.

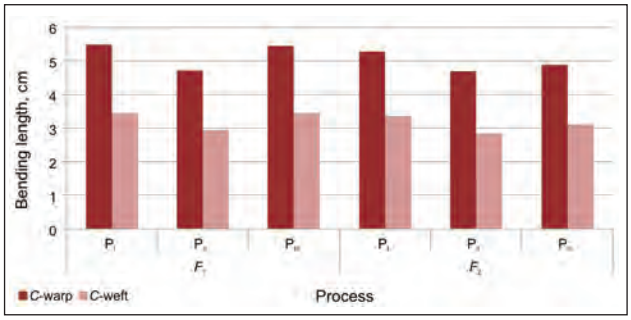

Fig. 1. Bending length of samples, cm

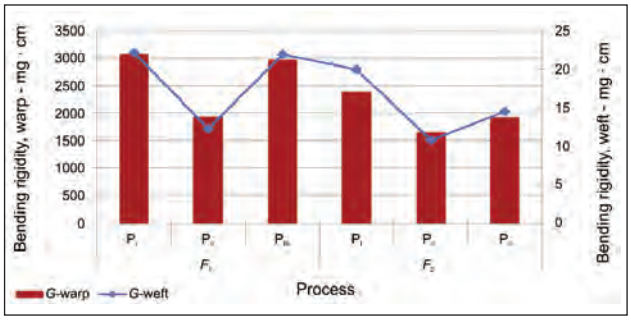

Fig. 2. Bending rigidity of the warp and weft direction of the samples, mg·cm

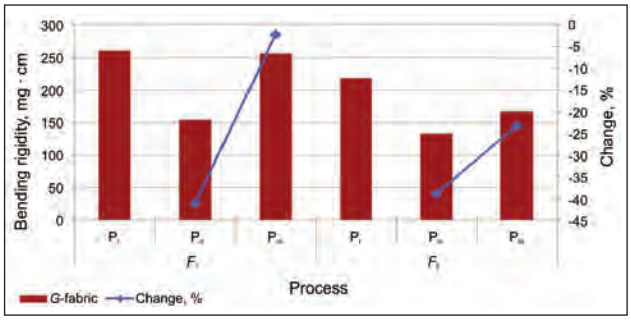

Fig. 3. Bending rigidity of the samples, mg·cm

If the results for F_1 were investigated, we could say that rigity results of the samples produced by P_I and P_{III} were almost same, but P_{II} showed the best results between them. If we set order the softness results for F_1 sample according to the enzyme process, we could order the performance as $P_{II} > P_{III} > P_I$. The total bending rigidity calculated according to the equation (3) is shown in figure 3. According to the graphic, the samples manufactured by P_{II} process are approximately 40% less rigid than samples produced without any enzyme (P_I). The bending rigidity of the samples processed with P_{II} is also less than produced by P_{III} process group.

These experimental results showed the positive contribution of the enzymatic processes to the handle properties of the woven fabric. In addition, it was clear that the sequence of the enzymatic application (before or after dyeing) was another important factor in order to be determined the handle performance.

Color measurement results

The results of the measured the CIELab and the calculated color differences values for F_1 and F_2 samples can be seen in table 1 and table 2, respectively.

In order to determine the color differences values, the accept tolerance limits must be displayed. For this experimental study, these tolerances were accepted as "± 1, ± 0.6, ± 0.6 and + 1" for ΔL^*, Δa^*, Δb^* and ΔE, respectively as mentioned in the previous studies, practical applications, especially commercial ones [18]. However, it must be mentioned that these tolerances could be showed differences depending on the quality standards of the manufacturers, especially on the industrial applications.

According to the results shown in table 1, the greatest color difference values were observed in the F_1 samples that had been treated with cellulase enzyme before dyeing process. All ΔE values for the samples treated by P_{II} is out of the tolerances limits mentioned above. However, the measured and the calculated color differences for samples treated by P_{III} was acceptable for this kind of experimental application. Based on the measured results in table 1, after the enzyme applications (P_{II} and P_{III}), the color was generally got lighter, greener and bluer than non-enzymed samples. These changes are in the tolerance limits for samples produced by P_{III} reverse the P_{II}. For the F_2 samples, the similar results were obtained that of F_1.

Table 1

THE COLOR MEASUREMENT RESULTS OF THE F_1 SAMPLES

Fabric	Process	Sample no	L^*	a^*	b^*	C^*	h	ΔL^*	Δa^*	Δb^*	ΔE
F_1	P_I	1	55.35	51.59	–4.23	51.76	355.31	Reference specimens			
		2	45.57	58.53	–0.55	58.53	359.46				
		3	42.85	59.07	1.80	59.09	1.75				
		4	45.33	–7.93	–19.16	20.74	247.52				
		5	29.40	–5.74	–18.54	19.41	252.80				
		6	24.79	–4.18	–16.28	16.80	255.59				
		7	80.71	17.25	62.19	64.54	74.49				
		8	74.66	27.92	77.02	81.92	70.07				
		9	72.37	31.69	80.04	86.09	68.40				
	P_{II}	10	57.07	49.73	–4.20	49.90	355.17	1.72	–1.86	0.03	2.53
		11	47.25	57.08	–1.55	57.10	358.44	1.68	–1.45	–1	2.43
		12	44.59	57.93	0.27	57.93	0.26	1.74	–1.14	–1.53	2.58
		13	47.07	–7.76	–18.42	19.99	247.15	1.74	0.17	0.74	1.89
		14	32.11	–6.26	–18.44	19.47	251.23	2.71	–0.52	0.1	2.76
		15	27.17	–4.89	–16.74	17.44	253.71	2.38	–0.71	–0.46	2.52
		16	81.29	15.94	58.71	60.83	74.81	0.58	–1.31	–3.48	3.76
		17	75.54	25.91	73.09	77.55	70.48	0.88	–2.01	–3.93	4.50
		18	73.30	29.76	76.72	82.29	68.80	0.93	–1.93	–3.32	3.95
	P_{III}	19	55.67	51.35	–3.95	51.50	355.6	0.32	–0.24	0.28	0.48
		20	46.14	58.51	–0.34	58.51	359.67	0.57	–0.02	0.21	0.60
		21	43.64	58.98	1.75	59.00	1.70	0.79	–0.09	–0.05	0.79
		22	45.90	–7.92	–18.78	20.38	247.14	0.57	0.01	0.38	0.68
		23	30.40	–5.93	–18.39	19.32	252.12	1	–0.19	0.15	1.02
		24	25.56	–4.43	–16.16	16.76	254.67	0.77	–0.25	0.12	0.81
		25	80.74	17.12	61.65	63.98	74.48	0.03	–0.13	–0.54	0.55
		26	74.72	27.59	76.06	80.91	70.06	0.06	–0.33	–0.96	1.01
		27	72.36	31.43	79.18	85.19	68.35	–0.01	–0.26	–0.86	0.89

Table 2

THE COLOR MEASUREMENT RESULTS OF THE F_2 SAMPLES

Fabric	Process	Sample no	*L**	*a**	*b**	*C**	*h*	Δ*L**	Δ*a**	Δ*b**	Δ*E*
F_2	P_I	*28*	55.13	51.97	–3.96	52.12	355.64	**Reference specimens**			
		29	45.46	58.76	–0.14	58.76	359.87				
		30	42.93	59.19	2.10	59.23	2.04				
		31	44.98	–7.92	–19.08	20.66	247.45				
		32	28.63	–5.63	–18.28	19.13	252.88				
		33	24.52	–4.21	–16.15	16.69	255.39				
		34	80.29	17.62	62.75	65.18	74.31				
		35	74.31	28.16	77.21	82.19	69.96				
		36	72.09	31.95	80.34	86.46	68.31				
	P_{II}	*37*	56.39	50.05	–3.91	50.2	355.53	1.26	–1.92	0.05	2.29
		38	46.88	57.29	–1.24	57.31	358.76	1.42	–1.47	–1.10	2.32
		39	44.37	58.11	0.49	58.11	0.48	1.44	–1.08	–1.61	2.41
		40	46.81	–7.81	–17.93	19.56	246.47	1.83	0.11	1.15	2.16
		41	31.75	–6.35	–18.15	19.23	250.71	3.12	–0.72	0.13	3.20
		42	26.74	–4.92	–16.5	17.21	253.39	2.22	–0.71	–0.35	2.35
		43	80.9	16.26	59.21	61.4	74.64	0.61	–1.36	–3.54	3.84
		44	75.09	26.46	73.86	78.45	70.29	0.78	–1.7	–3.35	3.83
		45	72.94	30.03	77.19	82.83	68.74	0.85	–1.92	–3.15	3.78
	P_{III}	*46*	55.33	51.11	–3.93	51.27	355.6	0.20	–0.86	0.03	0.78
		47	45.96	58.39	–0.24	58.39	359.77	0.50	–0.37	–0.10	0.39
		48	43.37	58.7	1.47	58.72	1.44	0.44	–0.49	–0.63	0.83
		49	45.72	–7.92	–18.56	20.18	246.89	0.74	0.00	0.52	0.81
		50	29.89	–5.89	–18.13	19.06	252.02	1.26	–0.26	0.15	1.67
		51	25.49	–4.44	–16.08	16.68	254.55	0.97	–0.23	0.07	0.99
		52	80.26	17.63	62.46	64.9	74.24	–0.03	0.01	–0.29	0.08
		53	74.37	27.78	76.15	81.06	69.96	0.06	–0.38	–1.06	1.27
		54	72.13	31.6	79.39	85.44	68.3	0.04	–0.35	–0.95	1.02

According to the principle of the enzymatic reaction, especially the EG part of the cellulase enzyme acts to the end of the cellulose molecule and cause damage on this part. Depending on this damage, the structure of the cotton fibre negatively changes in terms of dyeing mechanism of the fibre. As it is known, the dyeing of the cellulose with reactive dyestuff bases a chemical reaction between the reactive group of the dye molecule and OH^- group of the cellulose. It was thought that by reason of the negative chemical modification in the fibre structure, bonding possibility of the reactive dye to the cellulosic fibre reduced, and this state resulted with less dye and lighter color on the samples processed by the P_{II} comparing to the non-enzymed and P_{II} samples. In addition, it was also found out that the P_{III} process was affected the color parameters lesser than P_{II}, because the dye molecule had already bound to the fibre before enzyme was applied to the cotton samples. Therefore, the possible damage depending on the enzyme in the fiber did not seriously affect the color of these samples.

Fastness results

The fading results of the several fastness tests for F_1 and F_2 samples can be seen in table 3 and table 4, respectively. These results represent the color change after fastness tests for all samples.

If the non-enzymed samples (P_I samples *1–9* for F_1 and *28–36* for F_2) were accepted as reference in order to investigate the effect of the enzymatic processes on the color fastness performance, it could be said that any crucial negative or important positive changes on the whole fastness performances were not observed depending on either P_I or P_{II} enzymatic applications for both fabric specimens. It was only determined half (1/2) degree decreases on the color fastness to the water performance for the F_1 samples treated by P_{III}. In addition, the general fastness decrease (about 1/2 or 1 degree) was only observed on the rubbing fastness performance (dry and wet). As mentioned before, the cellulase enzymes especially affected the fibrillation and surface characters of the cotton fiber. With added the rubbing effect of this test, "the reducing end" remaining on the enzyme treated cotton fiber received supplemental dry and

Table 3

THE FASTNESS RESULTS (FADING) OF THE F_1 SAMPLES

Fabric	Process	Sample	Washing fastness	Water fastness	Perspiration Fastness		Artificial light	Light of textiles wetted with artificial perspiration		Rubbing fastness	
					Acidic	*Alkali*		*Acidic*	*Alkali*	Dry	Wet
F_1	P_I	*1*	4/5	4/5	4/5	4/5	3/4	*3*	*3*	4	3/4
		2	4/5	4	4	4	4	4	3/4	4	3/4
		3	4/5	4	4	4	4	4	3/4	3	3
		4	4/5	4/5	4/5	4/5	3	2/3	2/3	4/5	4
		5	4/5	4	4	4	3/4	3/4	3/4	4	3/4
		6	4/5	4	4	4	4	4	4	3	3
		7	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
		8	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	4
		9	4/5	4/5	4/5	4/5	4/5	4/5	4/5	3/4	3/4
	P_{II}	*10*	4/5	4	4	4/5	3	3/4	3	4	3/4
		11	4/5	4	4	4	3/4	4	3/4	3	3
		12	4/5	4	4	4	3/4	4	3/4	3	3
		13	4/5	4/5	4	4/5	2	3	2	4/5	4
		14	4/5	4/5	4/5	4/5	3	3/4	3	3/4	3/4
		15	4/5	4	4	4	3/4	4	3/4	3	3
		16	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	4
		17	4/5	4/5	4/5	4/5	4/5	4/5	4/5	3/4	3
		18	4/5	4	4	4	4/5	4/5	4/5	3	3
	P_{III}	*19*	4/5	4	4	4	3	3	3	3/4	3
		20	4/5	3/4	4	4	3/4	3/4	3/4	4/5	3
		21	4/5	3/4	4	4	3/4	4	3/4	3	3
		22	4/5	4/5	4	4	3	3	2/3	4/5	4
		23	4/5	4	4	4	4	3/4	3/4	3/4	3/4
		24	4/5	4	4	4	4	4	4	3	3
		25	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	3
		26	4/5	4	4/5	4/5	4/5	4/5	4/5	3	3
		27	4/5	4	4	4	4/5	4/5	4/5	3/4	3

wet mechanical force, and because of this effect, the change on the fastness performance came more possible for these kinds of enzymatic treated fabrics.

Variance analysis (ANOVA)

Beside the experimental study and the results, experimental instruments, methods and statistical contribution of each factor to these investigated parameters were discussed using the ANOVA. The results were evaluated at 5% significance level by Design-Expert Trial version [19]. The ANOVA of all results obtained from Part I and Part II can be seen in tables 5, 6 and 7.

While analyzing of the ANOVA results we focused on *F* and *p* values. While *F* and *p* values get bigger and respectively smaller, the significance contribution of the investigated factors on the variance increases. Especially, the *p* values must be less than 0.05 in order to define the factor as statistically significant.

According to the table 5, 6, 7, it is clear that all established models are significant. In addition the R^2 values of these models are satisfied. These data clearly show the reliability of our experimental design.

It was determined that *A, B, C* factors had significant effect on the tensile, *TS*, and tearing strength, *TeS*, performance for both warp and weft sides of the woven fabrics. It was found out that "Factor C-Type of Reactive Dye" was the factor having less significant effect on the *TS* and *TeS*. According to the results shown in table 5, it is obvious that the presence and the sequence of the enzymatic process is the crucial factor for both output, especially for weft side of the samples.

It was also realized that same factors as similar *TS* and *TsE* had also significant effect on the weight of the samples. However, for *W, ABC* interaction was significant, too. It means that while determining the effect of the factors, we should observe these three factors together.

For total color differences, ΔE, forming after enzymatic treatments, all main factors and *BC* interaction were important. It was clearly seen that the enzymatic

Table 4

THE FASTNESS RESULTS (FADING) OF THE F_2 SAMPLES

Fabric	Process	Sample	Washing fastness	Water fastness	Perspiration fastness		Artificial light	Light of textiles wetted with artificial perspiration		Rubbing fastness	
					Acidic	*Alkali*		*Acidic*	*Alkali*	Dry	Wet
F_2	P_I	*28*	4/5	4	4	4	3/4	3/4	3/4	4	4
		29	4/5	4	4	4	4	4	4	4	4
		30	4/5	4	4	4	4	4	4	3/4	3
		31	4/5	4/5	4/5	4	2/3	2	2/3	4/5	4
		32	4/5	4	4	4	3/4	3/4	3/4	4	4
		33	4/5	4	4	4/5	4	4	4	3/4	3/4
		34	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
		35	4/5	4/5	4/5	4/5	4/5	4/5	4/5	3/4	3/4
		36	4/5	4/5	4/5	4/5	4/5	4/5	4/5	3/4	3/4
	P_{II}	*37*	4/5	4	4	4	3/4	3	3	4	3/4
		38	4/5	4	4	4	4	3/4	3/4	3/4	3
		39	4/5	4	4	4	4	4	4	4/5	3
		40	4/5	4/5	4/5	4	2/3	2	2	4/5	4
		41	4/5	4/5	4/5	4/5	3/4	3	3	3/4	3
		42	4/5	4	4	4/5	4	4	4	3/4	3
		43	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4
		44	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	3/4
		45	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	3
	P_{III}	**46**	4/5	4	4	4	3/4	3/4	3/4	4/5	3/4
		47	4/5	4	4/5	4/5	4	4	4	4/5	3
		48	4/5	4	4	4	4	4	4	3/4	3
		49	4/5	4/5	4/5	4/5	2/3	2/3	2	4	3/4
		50	4/5	4	4/5	4/5	3/4	3/4	3/4	3/4	3
		51	4/5	4	4	4	4	4	4	3	3
		52	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4
		53	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	3/4
		54	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4	3

Table 5

ANOVA RESULTS

Factor	Parameters									
	TSW		***TSWe***		***TeSW***		***TSeWe***		***W***	
	F value	*p value*	*F value*	*p value*	*F value*	*p value*	*F value*	*p value*	*F value*	*p value*
Main model	6.69	<0.0001	133.31	<0.0001	15.27	<0.0001	12.77	<0.0001	61.28	<0.0001
A - type of fabric	15.90	0.0003	236.81	<0.0001	30.40	<0.0001	14.45	0.0004	611.69	<0.0001
B - the presence of enzyme	10.93	0.0002	343.85	<0.0001	29.73	<0.0001	32.02	<0.0001	13.20	<0.0001
C - type of reactive dye	5.01	0.0114	3.81	0.0292	6.89	0.0024	7.23	0.0019	10.71	0.0002
D - color strength	2.62	0.0848	0.52	0.5930	1.32	0.2765	0.15	0.8585	0.86	0.4279
ABC interaction	-	-	-	-	-	-	-	-	3.21	0.0217
R^2 values of model	0.53		0.95		0.70		0.66		0.94	
Standard deviation	2.31		0.84		66.34		84.70		2.53	
CV	4.59		4.19		6.32		7.92		1.46	

Note: TSW is tensile strenght - warp, *TSWE* is tensile strenght - weft, T*ESW* is tearing strength - warp, *TSEWE* is istearing strength - weft, w is weight

Table 6

ANOVA RESULTS FOR TOTAL COLOR DİFFERENCES		
Factor	**ΔE**	
	F value	*p value*
Main model	82.72	<0.0001
A - type of fabric	0.02	0.8729
B - the presence of enzyme	528.12	<0.0001
C - type of reactive dye	29.49	<0.0001
D - color strength	7.20	0.0031
BC interaction	30.11	<0.0001
R^2 values of model	0.96	
Standard deviation	0.27	
CV	14.8	

Table 7

ANOVA RESULTS FOR BENDİNG RİGİDİTY		
Factor	***BR****	
	F value	*p value*
Main model	68.77	0.0005
A - type of fabric	9.43	0.0373
B - the presence of enzyme	6.49	0.0455
C - fabric direction	437.30	<0.0001
AC interaction	9.22	0.0385
BC interaction	6.23	0.0490
R^2 values of model	0.99	
Standard deviation	191.26	
CV	16.32	

* *BR* is bending rigidity

applications set the color change because the *F* value of *C* factor was the highest one in all inputs. It was also found out that the effect of the type of the reactive dye on the Δ*E* could show differences depending on the sequence of the enzymatic application in the finishing line when the ANOVA results were investigated from table 6. Therefore, it could be said that it must be taken care the application of the cellulase enzyme in the finishing mill related to the type of the dye in order to control the possible color change on the fabric. After analyzing the ANOVA results, the reliability of the established models were discussed. "The % normal probability versus Residuals" and "Residuals versus Run Number" diagrams which are used in order to check the reliability and accuracy of the ANOVA results can be seen in figures 4 and 5.

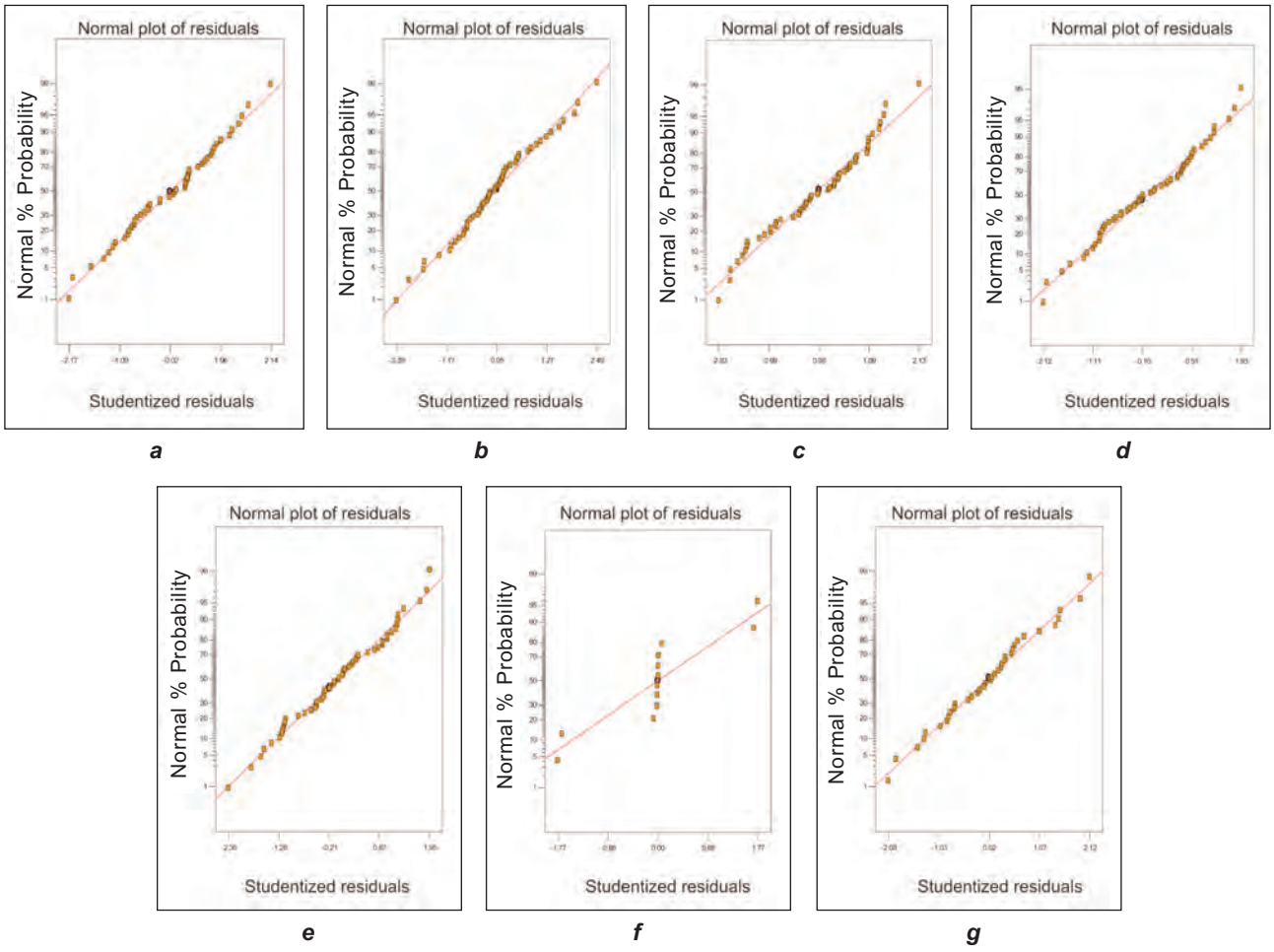

Fig. 4. Normal probability, %, plot of the models for all outputs:
a *– TSW;* ***b*** *– TSWE;* ***c*** *– TESW;* ***d*** *– TSEWE;* ***e*** *– W;* ***f*** *– BR;* ***g*** *– ΔE*

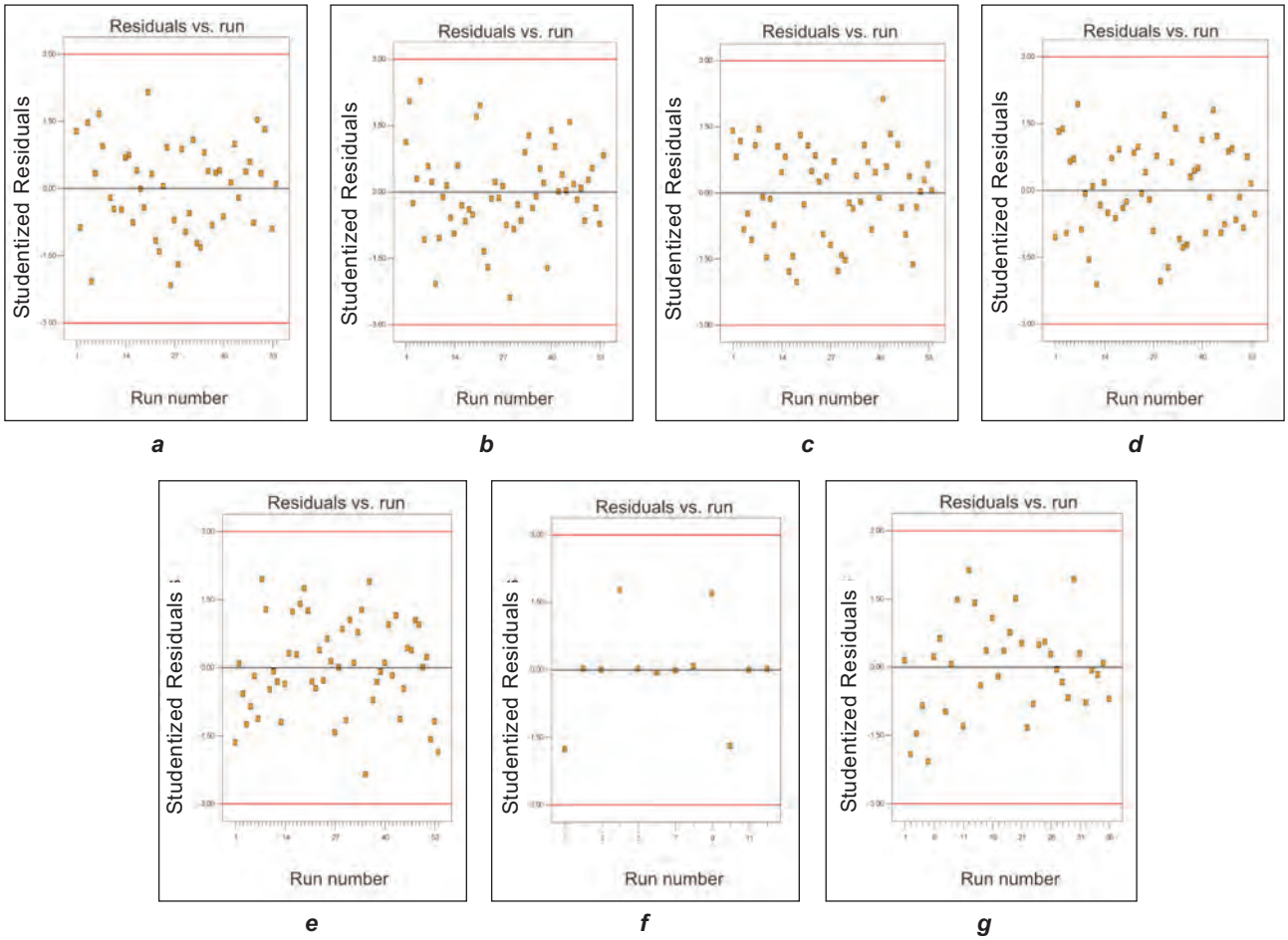

Fig. 5. Control plots of the ANOVA for all outputs:
a *– TSW;* ***b*** *– TSWE;* ***c*** *– TESW;* ***d*** *– TSEWE;* ***e*** *– W;* ***f*** *– BR;* ***g*** *– ΔE*

The crucial signal is the diagnostics for checking the accuracy of the statistical analysis. The normal probability indicates whether the residuals follow a normal distribution, in which the points will follow a straight line. This plot consists of the number of standard deviations of the actual values from their respective predicted values. Ideally, it should be straight line, indicating no abnormalities. Therefore, when it is analyzed results from figure 4, it can be seen that there are not any problems on any plots formed for each outputs [19].

The diagnostics shown in figure 5 are plot of the residuals versus the experimental run order. It checks for lurking variables that may have influenced the response during the experiment. The plot shows a random scatter. The size of the residual should be independent of its run number. In other words, the spread of the residuals should be approximately the same across all levels of the run numbers. In this case, the plots do not have any problem because the distribution of the residuals is random. According to the diagnostics, there is not any problem about the model that it is established for outputs [19].

CONCLUSIONS

In the second part of the study, we discussed the necessity of the enzymatic application for woven fabrics processed with singeing in the pretreatment line. In addition, we tried to find out the sequence of the enzymatic process. In order to reach these aims, the research was performed in terms of softness (handle), fastness and color change performances.

Based on the results obtained from this experimental study, it could be said that:

- It was clearly seen that enzymatic applications increased the handle properties, softness of the woven fabric in both warp and weft direction. In addition, the place of the enzymatic application (before or after dyeing) was crucial in order to provide improvement the softness properties of the woven fabric. In terms of handle, the samples produced by P_{II} had better results. On the contrary, these samples showed worse performance (strength, weight loss, abrasion resistance or color change) than fabrics produced by P_{III};
- The presence and the sequence of the enzymatic process did not affect the fastness character of the dyed samples;
- We observed big changes on the CIELab values for both processes. In addition, it was clearly confirmed that the amount of the change had to do with the presence and sequence of enzymatic treatment. Especially, if the dyeing process was carried on the cellulase enzyme treated fabric, it should be taken more care than other ones,

because the highest color difference was measured and calculated on the samples processed by P_{II} treatment.

- The statistical analyze showed that the experimental design and results had high accuracy, and especially *A, B, C* factors had significant effect on all outputs. Especially, it was identified that enzymatic application, especially sequence of application, (factor *B*) was the major factor having effect on the different performance criteria.

As a result, even the singeing process can be effective on the removing the fuzzy fibres from the surface and preventing the pill formation for the woven fabrics, the cellulase enzyme treatment are necessary in the finishing line. Especially, if excellent handle properties are expected from the woven fabric, the enzymatic processes can be definitely applied. However, the change on the physical and chemical performance on the fabric must also be observed. The other important point which should be focused for the true application of the cellulase enzyme is the sequence of the process according to the dyeing, because the fact is that it has very obvious negative or positive change of all performance properties of the woven fabrics. If one desires the handle properties of fabrics to increase, the acid cellulase enzyme can be used before dyeing.

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Antibacterial and colorimetric evaluation of cotton fabrics dyed with direct dyes and loaded with Ag nanoparticles

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REZUMAT – ABSTRACT

Evaluarea antibacteriană şi colorimetrică a ţesăturilor din bumbac tratate cu nanoparticule de Ag şi vopsite cu coloranţi direcţi

Lucrarea prezintă relaţia dintre procesele de tratare a ţesăturilor din bumbac cu nanoparticule de Ag coloidal şi de vopsire a acestora cu coloranţi direcţi – C.I. Direct Yellow 86, C.I. Direct Red 79 şi C.I. Direct Blue. S-au studiat atât influenţa ordinii celor două procese, cât şi a concentraţiei colorantului utilizat asupra activităţii antibacteriene şi a modificării culorii ţesăturilor. A fost testată activitatea antibacteriană împotriva E. coli – bacterie gram-negativă, şi S. aureus – bacterie gram-pozitivă. Ţesăturile din bumbac vopsite şi tratate cu nanoparticule de Ag au prezentat excelente proprietăţi antibacteriene, independent de concentraţia colorantului şi de ordinea proceselor de vopsire şi de încărcare cu nanoparticule de Ag. În schimb, în prezenţa nanoparticulelor de Ag, schimbarea culorii ţesăturilor din bumbac este puternic influenţată de ordinea în care se efectuează operaţiile, de colorantul folosit şi de concentraţia acestuia. Stabilitatea acestor materiale textile nanocompozite a fost testată în mediu de transpiraţie artificială, acidă şi alcalină. Eliberarea nanoparticulelor de Ag a avut loc independent de valoarea pH-ului transpiraţiei.

Cuvinte-cheie: bumbac, nanoparticule de Ag, coloranţi direcţi, activitate antibacteriană, transpiraţie artificială

Antibacterial and colorimetric evaluation of cotton fabrics dyed with direct dyes and loaded with Ag nanoparticles

This study discusses the relationship between loading of cotton fabric with colloidal Ag nanoparticles and dyeing with direct dyes – C.I. Direct Yellow 86, C.I. Direct Red 79 and C.I. Direct Blue 78. The influence of order of Ag nanoparticles loading and dyeing of cotton fabrics as well as the concentration of applied dye on their antibacterial activity and colour change were studied. Antibacterial activity was tested against gram-negative bacterium E. coli and Gram-positive bacterium S. aureus. Dyed cotton fabrics loaded with Ag nanoparticles exhibited excellent antibacterial properties independently of dye concentration and order of dyeing and loading of Ag nanoparticles. Colour change of cotton fabrics due to presence of Ag nanoparticles is highly influenced by the order of operations, applied dye and dye concentration. The stability of these nanocomposite textile materials was tested in acidic and alkaline artificial sweat. The release of silver occurred independently of the pH value of the sweat.

Key-words: cotton, Ag nanoparticles, direct dyes, antibacterial activity, artificial sweat

Lately, the development of novel materials with antimicrobial properties and low susceptibility to bacterial resistance that are benign to human cells gained much scientific interest. Some nanoscale materials emerged up as potential antimicrobial agents primarily due to high surface to volume ratio and extraordinary reactivity. Silver nanoparticles (Ag NPs) seem to be particularly efficient in killing a wide spectrum of bacteria, viruses and other eukaryotic microorganisms [1]. High efficiency, simple routes for their synthesis and application make them especially attractive and thus, they are slowly becoming common integral components of room sprays, cosmetic products, detergents, wall paints, etc. Recent studies demonstrated that small amount of colloidal Ag NPs can also impart antimicrobial properties to different textile materials [2–9]. The major research so far was oriented towards cotton and polyester fibres that are broadly used for medical, protective, hygiene and sports textiles i.e. materials that require exquisite antimicrobial activity. Cotton fabrics are particularly appropriate for a wide range of utilities basically because they provide a great comfort. On the other hand cotton is prone to microbial attack due to its high higroscopy and in certain environment (humidity and temperature) it may act as a nutritient, becoming a suitable medium for microbial growth [9–10]. Therefore, cotton fibres require adequate antimicrobial finishing which can be achieved with different forms of silver.

Although very efficient antimicrobial agent, silver nitrate stains the fabrics to black-brown when exposed to air

and light, due to uncontrolled reduction processes [5]. This can be serious obstacle for dyeing of fabrics especially in pale shades. Unlike silver nitrate, Ag NPs stain the cotton fabrics to light yellow. The colour yield depends on the initial concentration of colloidal solution of Ag NPs and consequently, the amount of deposited Ag NPs [12]. Yellow shade of fabrics due to presence of Ag NPs may also influence the dyeing effects. Much work has been done on the application of Ag NPs to cotton fabrics and their antimicrobial properties, but the aspect of this finishing treatment in relation to dyeing of cotton fabrics was certainly neglected [4–9]. Since this feature is equally important from both antimicrobial and colorimetric points of view, more extensive work has to be addressed to this issue. Gorenšek and Recelj reported that simultaneous application of Ag NPs and exhaust dyeing with reactive dyes can impart antibacterial activity to cotton fabrics that varies with bacterium type [9]. Additionally, they pointed out that the presence of Ag NPs highly affected the colour of dyed cotton fabrics. This was more pronounced on the fabrics that were dyed in light and deep blue shades (0.1% and 5% o.w.f. of dye Cibacron navy S-G) compared to fabrics dyed with Cibacron deep red S-B. Our research group demonstrated that order of dyeing with C.I. direct red 81 and loading of Ag NPs did not influence the antimicrobial activity of cotton fabrics i.e. maximum bacterial reduction was reached [11]. However, loading of Ag NPs after dyeing led to a significant colour change. Taking into account the significance of relationship between dyeing and antimicrobial finishing with colloidal Ag NPs for the overall quality of textile product, one of the aims of this study was to discuss the effect of dye type, dye concentration, presence of Ag NPs and order of dyeing and loading of Ag NPs on antibacterial activity and colour change of cotton fabrics.

In addition to antimicrobial efficiency, the stability and durability of developed textile materials with incorporated Ag NPs during the exploitation and maintenance has to be ensured. Most of the published papers mainly considered the maintenance of such systems i.e. laundering durability of achieved antibacterial properties. However, wearing of such products and performance of Ag NPs in contact with human skin received less attention. The behaviour of Ag NPs deposited onto cotton fabrics in contact with artificial sweat was recently studied by Kulthong et al. [13]. They reported that the amount of silver released from the fabrics into artificial sweat depends on the initial amount of deposited silver, the quality of the fabric, *p*H and artificial sweat formulation. Keeping in mind the importance of perspiration fastness of textile materials, this study also considers the stability of Ag NPs on dyed cotton fabrics in alkaline and acidic artificial sweat.

EXPERIMENTAL PART

Materials and chemicals

Desized and bleached cotton woven fabric (Co, 168 g/m^2) has been used as a substrate in this study. To eliminate the surface impurities, the fabric was washed in the bath (liquor-to-fabric ratio of 50:1) containing 0.5% nonionic washing agent Felosan RG-N (Bezema) for 15 minutes at 50ºC. After the single rinsing with warm water (50ºC) for 3 minutes and triple rinsing (3 minutes) with cold water, the samples were dried at room temperature.

Synthesis of colloidal Ag NPs

The synthesis of colloidal Ag NPs was based on the reduction of $AgNO_3$ with strong reducing agent $NaBH_4$, without using any stabilizer [14–15]. The concentration of the stable colloid was 50 ppm. Synthesized Ag NPs were nearly spherical with an average diameter of 10 nm and they were not prone to agglomeration in the colloid [16].

Treatment of Co fabrics with colloidal Ag NPs

One gram of Co fabric was immersed in 45 mL of colloid of Ag NPs for 5 minute and dried at room temperature. After 5 minutes of curing at 100°C, the samples were rinsed twice (5 minutes) with deionized water and dried at room temperature. The whole procedure was performed before and after dyeing.

Dyeing of Co fabrics

Co fabrics were dyed with direct dyes (Bezema): Tubantin yellow GR, Tubantin red 6BLL and Tubantin blue GLL 300. The characteristics of the dyes are summarized in table 1.

Dyeing was performed in accordance with manufacturer (Bezema) recommendation. Co fabrics were dyed in polycolor laboratory beaker (Werner Mathis AG) at liquor-to-fabric ratio of 30:1. Samples were initially treated in the bath containing Na_2CO_3 (1 g/L) and Sarabid SBF (Bezema, 0.5 g/L) for 10 minute at 50ºC, when the appropriate amount of dyestuff was added. Sarabid SBF is nonionic/anionic low foaming levelling agent for dyeing with direct dyes that enables an even dye distribution by temporary dyestuff retarding. The bath contained 0.5, 1.0 and 2.0% (o.w.f.) of dye, respectively. After further processing of Co fabrics at 50ºC for 10 minutes, the temperature of the dyebath was raised up to 100ºC in the next 40 minutes and Na_2SO_4 (5 g/L) was added. Dyeing at 100ºC for 45 minutes was followed by rapid cooling of the dyebath. Subsequently, the samples were rinsed 10 minute in deionised water at 35ºC and 5 minutes at 30ºC. In order to increase their wet fastness, Co fabrics were treated with CH_3COOH (0.3 mL/L) and cationic after-treatment agent Rewin MRT (Bezema, 3.0%) at 40ºC for 20 minutes. Afterwards, the samples were rinsed in deionised water and dried at room temperature.

For clearer interpretation of results, the abbreviations of differently modified Co fabrics are specified in table 2.

Table 1

CHARACTERISTICS OF THE DYES

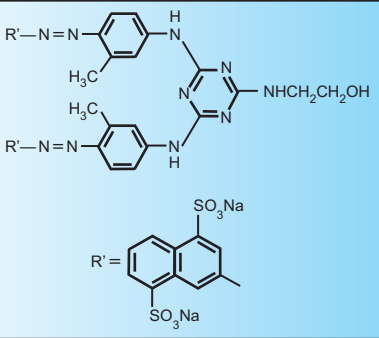
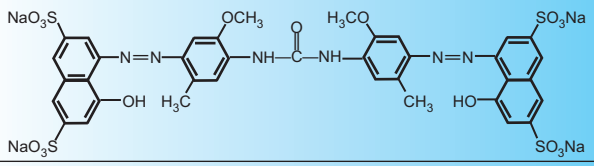
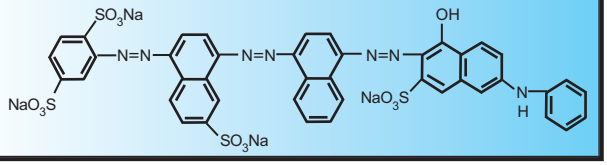
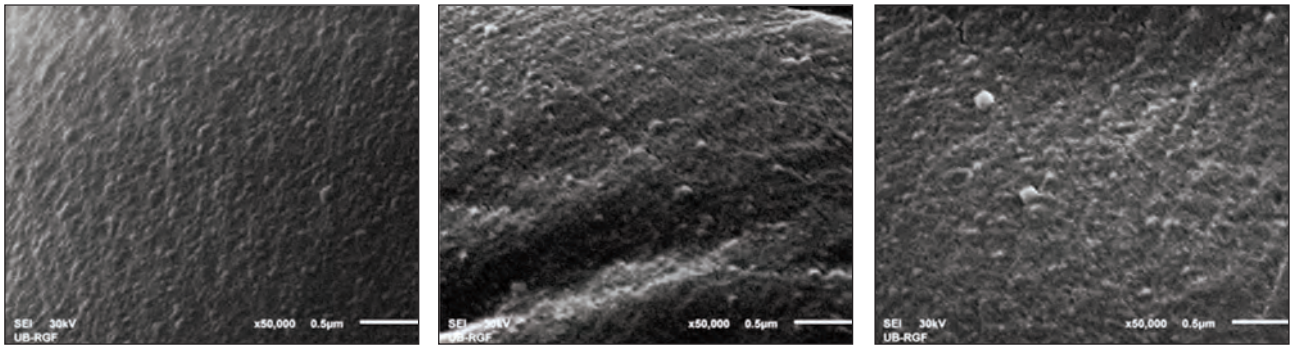
Dye	Commercial name	C. I. number	Relative molecular mass	λ_{max}, nm	Structure
DY86	Tubantin yellow GR	C.I. Direct Yellow 86	969.81	506	
DR79	Tubantin red 6BLL	C.I. Direct Red 79	1 020.85	362	
DB78	Tubantin blue GLL 300	C.I. Direct Blue 78	1 059.95	604	

Table 2

SPECIFICATION OF DIFFERENTLY MODIFIED Co FABRICS

Sample	Treatment
Co + DY86 0.5%	Dyeing with DY86 (0.5% o.w.f.)
Co + Ag + DY86 0.5%	Loading of Ag NPs and dyeing with DY86 (0.5% o.w.f.)
Co + DY86 0.5% + Ag	Dyeing with DY86 (0.5% o.w.f.) and loading of Ag NPs
Co + DY86 1%	Dyeing with DY86 (1% o.w.f.)
Co + Ag + DY86 1%	Loading of Ag NPs and dyeing with DY86 (1% o.w.f.)
Co + DY86 1% + Ag	Dyeing with DY86 (1% o.w.f.) and loading of Ag NPs
Co + DY86 2%	Dyeing with DY86 (2% o.w.f.)
Co + Ag + DY86 2%	Loading of Ag NPs and dyeing with DY86 (2% o.w.f.)
Co + DY86 2% + Ag	Dyeing with DY86 (2% o.w.f.) and loading of Ag NPs
Co + DR79 0.5%	Dyeing with DR79 (0.5% o.w.f.)
Co + Ag + DR79 0.5%	Loading of Ag NPs and dyeing with DR79 (0.5% o.w.f.)
Co + DR79 0.5% + Ag	Dyeing with DR79 (0.5% o.w.f.) and loading of Ag NPs
Co + DR79 1%	Dyeing with DR79 (1% o.w.f.)
Co + Ag + DR79 1%	Loading of Ag NPs and dyeing with DR79 (1% o.w.f.)
Co + DR79 1% + Ag	Dyeing with DR79 (1% o.w.f.) and loading of Ag NPs
Co + DR79 2%	Dyeing with DR79 (2% o.w.f.)
Co + Ag + DR79 2%	Loading of Ag NPs and dyeing with DR79 (2% o.w.f.)
Co + DR79 2% +Ag	Dyeing with DR79 (2% o.w.f.) and loading of Ag NPs
Co + DB78 0.5%	Dyeing with DB78 (0.5% o.w.f.)
Co + Ag + DB78 0.5%	Loading of Ag NPs and dyeing with DB78 (0.5% o.w.f.)
Co + DB78 0.5% + Ag	Dyeing with DB78 (0.5% o.w.f.) and loading of Ag NPs
Co + DB78 1%	Dyeing with DB78 (1% o.w.f.)
Co + Ag + DB78 1%	Loading of Ag NPs and dyeing with DB78 (1% o.w.f.)
Co + DB78 1% + Ag	Dyeing with DB78 (1% o.w.f.) and loading of Ag NPs
Co + DB78 2%	Dyeing with DB78 (2% o.w.f.)
Co + Ag + DB78 2%	Loading of Ag NPs and dyeing with DB78 (2% o.w.f.)
Co + DB78 2% + Ag	Dyeing with DB78 (2% o.w.f.) and loading of Ag NPs



a *b* *c*

Fig. 1. SEM images of the: ***a*** – Co + DY86 2% + Ag; ***b*** – Co + DR79 2% + Ag; ***c*** – Co + DB78 2% + Ag fibres

Methods used

Fibre morphology was investigated by scanning electron microscopy (SEM, JEOL JSM–6610LV). Gold layer was deposited on the samples before the analysis. The total content of Ag in the Co fabrics was quantitatively determined using a Spectra AA 55 B (Varian) atomic absorption spectrometer (AAS).

The antibacterial activity of Co fabrics was quantitatively assessed using a gram-negative bacterium E. coli ATCC 25922 and Gram-positive bacterium S. aureus ATCC 25923. The antibacterial activity of Co fabrics was evaluated using the standard test method ASTM E 2149-01.

The percentage of bacterial reduction (R, %) was calculated using the following equation:

$$R = \frac{C_0 - C}{C_0} 100\% \quad (1)$$

where:

C_0 (CFU) is the number of bacterial colonies on the control Co fabric (untreated Co fabric without Ag);

C (CFU) – the number of bacterial colonies on the Co fabric loaded with Ag NPs;

CFU – colony forming units.

Colour coordinates of the dyed fabrics (L^* – lightness, a^* – red/green axis, b^* – yellow-blue axis, C^* – chromaticity, h^* – hue) were determined with Datacolor SF300 spectrophotometer under illuminant D_{65} using the 10º standard observer. On the basis of measured CIE colour coordinates, the colour difference (ΔE^*) between dyed samples and dyed samples loaded with Ag NPs was determined.

Artificial sweat at *p*H 5.5 and 8.0 was prepared according to ISO 105-E04:1989E. A 1 L of acidic artificial sweat (*p*H 5.5) contained: 0.5 g of *l*-histidine monohydrochloride monohydrate, 5 g of sodium chloride and 2.2 g of sodium dihydrogen orthophosphate dihydrate. A 1 L of alkaline artificial sweat (*p*H 8.0) contained: 0.5 g of l-histidine monohydrochloride monohydrate, 5 g of sodium chloride and 5 g of disodium hydrogen orthophosphate dodecahydrate. The solutions were brought to *p*H 5.5 and 8.0 with 0.1 M solution of sodium hydroxide. A 0.300 g of Co fabric was soaked in artificial sweat at liquor-to-fabric ratio 1:50. The samples were incubated in a water bath at 37ºC. After 24 hours of incubation, the artificial sweat was collected and silver content was determined by AAS.

RESULTS AND DISCUSSIONS

Morphology of Co fabrics modified with Ag NPs

The morphology of Co fabrics modified with Ag NPs was followed by SEM analysis. Typical SEM images of the Co + DY86 2% + Ag, Co + DR79 2% + Ag and Co + DB78 2% + Ag fibres are presented in figure 1. SEM images reveal uniform distribution of nearly spherical agglomerates of Ag NPs mostly with dimensions of approximately 40 nm. Several bigger agglomerates with dimensions between 110–130 nm can be also observed. Similar topography was noticed on the Co fibres that were only loaded with colloidal Ag NPs [12].

Colour assessment of dyed fabrics loaded with Ag NPs

Our previous results indicated that Co fabrics turned from white to yellow after deposition of Ag NPs [12]. The higher the initial concentration of the colloid, the larger the colour difference. Significant change of the shape of reflectance curve particularly in the high energy region indicated the appearance of plasmon resonance band of Ag NPs. Accordingly, it could be expected that the presence of Ag NPs may also influence the colour of dyed Co fabrics. The colour of the dyed Co fabrics modified with Ag NPs was assessed by reflectance spectrophotometer. Dyed Co fabrics were colorimetrically evaluated using a CIE $L^*a^*b^*$ colour system. The colour coordinates and colour difference between dyed Co fabrics and Co fabrics that were loaded with Ag NPs after dyeing or Co fabrics that were finished in opposite order are summarized in table 3. It is evident that the order of dyeing and loading with Ag NPs significantly affected the colour of Co fabrics irrespectively of dye employed. The loading of Co fabrics with Ag NPs after dyeing caused considerable colour change that can be easily visually detected ($\Delta E^* > 1$). The colour change was more prominent on the Co fabrics that were dyed in lighter shades (0.5%). The higher the dye concentration the smaller the colour change. The strongest colour changes due to presence of Ag NPs were observed on the samples that were dyed with DY86

Table 3

CIE $L^*a^*b^*$ COORDINATES OF Co FABRICS DYED WITH DIRECT DYES AND LOADED WITH Ag NANOPARTICLES

Sample	L^*	a^*	b^*	C^*	h^*	ΔE^*
Co + DY86 0.5%	83.32	8.14	67.92	68.41	83.17	
Co + Ag + DY86 0.5%	81.26	7.37	62.65	63.08	83.29	5.43
Co + DY86 0.5% + Ag	70.24	7.28	58.70	59.15	82.93	15.22
Co + DY86 1%	78.13	15.45	76.00	77.56	78.51	
Co + Ag + DY86 1%	77.82	15.26	77.07	78.57	78.80	1.13
Co + DY86 1% + Ag	67.71	14.31	66.91	68.43	77.93	13.87
Co + DY86 2%	74.10	21.76	79.82	82.73	74.75	
Co + Ag + DY86 2%	73.33	20.86	78.02	80.76	75.03	2.15
Co + DY86 2% + Ag	65.63	21.86	71.82	75.07	73.07	11.65
Co + DR79 0.5%	50.38	45.64	4.57	45.86	5.72	
Co + Ag + DR79 0.5%	50.19	44.88	4.10	45.07	5.22	0.91
Co + DR79 0.5% + Ag	46.34	38.95	7.87	39.74	11.42	8.48
Co + DR79 1%	42.86	47.71	8.09	48.39	9.62	
Co + Ag + DR79 1%	42.86	47.43	8.08	48.11	9.67	0.28
Co + DR79 1% + Ag	40.65	41.32	9.93	42.50	13.51	7.00
Co + DR79 2%	36.16	44.15	10.73	45.44	13.66	
Co + Ag + DR79 2%	35.87	44.28	10.98	45.62	13.92	0.40
Co + DR79 2% + Ag	35.38	41.60	11.92	43.27	15.99	2.92
Co + DB78 0.5%	42.55	-4.43	-27.59	27.94	260.88	
Co + Ag + DB78 0.5%	42.38	-4.55	-27.08	27.46	260.47	0.55
Co + DB78 0.5% + Ag	41.08	-8.55	-18.06	19.98	244.67	10.49
Co + DB78 1%	34.45	-1.73	-26.89	26.94	266.33	
Co + Ag + DB78 1%	33.98	-1.46	-26.60	26.65	266.86	0.61
Co + DB78 1% + Ag	33.17	-5.24	-18.84	19.56	254.47	8.87
Co + DB78 2%	26.82	0.79	-23.43	23.45	271.93	
Co + Ag + DB78 2%	26.87	0.51	-22.92	22.93	271.28	0.58
Co + DB78 2% + Ag	26.66	-2.31	-15.99	16.16	261.78	8.06

where ΔE^* was mainly induced by the change of lightness (L^*) and chromaticity (C^*) and only slightly by the change of hue (h^*). These samples became darker and duller i.e. less saturated as C^* considerably decreased. On the other hand, the presence of Ag NPs caused the colour change of the Co fabrics dyed with DR79 and DB78 that was predominantly influenced by the change of C^* and h^*. Dyeing in higher concentrated dyebaths (1 and 2%) led to a negligible change of L^* which was particularly pronounced in case of the Co + DB78 2% + Ag fabric. In general, these samples also became darker and duller.

The opposite order of operations i.e. loading of Ag NPs prior to dyeing brought about considerably smaller colour changes. Colour difference of the Co fabrics that were dyed with DR79 and DB78 could not be visually detected as $\Delta E^* < 1$. Unlike these samples, Co fabrics dyed with DY86 underwent stronger colour change. This colour change dominated again on the sample which was dyed in lighter shade (0.5%) and it was mainly affected by the change of L^* and C^*.

Larger colour change of Co fabrics that were loaded with Ag NPs after dyeing can be attributed to larger amount of deposited Ag NPs as can be seen in figure 2. Namely, AAS analysis demonstrated that one gram of Co fabric which was only modified with Ag NPs and was not dyed contained approximately 64 μg of Ag. The results from figure 2 clearly indicate that the amount of deposited Ag NPs strongly depends on the order of dyeing and loading of Ag NPs. Dyeing after loading of Ag NPs resulted in decrease of Ag content because of the release of Ag NPs from Co fabrics during dyeing. In this case, Ag content ranged from 14–25 μg per g of Co fabric. Unexpectedly, Ag content in the samples that were dyed prior to loading of Ag NPs was two to four times higher compared to the samples that were only modified with Ag NPs and six to fourteen times higher compared to the samples that were loaded with Ag NPs before dyeing. It can be assumed that the presence of dyes on the Co fabric facilitates the binding of Ag NPs. It is well known that silver ions have affinity to atoms which donate pairs of electrons such as nitrogen and sulphur [17]. Hence, the interaction between sulphonic groups of

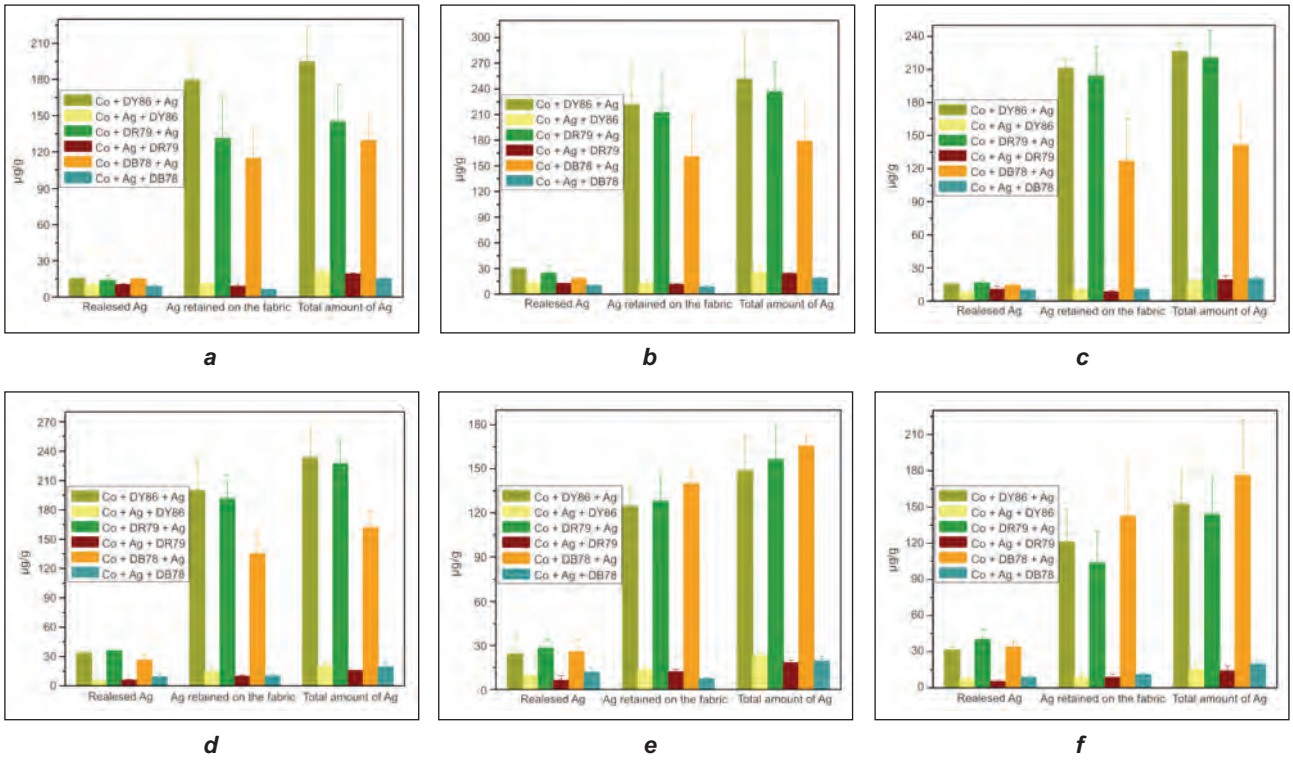


Fig. 2. Release of Ag in artificial sweat from:
a – Co fabrics dyed with 0.5% dye (*p*H 5.5); ***b*** – Co fabrics dyed with 0.5% dye (*p*H 8.0);
c – Co fabrics dyed with 1% dye (*p*H 5.5); ***d*** – Co fabrics dyed with 1% dye (*p*H 8.0);
e – Co fabrics dyed with 2% dye (*p*H 5.5); ***f*** – Co fabrics dyed with 2% dye (*p*H 8.0)

dye molecules and Ag NPs may be involved, eventually resulting in improved deposition of Ag NPs.

The stability of Ag NPs on Co fabrics in artificial sweat

The stability of Ag NPs deposited onto Co fabrics was tested in acidic and alkaline sweat. The data on perspiration fastness are presented in figure 2. Obtained results suggested that release of Ag occurred during the 24 hours long incubation in artificial sweat regardless of *p*H value. 34–61% of Ag was released in acidic sweat from the samples that were loaded with Ag NPs after dyeing. In acidic condition, all samples that were loaded with Ag NPs after dyeing with 0.5 and 1% of dye exhibited similar trend of Ag release (7–11%) independently of dye explored. Larger amount of Ag was released from the samples dyed with 2% of dye (16–18%). No specific behaviour was observed in regard to dye applied i.e. all dyes showed similar behaviour.

The Co fabrics that were loaded with Ag NPs after dyeing released significantly more Ag in alkaline (10–28%) than in acidic sweat. Similar observations were reported by Kulthong et al. [12]. No significant difference between Ag release in acidic and alkaline sweat from the Co fabrics that were loaded with Ag NPs and subsequently dyed was observed. Only slightly lower Ag release in alkaline sweat from the Co + Ag + DR79 and Co + Ag + DY86 samples occurred.

In general, the amount of released Ag in both, alkaline and acidic sweat is dependent on initial Ag content in the modified Co fabrics. Remarkably larger amount of Ag NPs remained on the fabrics that were loaded with Ag NPs after dyeing. In contrast, only small amount of Ag NPs are left on the samples that were finished in opposite way. Achieved results can be also the basis for some conclusions concerning the total amount of Ag in the samples. Namely, the total Ag content was calculated as a sum of Ag released from the samples into artificial sweat and Ag retained on the fabric. The results from figure 2 clearly indicate that the total content of Ag in the same Co fabrics that were exposed to alkaline and acidic sweat differs significantly. This was particularly pronounced in the samples that were loaded with Ag NPs after dyeing. Since the initial amount of Ag is independent of testing conditions during the perspiration fastness examination, it can be assumed that non-uniform deposition of Ag NPs onto Co fabrics is obtained and consequently, discrepancies in Ag content occurred.

Antibacterial activity of dyed Co fabrics loaded with Ag NPs

In order to study the bactericidal efficiency, Co fabrics loaded with Ag NPs before and after dyeing were subjected to antibacterial assay against gram-positive bacterium S. aureus and gram-negative bacterium E. coli. The results from table 4 and table 5 indicate that maximum bacterial reduction (R = 99.9%)

Table 4

BACTERICIDAL EFFICIENCY OF Co FABRICS MODIFIED WITH Ag NANOPARTICLES BEFORE AND AFTER DYEING AGAINST S. AUREUS		
Sample	**Number of bacterial colonies,** *CFU*	***R*,** %
Control Co	1.4×10^4	
Co + Ag + DY86 0.5%	<10	99.9
Control Co	3.1×10^4	
Co + Ag + DY86 1%	<10	99.9
Control Co	1.0×10^5	
Co + Ag + DY86 2%	115	99.8
Control Co	5.1×10^5	
Co + DY86 0.5% + Ag	30	99.9
Control Co	8.3×10^4	
Co + DY86 1% + Ag	10	99.9
Control Co	2.2×10^4	
Co + DY86 2% + Ag	<10	99.9
Control Co	8.5×10^4	
Co + Ag + DR79 0.5%	<10	99.9
Control Co	3.7×10^4	
Co + Ag + DR79 1%	10	99.9
Control Co	1.6×10^5	
Co + Ag + DR79 2%	<10	99.9
Control Co	2.3×10^4	
Co + DR79 0.5% + Ag	<10	99.9
Control Co	5.8×10^4	
Co + DR79 1% + Ag	20	99.9
Control Co	2.6×10^4	
Co + DR79 2% + Ag	<10	99.9
Control Co	9.0×10^4	
Co + Ag50 + DB78 0.5%	70	99.9
Control Co	6.6×10^4	
Co + Ag + DB78 1%	<10	99.9
Control Co	8.1×10^4	
Co + Ag + DB78 2%	25	99.9
Control Co	1.4×10^5	
Co + DB78 0.5% + Ag	15	99.9
Control Co	6.6×10^4	
Co + DB78 1% + Ag	<10	99.9
Control Co	4.9×10^4	
Co + DB78 2% + Ag	20	99.9

Table 5

BACTERICIDAL EFFICIENCY OF Co FABRICS MODIFIED WITH Ag NANOPARTICLES BEFORE AND AFTER DYEING AGAINST E. COLI		
Sample	**Number of bacterial colonies,** *CFU*	***R*,** %
Control Co	3.2×10^4	
Co + Ag + DY86 0.5%	<10	99.9
Control Co	8.5×10^4	
Co + Ag + DY86 1%	25	99.9
Control Co	1.2×10^5	
Co + Ag + DY86 2%	265	99.8
Control Co	1.1×10^5	
Co + DY86 0.5% + Ag	20	99.9
Control Co	2.2×10^5	
Co + DY86 1% + Ag	<10	99.9
Control Co	1.2×10^5	
Co + DY86 2% + Ag	15	99.9
Control Co	2.2×10^4	
Co + Ag + DR79 0.5%	<10	99.9
Control Co	9.1×10^4	
Co + Ag + DR79 1%	<10	99.9
Control Co	9.0×10^4	
Co + Ag + DR79 2%	<10	99.9
Control Co	3.2×10^4	
Co + DR79 0.5% + Ag	70	99.8
Control Co	9.1×10^4	
Co + DR79 1% + Ag	95	99.9
Control Co	5.7×10^4	
Co + DR79 2% + Ag	<10	99.9
Control Co	8.4×10^4	
Co + Ag + DB78 0.5%	<10	99.9
Control Co	1.2×10^5	
Co + Ag + DB78 1%	25	99.9
Control Co	8.4×10^4	
Co + Ag + DB78 2%	35	99.9
Control Co	2.4×10^5	
Co + DB78 0.5% + Ag	<10	99.9
Control Co	4.4×10^4	
Co + DB78 1% + Ag	15	99.9
Control Co	7.5×10^4	
Co + DB78 2% + Ag	<10	99.9

was obtained with most of the samples. Only few samples provided negligibly lower bacterial reduction of 99.8%. Excellent antimicrobial activity can be achieved independently of order of loading of Ag NPs and dyeing as well as on the dye applied and its concentration. Obviously, dyeing did not affect the antibacterial activity of Co fabrics loaded with Ag NPs. Equivalent results were obtained with dye C.I. direct red 81 in our previous research [12]. On the contrary, Lee at al. concluded that bacterial reduction was larger when the samples were treated with colloidal Ag NPs after dyeing than before dyeing, though the applied type of dye was not specified [2].

CONCLUSIONS

Cotton fabrics dyed with C.I. Direct Yellow 86, C.I. Direct Red 79 and C.I. Direct Blue 78 and loaded with colloidal silver nanoparticles provided excellent antibacterial activity against gram-positive bacterium S. aureus and gram-negative bacterium E. coli inde-

pendently of order of dyeing and nanoparticles loading, dye and dye concentration used.

The presence of silver nanoparticles influences the colour of dyed cotton fabrics. The colour of cotton fabric dyed with C.I. Direct Yellow 86 was considerably changed in the presence of silver nanoparticles. This was particularly pronounced when dyeing was performed before silver nanoparticles deposition. This order of operations led to similar effects on the fabrics that were dyed with two other dyes. However, in their case, opposite order of operations caused colour changes that cannot be visually detected.

The release of deposited silver nanoparticles in artificial sweat depends on the *p*H of the sweat as well as on the initial amount of silver in the fabrics. Stronger silver release from the samples that were loaded with silver nanoparticles after dyeing occurred in alkaline than in the acidic sweat, independently of dye and dye concentration. No considerable difference between silver release in acidic and alkaline sweat from the cotton fabrics that were loaded with silver nanoparticles and subsequently dyed was observed.

Obtained results pointed out that application of silver nanoparticles to textile materials must be carefully planed and many different aspects should be considered. Since antibacterial properties are equally good independently of order of dyeing and loading of silver nanoparticles, more attention should be paid on colouristic aspect. Obviously, dye hue and dye concentration should be delicately selected in order to diminish the negative effect of silver nanoparticles on the colour of the fabric. Loading of silver nanoparticles after dyeing of cotton fabric results in unacceptable colour change. On the other hand, this order of operations provides higher amount of deposited silver nanoparticles and better perspiration fastness. Thus, the final utilization of the textile product will dictate the selection of optimum conditions during finishing process.

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DOCUMENTARE

Noi tehnologii

O NOUĂ TEHNOLOGIE ÎN DOMENIUL SCAUNELE AUTO

Compania ***Johnson Controls*** în colaborare cu compania britanică ***Harrison Spinks***, specializată în producerea saltelelor de lux, a extins tehnologia dezvoltată în domeniul saltelelor şi la scaunele destinate automobilelor.

În anul 2012, companiei i s-a conferit premiul internațional *ÖkoGlobe,* pentru noul scaun auto *ComfortThin*, în cadrul categoriei "Optimizarea Resurselor, Materialelor şi Proceselor". Noua tehnologie elaborată de Johnson Controls se bazează pe transferul unor materiale uşoare şi reciclabile din alte industrii către un produs auto. Noul scaun creează un mare potențial de economisire a energiei, prin reducerea consumului de carburant, datorită caroseriei mai scurte.

Profilul subțire al scaunelor oferă pasagerilor un grad de confort ridicat, căptuşeala tradițională din spumă poliuretanică fiind înlocuită cu arcuri elicoidale cu buzunare, amortizate şi fixate de materialele nețesute. Astfel, se creează mai mult spațiu pentru pasageri, de exemplu, în cazul autoturismelor, spațiul este cu până la 35 mm mai mare pentru picioare şi genunchi – la locurile din spate, fără modificarea spațiului interior. Pe lângă faptul că această alternativă este 100% reciclabilă, aplicarea ei are ca rezultat o reducere a greutății cu 20%, ceea ce, în cazul unui vehicul de categorie mică sau medie, reprezintă 4,5 kg. Gradul de confort rămâne acelaşi, dar vehiculele sunt mai uşoare şi mai compacte şi pot fi dotate cu motoare mai eficiente, cu capacitate mai mică. Testarea scaunului acestor maşini a avut un rezultat pozitiv şi a stârnit interesul producătorilor de autovehicule.

Noua tehnologie va fi disponibilă pentru modelele de vehicule care vor apărea pe piață în anul 2015.

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Color and fastness properties of printed with reactive dye viscose fabrics and fixed with radio frequency energy

ARZU YAVAS

REZUMAT – ABSTRACT

Performanța culorii şi proprietățile de rezistență a vopsirii materialelor textile din viscoză, imprimate cu coloranți reactivi şi fixate cu unde de radiofrecvență

În cadrul acestui studiu, textile din viscoză, tratate şi netratate alcalin, au fost imprimate cu coloranți reactivi. Fixarea țesăturilor din viscoză imprimate cu coloranți reactivi a fost posibilă doar în condiții de aburire. Mostrele imprimate cu coloranți reactivi – netratate şi tratate alcalin – au fost fixate concomitent cu abur şi frecvențe radio. Eficacitatea vopsirii mostrelor fixate cu abur şi unde de radiofrecvență a fost comparată cu cea a mostrelor fixate prin metoda clasică cu abur, la 102ºC, timp de 10 minute. Aplicarea concomitentă de abur şi frecvențe radio pe textilele tratate alcalin nu a condus la o eficiență mai mare a vopsirii, comparativ cu metoda clasică de fixare cu abur. Cu toate acestea, s-au obținut valori similare, însă numai pentru perioade scurte de timp. Nu s-a constatat niciun efect negativ al fixării cu unde de radiofrecvență şi abur asupra proprietăților de rezistență a vopsirii.

Cuvinte-cheie: radiofrecvență, abur, imprimare cu coloranți reactivi, materiale textile, viscoză, caustificare, fixare, proprietăți tinctoriale, eficacitatea vopsirii

Color and fastness properties of printed with reactive dye viscose fabrics and fixed with radio frequency energy

In this study, causticized and un-causticized viscose fabrics were printed with reactive dye. Fixation of printed viscose fabrics with reactive dyes was only possible under steaming conditions. Reactive printed samples (untreated and causticized) were treated with radiofrequency and steam combination. Color efficiencies of the samples fixated with radiofrequency and steam combination were compared with a conventional steam, at 102ºC for 10 minutes. An application of steam combination with radiofrequency energy on causticized fabrics did not lead to a higher color performance in comparison to the color performance resulting from classical steaming method. However similar values were obtained for shorter durations. There was no negative effect of fixation with radiofrequency and steam combination on color fastness properties.

Key-words: radio frequency, steam, reactive printing, fabrics, viscose, causticising, fixating, color properties, color efficiency

As it is known, viscose fiber is produced from tree cellulose. Some of the important advantages of this fiber are its purity, high clothing comfort, high absorbency, natural and high luminiscence, skin-friendly nature and breathing capability [1, 2]. Viscose fibers are clean fibers as a result of their structures and production type, due to this reason and their low durability aganist alkaline; an alkaline treatment is not needed. However, it is useful to perform a good washing prior to bleaching and dyeing. Causticization application is generally recommended before the application of reactive printing in order to obtain high color performances. Fiber swelling in caustic soda solution of 4–6°Bé at room temperature, under tensionless conditions, improves the color strength of the fabric print. The fabric should be well rinsed, but not neutralised, to accomplish the maximum swelling effect [3]. Causticisation process modifies the surface or skin of the viscose fibre in order to enable more rapid diffusion of dye into the fibre. Causticizing process is especially recommended for the repeatable results of printing and dyeing processes. Viscose fibers swell and get smoother and the pilling tendency of viscose fabrics are slightly reduced after causticizing. Additionally, since causticizing alone is adequate as a pre-treatment process for white greige viscose fabrics, the risk of catalytic damage during the bleaching process will be entirely eliminated [4]. The color efficiency of the printed and dyed fabric was increased with the causticizing pre-treatment process [5–8].

Reactive printed products constitue nearly 25–27% of total printing production in the world [9, 10]. Reactive dyes generally exhibit high wet fastness, bright colors and diverse color range and they are the second most used colorants after pigment dyes. The fixation of most reactive dyes is effected by saturated steam at 100–103°C for 10 minutes [3].

Significant effects of water steam on reactive printing process are listed below [11]:

- It is the producer of water in each single step methods due to the condensation;
- It enables water condensation on dry and cold fabric which is processed in the steamer;

- It provides energy for dyestuff difusion acceleration;
- It provides energy for chemical reactions of fixation process.

Radio frequency, *RF*, drying is a drying technique in which the material to be dried is passing through a high frequency electric field generated by a radiofrequency generator, between a set of parallel plate or bar electrodes/applicators (fig. 1). The industrial frequencies in the *RF* region are 13.56, 27.12 ve 40.68 MHz, the region for the microwave, *MW*, is between 910 and 2850 MHz [13].

Radio frequency heats volumetrically at molecular level, heating selectively wetter areas in the material. In high frequency drying, different from conventional drying methods, the required heat is not introduced from outside, yet it is generated inside of the material itself. If an alternating field set up by a high frequency generator is applied to a wet textile substrate, it excites the water molecules so that they rapidly and continuously change their polarity and oscillate about their position [14].

When frequency is applied to any product located between two electrodes which work as capacitor plates, the polarity of the potantiel changes according to the applied frequency. For example, 27.12 MHz means 27 120 000 polarization in a second [15]. Heat is occurred due to the work done by polar molecules. The materials that are not dipolar (un-chargeable) can not be heated. Moreover, the usage of *RF* for drying, another key properties of the *RF* drying which makes it attractive for dye fixation are the uniform and heating speed abilities under the appropriate conditions [16].

Microwave-promoted organic reactions (known as environmentally benign methods) can accelerate a great number of chemical processes [17]. High frequency energy can be used for dye fixation. There are some studies in which microwave energy is used in textile treatments, especially in pre-treatment and dyeing processes. For example, microwave energy is used in dyeing of cotton fibers with reactive dyestuff [16, 18] and dyeing of wool fibers with reactive dyestuff [19]. Dupont G. [20] used radiofrequency energy in the fixation of 1:2 metal complex dyestuffs into wool fibers. Kale J. et. al. [21] performed microwave pre-process for PES fiber in the existence of solvents and then pes fiber was dyed in varying temperatures and durations with selected commercial disperse dyestuffs (C.I. Disperse Red 91, C.I. Disperse Blue 26). According to the results of scanning electron microscope (SEM), pre-process of PES with microwave in company with solvents led to some structural changes such as surface roughness and gap formation. As a result, dye exhauastion has increased three times compared to classical methods. In the studies conducted by Kim S.S et. al. [22], polyester fibre was padded with urea and sodium chloride solution for ten minutes and then dyed using microwave technology (2 450 MHz, 700 W) for 7 minutes. It was ascertained that the solvent that was added into the padding bath, its type and concentration was effective on *K/S* values of dyed PES fiber.

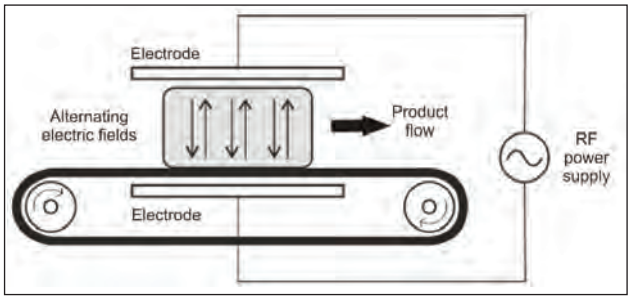

Fig. 1. Working principle of *RF* dryer [12]

Weilin and Yang [23] treated PES fiber with sodium hydroxide solvent under microwave radiation. It was observed that the increase in microwave power and sodium hydroxide concentration led to an increase in weight loss along with an increase in the decrease of thickness of the PES fiber. In comparison to the classical methods, it was determined that there was an increase on hydrolysis with microwave. Treated PES fabric which was dyed via microwave energy exhibited increased dye exhaustion as the weight loss of hydrolized PES fibre was increased. Microwave energy utilization in finishing processes has been also investigated in the recent years. For example, the applicability of microwave in finishing processes was investigated by Katović D. et. al. [24]. In order to achieve water and/or oil repellent, flame retardent and crease resistant cellulosics fiber, drying and fixation processes were performed via benefiting from both classical methods and microwave energy. The usage of microwave energy led to some improvements on crease resistant finishing processes which formaldehite oscillation decreased. In the studies conducted by Xue et. al. [25], antimicrobial finishing fixation of wool fiber with chitosan biguanidine hydrochloride was conducted via microwave energy. It was stated that fixation with microwave energy was much more efficient in comparision to classical method. In the event of microwave usage, drying step can be eliminated and fixation can be completed in two minutes, on the other hand, classical method fixation can be completed in ten minutes. It was concluded that the samples which were fixed using microwaves at 700 W irradiation power for 2 minutes exhibited slightly more crosslinking formation and slightly higher antimicrobial activity without losing substantial strength loss. Easy care and antibacterial properties were obtained on cotton fibers using glyoxal, glutaraldehyde and 1, 2, 3, 4 butanetetracarboxylic acid (BTCA) and water soluble chitosan with microwave fixation [26]. It was stated that microwave curing system was beneficial for an easy care and antibacterial cotton fabric production without high strength losses. We investigated the fixation of reactive printed cotton fabrics with microwave and radio frequency energy in our earlier studies [27, 28]. In this current study, viscose fabrics were subjected to causticization process. After causticing, reactive printing process was

applied. Steam fixation method is used for the fixation of the reactive printed viscose fabrics. In this study, which is different from the conventional methods, reactive printed goods were fixed through the use of combination of *RF* energy and steam. With this combination, the need for steam in heat formation in radio frequency environment was solved and steam energy was used for the dye fixation. Color efficiency, color and fastness properties of samples which were fixed via both methods were investigated.

EXPERIMENTAL PART

Fabrics used

In this study, a plain woven 100% viscose fiber fabric with the following characteristics: in warp 28 threads/cm, in weft 27 threads/cm, fabric weight 140 g/m^2, whiteness degree: 78.48 (Stensby).

Methods used

Causticizing process was carried out in laboratory conditions with the involvement of a domestic washing machine (Raks). The thickeners used were low viscosity and high viscosity sodium alginates. Lamitex L (8%) low-viscosity and Lamitex S (4%) high-viscosity alginates were provided by ProChem Tekstil Kimya Sanayi ve Tic. A.S., Turkey. The selected dye was Novacron Red P-4B (C.I. Reactive Red 245; small molecule low reactivity MCT-Monoazo reactive dye) supplied from Huntsman (fig. 2). In printing paste 30 g/kg Novacron Red P-4B was used.
Different printing pastes were prepared which contained 100, 150 and 200 g/kg urea (table 1) in order to investigate the polarization increasing effect of the urea. Viscosity degree of printing paste was measured with a SC4-28 spindle using a Brookfield DV3 Rheometer and measuring viscosity degree 60 000 mPas as a base. Fabrics were printed at 4 m/minutes at press

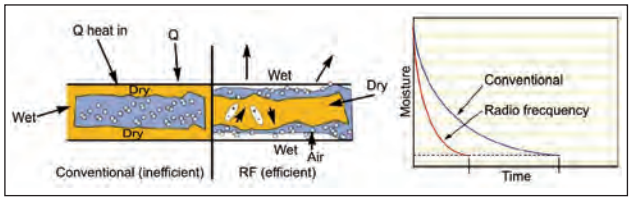

Fig. 2. Comparasion of *RF* drying with conventional drying [14]

Table 1

PROCESS CONDITIONS	
Causticizing	**Printing paste**
10^{0}Bé NaOH	30 g Reactive dye
35ºC, 7 minutes	*X* (100, 150, 200) g Urea
LR 1/15	25 g Sodiumbicarbonate
	10 g Ludigol
	500 g Thickener*
	Y water/paste, 1 000 g

* low viscosity and high viscosity sodium alginates

5 on J. Zimmer MDK laboratory type printing machine with 70 Nr PES gauze and a doctor blade 10 mm in diameter in laboratory conditions. Printed fabrics were dried in a laboratory type Rapid Drying machine at 100°C for 2 minutes.

The dye fixation

The printed fabrics were steamed for 10 minutes at 102°C with a laboratory-type steamer (Mathis) for the dye fixation. Fabrics were treated in *RF* machine with only steam and steam and *RF* combination in order to observe the effect of *RF*. To determine the optimum *RF* treatment time, different time intervals were tried as 1, 3, 5 minutes. In addition to different time intervals, experiments were carried out under two different current values as 300 A and 500 A. Properties of prototype stray-field *RF* dryer which was used in experiments are shown on table 2.

Table 2

PROPERTIES OF PROTOTYPE STRAY-FIELD *RF* DRYER	
Prototype stray-field RF dryer	
Frequency	27.12 MHz
Maximum output power	10 kW
Oscillator type	BR1196 F-air cooling triod tube

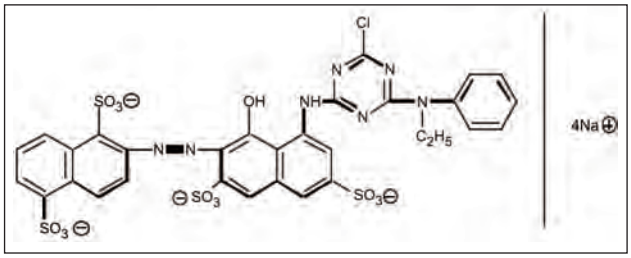

Fig. 3. Structural formula of Novacron Red P-4B

The cooling ventilator was a 220 V, with a snail-helix silicone diode, and with 3 phase full wave plate output condensator. Resistances were located in the upper side of the cabin in order to prevent the vapour condensation during the radio frequency and vapour combination. If not, condensed vapour may drop onto the printed fabric which may disorder-disrupt the printed pattern. In the reaction cabin, there are some vantilators for excessive vapour removal. In the upper side of the electrodes, there were two perforated vapour pipes that transport the vapour coming from the generator. Moreover, there is a perforated plate on these pipes that prevents the direct vapour transport to the fabric. Fabric transport was carried out by using a needled chain system akin as in conventional drying systems that provides non-contact, stretch mode to the electrodes (fig. 3).

Washing process

The fabrics were washed off to remove unfixed dyes and residual materials on the surface. After the fixation,

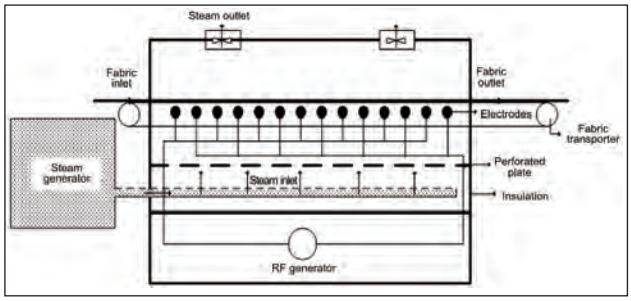

Fig. 4. The schematic view of the prototype *RF* dryer combined with steam generator [28]

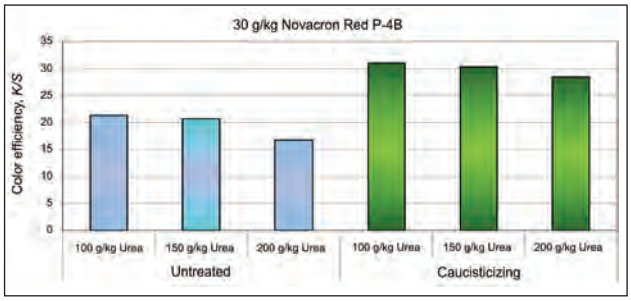

Fig. 5. Effect of causticizing on the color efficiency

fabrics were rinsed: cold rinse for 10 minutes, hot rinse for 5 minutes, hot washing for 5 minutes, cold rinse for 5 minutes and dried at room temperature.

Color measurements

Datacolor 600 (USA) was used for the evaluation of color efficiency. A fabric which was steamed at 102°C for 10 minutes was selected as a reference fabric.

Color fastness measurements

The color fastness to washing and rub (crocking) of printed fabrics was carried out and assessed according to ISO 105-C06/C2S and ISO 105-X12, respectively.

RESULTS AND DISCUSSIONS

Color efficiency of causticizatized and non-causticizatized printed samples, which were fixed with conventional methods are seen in figure 4. The effect of causticiting on the increase of color efficiency is quite clear. When the quantity of urea on the printing paste increased up to 200 g/kg, it was observed that there was a decrease in color efficiency of both caustisized and non-causticized samples.

Effect of fixation methods

The samples printed with 100–150–200 g/kg urea were fixed in the *RF* machine with only steaming (with the steam fed in radiofrequency dryer), radiofrequency energy and steam combined *RF* (under different power). The highest color yield (21.22) was achieved with fixation of reactive printed samples via saturated steam, which is a conventional method – 102°C for 10 minutes, Mathis AG, laboratory-type steamer (fig. 5).

In the event of application of radiofrequency energy with steam combination, the results obtained in a short duration like 1 minute are very similar to that of steaming. Fixation conducted via radiofrequncy with steam combination (300 A) for 5 minutes resulted in the same color efficiency with the classical method (21.04).

The amount of urea increase on printing paste did not have a positive effect on radiofrequncy and steam combination. Morever, it resulted in a slight reduction in color efficiency. The usage of urea, when printing with MCT based reactive dyes, improves the dissolution of the dyes. However, in the case DCT based reactive dyes, there are both very good soluble and poor soluble dyes [29]. Therefore, the amount of urea, which should be chosen according to the solubility of used reactive dye, and color yield of the sample can change accordingly. Novacron Red P-4B reactive dyes, based on MCT, has high solubility (more than 300 g/L) in water at 20°C (*p*H 7.3). Therefore, an increase on the amount of urea used in printing paste resulted in a decrease on the color yield of the printed substrate. The best results are obtained in the application of radiofrequncy energy when it is worked with 100 g/kg urea on the printing paste. Causticizing greatly increased color efficiency in fixation compared to both steaming and radiofrequncy methods (fig. 6). The change in the content of urea on the printing paste in the fixations conducted via radiofrequency energy had no important role in the color efficiencys of the samples that have experienced causticization process. Neverthless, it can be stated that the most convenient urea concentration was 100 g/kg.

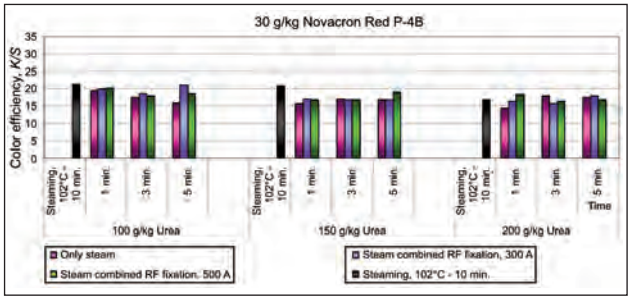

Fig. 6. Effect of fixation method on the color efficiency of un-treated viscose fabrics printed with Novacron Red P-4B

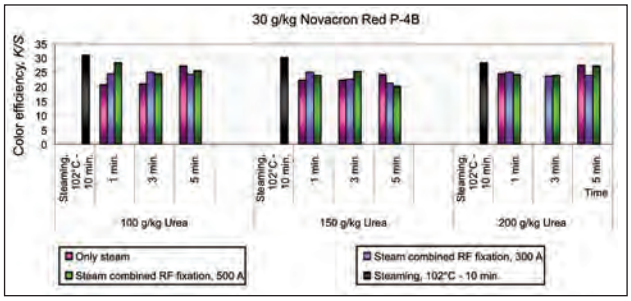

Fig. 7. Effect of fixation method on the color efficiency of the causticized viscose fabrics printed with Novacron Red P-4B

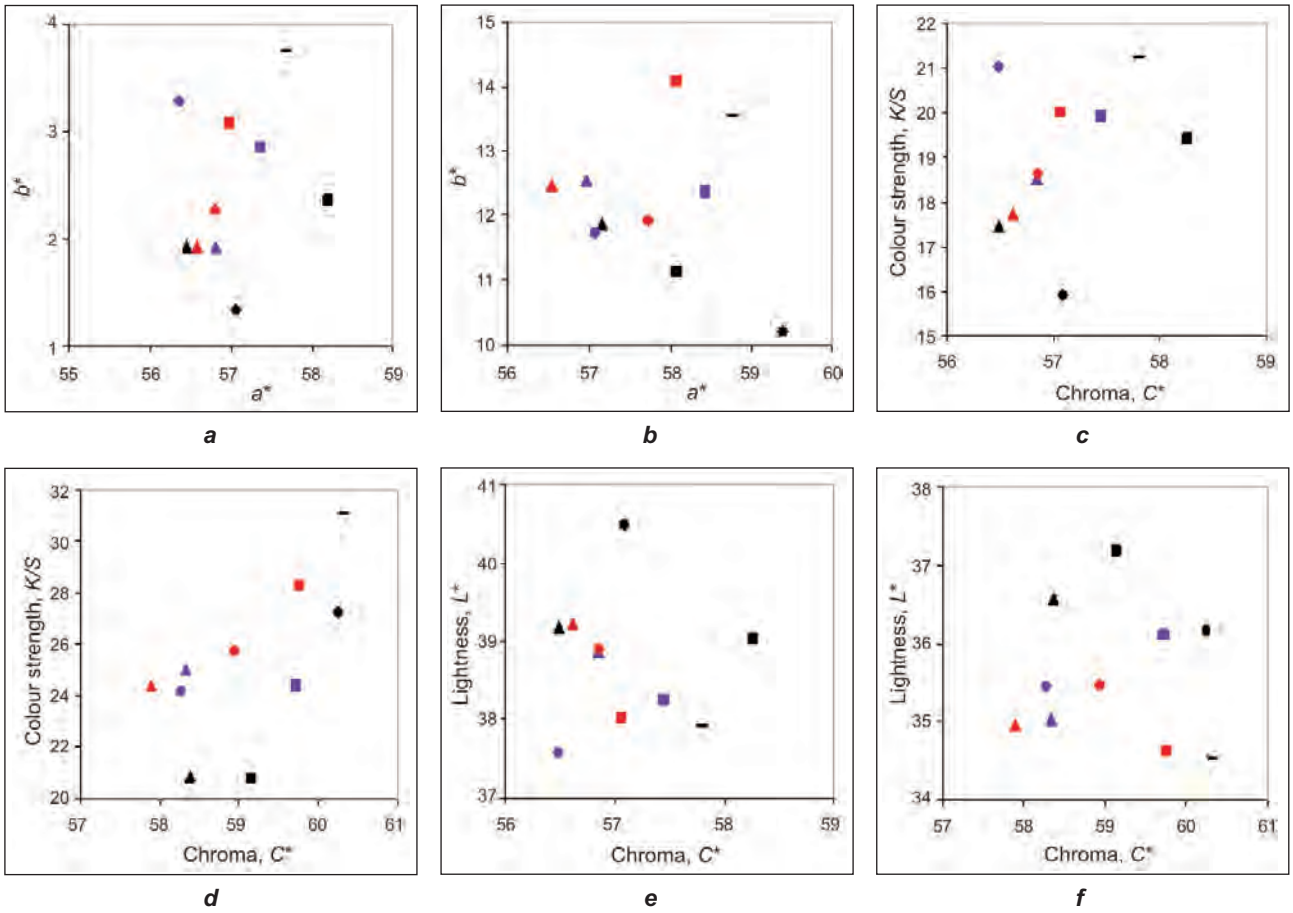

Fig. 8. 100 g/kg urea, $a^* - b^*$, $K/S - C$, $L - C$ diagrams*:
a – untreated samples, $a^* - b^*$ diagram; **b** – causticizing samples, $a^* - b^*$ diagram;
c – untreated samples, $K/S - C^*$ diagram; **d** – causticizing samples, $K/S - C^*$ diagram;
e – untreated samples, $L^* - C^*$ diagram; **f** – causticizing samples, $L^* - C^*$ diagram

* Black line = Steaming 102°C for 10 min.; Black square = Only steaming 1 min.; Blue square = Steam combined RF fixation (300 A) 1 min.; Red square = Steam combined RF fixation (500 A) 1 min.; Black triangle = Only steaming 3 min.; Blue triangle = Steam combined RF fixation (300 A) 3 min., Red triangle = Steam combined RF fixation (500 A) 3 min.; Black circle = Only steaming 5 min.; Blue circle = Steam combined RF fixation (300 A) 5 min.; Red circle = Steam combined RF fixation (500 A) 5 min.

When the printing paste contains 100 g/kg urea, the color efficiency of the sample that is fixed with steam in radiofrequency dryer (without radiofrequency energy) for one minute was 20.75, while the color efficiency of the sample that was fixed with the combination of radiofrequncy with steam combination (500 A) for the same duration reached to 28.25. In this case, the color efficiency of the sample that was fixed with the combination of radiofrequency with steam combination (28.25) reaches to the color efficiency that was obtained via classical steaming (31.02), which was taken as a referrence.

While better results were obtained in all urea concentrations worked out via classical steaming, especially in 100 g/kg urea concentrations, radiofrequency energy provide an advantage with shorter durations.

Color properties

The color properties of the samples causticized (having 100 g/kg urea) are compared with that of un-causticized samples. When figures 8 *a* and *b* are analyzed, it is observed that there was a significant increase in b^* values (blue-yellow axis) of samples after causticizing; in other words, the samples became more yellow. Processed samples were more red, with an incrase on their values (red-green axis), in comparison to unprocessed samples.

The samples, which had the closest *a* and *b* values to the reference (fixed with classical method), were the ones that were fixed via radiofrequency energy and steam combination at 300 A for 1 minute and the ones that were fixed again with radiofrequency energy and steam combination in 500 A for 1 minute.

The increase in C^* value means that the samples' distance to the colorlessness axis increases. Lustrous colors are better expressed with chroma. Figures 8 *c* and *d* show that C^* (Chroma) values of processed samples; in other words, their saturation, were higher than those of unprocessed samples. The color efficiencys of proceesed samples have also increased prominently. The sample, that has the closest color efficiency value to the reference sample, is the sample which was fixed with radiofrequency and stream combination at 500 A for 1 minute duration.

In unprocessed samples, the sample that has the closest color efficiency value *K/S* to the reference

sample, is the sample which was fixed with radiofrequency and stream combination in 300 A for 5 minutes. Having analyzed *L** (lightness) and *C** (Chroma) graphics of proceesed and unprocessed samples, it was observed that *L** values processed samples were decreased; in other words, colors of samples became darker (figures 8 *e* and *f*). The samples with the lowest *L** values are the reference fabric and the sample that was fixed with radiofrequency and steam combination at 500 A for 1 minute. While the *C** value of the sample that is fixed with only steam in radiofrequency dryer was very close to the reference sample, its *L** value was higher than that of reference sample. The samples with high *L** values are the ones that were only fixed with the steam in radiofrequency dryer, which was also confirmed by their *K/S* values. In un-processed samples, following both samples, radio frequency and steam combination with 300 A for 1 minute and radio frequency and steam combination with 500 A for 1 minute, exhibited the smallest color differences by 1 and 0.98 in comparison to the sample fixed with classical method (table 3). The lowest color difference value in processed samples was 0,87 and it belongs to the sample that is fixed via radiofrequency and steam combination with 300 A for one minute (table 4). Caustisizing process resulted in an increase on *h** values. For both processed and un-processed samples, the closest *h** values to the reference sample were obtained via samples that

Table 3

COLOR PROPERTIES OF UNTREATED FABRICS							
100 g/kg urea (untreated) samples	***K/S***	***L****	***a****	***b****	***C****	***h°***	***dE***
Steaming* (102ºC - 10 min.)	21.2	37.91	57.68	3.74	57.8	3.71	Referans
Only steam** 1 min.	19.4	39.03	58.21	2.35	58.26	2.31	1.86
Steam combined *RF* fixation*** (300 A) 1 min.	19.9	38.25	57.38	2.85	57.45	2.85	1.00
Steam combined *RF* fixation**** (500 A) 1 min.	20	38.02	56.98	3.07	57.06	3.09	0.98
Only steam 3 min.	17.5	39.17	56.46	1.92	56.49	1.95	2.53
Steam combined *RF* fixation (300 A) 3 min.	18.5	38.86	56.81	1.9	56.84	1.92	2.25
Steam combined *RF* fixation (500 A) 3 min.	17.7	39.21	56.59	1.92	56.62	1.95	2.49
Only steam 5 min.	15.9	40.48	57.07	1.32	57.09	1.33	3.58
Steam combined *RF* fixation (300 A) 5 min.	21	37.57	56.39	3.28	56.48	3.33	1.41
Steam combined *RF* fixation (500 A) 5 min.	18.6	38.89	56.81	2.26	56.85	2.27	1.98

* *Steaming* is conventional method (Steaming in Mathis steamer at 102ºC for 10 minutes);
** *Only steam* is fixation with steam fed in radiofreqeucy dryer (without radiofreqeuncy energy);
*** *Steam combined RF fixation (300 A)* is fixation with steam fed in radiofreqeucy dryer and radiofreqency energy (while the machine is working with 300 A) applied simultaneously;
**** *Steam combined RF fixation (500 A)* is fixation with steam fed in radiofreqeucy dryer and radiofreqency energy (while the machine is working with 500 A) applied simultaneously.

Table 4

COLOR PROPERTIES OF UNTREATED FABRICS							
100 g/kg urea (untreated) samples	***K/S***	***L****	***a****	***b****	***C****	***h°***	***dE***
Steaming* (102ºC - 10 min.)	31.1	34.54	58.78	13.56	60.32	12.99	Referans
Only steam** 1 min.	20.8	37.17	58.09	11.14	59.15	10.86	3.64
Steam combined *RF* fixation*** (300 A) 1 min.	24.4	36.1	58.43	12.37	59.73	11.95	1.99
Steam combined *RF* fixation**** (500 A) 1 min.	28.3	34.63	58.09	14.08	59.77	13.62	0.87
Only steam 3 min.	20.9	36.57	57.16	11.87	58.38	11.73	3.10
Steam combined *RF* fixation (300 A) 3 min.	25.1	35.04	56.97	12.55	58.34	12.42	2.13
Steam combined *RF* fixation (500 A) 3 min.	24.4	34.97	56.53	12.48	57.9	12.45	2.53
Only steam 5 min.	27.3	36.15	59.4	10.19	60.27	9.74	3.79
Steam combined *RF* fixation (300 A) 5 min.	24.1	35.44	57.09	11.73	58.28	11.61	2.65
Steam combined *RF* fixation (500 A) 5 min.	25.8	35.47	57.74	11.92	58.95	11.66	2.15

* *Steaming* is conventional method (Steaming in Mathis steamer at 102ºC for 10 minutes);
** *Only steam* is fixation with steam fed in radiofreqeucy dryer (without radiofreqeuncy energy);
*** *Steam combined RF fixation (300 A)* is fixation with steam fed in radiofreqeucy dryer and radiofreqency energy (while the machine is working with 300 A) applied simultaneously;
**** *Steam combined RF fixation (500 A)* is fixation with steam fed in radiofreqeucy dryer and radiofreqency energy (while the machine is working with 500 A) applied simultaneously.

Table 5

COLOR FASTNESS PROPERTIES OF UNTREATED AND CAUSTICIZED FABRICS													
Amount of urea (g/kg), in paste	**Untreated**												
100 g/kg	***Fixation methode***	***Wash fastness***						***Crock fastness***					
		Color change			*Staining of cotton*			*Dry*			*Wet*		
	Steaming (102ºC, 10 min.)	-			-			5			3		
	Fixation time	1 min.	3 min.	5 min.	1 min.	3 min.	5 min.	1 min.	3 min.	5 min.	1 min.	3 min.	5 min.
	Only steam (without *RF* energy)	5	5	5	5	5	5	4-5	5	5	3	3-4	3-4
	Steam combined *RF* fixation (300 A)	5	5	5	5	5	5	5	5	5	3	3-4	3-4
	Steam combined *RF* fixation (500 A)	5	5	5	5	5	5	5	5	5	3	3-4	3-4
Amount of urea (g/kg), in paste	**Causticizing**												
100 g/kg	***Fixation methode***	***Wash fastness***						***Crock fastness***					
		Color change			*Staining of cotton*			*Color change*			*Staining of cotton*		
	Steaming (102ºC, 10 min.)	-			-			5			3		
	Fixation time	1 min.	3 min.	5 min.	1 min.	3 min.	5 min.	1 min.	3 min.	5 min.	1 min.	3 min.	5 min.
	Only steam (without *RF* energy)	5	5	5	5	5	5	4-5	4-5	4-5	3-4	3-4	3
	Steam combined *RF* fixation (300 A)	5	5	5	5	5	5	4-5	4-5	4-5	3-4	3	3
	Steam combined *RF* fixation (500 A)	5	5	5	5	5	5	4-5	4-5	4-5	3-4	3	3

were fixed with radiofrequncy and steam combination. Similar *h** values show that there was no color shift in samples.

As a result, both caustisized and un-causticized samples can be fixed with radio frequency energy with steam combination without significant changes in their color properties.

Fastness properties

Fastness properties of printed samples were analyzed for printings conducted via paste including 100 g/kg urea, which led to the highest color efficiency values (table 5). The wash and dry rub (crock) fastness of the printed fabrics were good enough for all fixation types. Caustizised printed samples have lower wet and dry rubbing fastness values in comparision to un-causticized fabrics. This difference was 0.5 points by gray scale rating. It is considered that this difference results from the fact that causticized fabrics have higher color efficiency. Fixation with radiofrequency with steam combimation results in no major change in both rubbing and washing fastness of samples compared to the fastness properties of samples fixed with classical method (table 5).

CONCLUSIONS

It is generally recommended that causticization should be conducted on viscose fabrics before printing as a result of its color efficiency improvement property. In this study, causticized and non-causticized samples were subjected to fixation with classical steaming and radiofrequency with steam combination methods.

When the color efficiencies of printed (with monochlortriazin based reactive dyestuff) causticized and non-causticized viscose fibers are compared, color efficiencies obtained via radiofrequency with steam combination and classical method (steamed for 10 minutes at 102°C) were similar.

Fastness properties of samples that are printed with 30 g/kg Novacron Red P 4B and fixed with radiofrequency energy were at the same level with the fastness properties obtained via classical fixation method. Radiofrequency with steam combination can be applied as an alternative method for the reactive printing of viscose fibers and it can be applied to causticized fibers before printing.

Optimum urea quantity was 100 g/kg and the most convenient fixation conditions are radiofrequency and steam combination for 1 minute, which gives the closest results to the classical steaming reference method.

Optimum urea quantity on printing paste and fixation durations for the dyestuffs with different molecular size should be determined in the further studies.

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Composite materials with conductive polymers content

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REZUMAT – ABSTRACT

Materiale compozite cu conținut de polimeri conductivi

În lucrare s-a urmărit obținerea unor materiale textile cu proprietăți electroconductive îmbunătățite, prin acoperirea țesăturilor din poliamidă şi bumbac cu polianilină dopată. Polimerizarea anilinei s-a realizat in situ şi prin dopare directă cu DBSA şi DBSNa. Scopul cercetării l-a constituit evidențierea influenței acidului DBSA şi a sării DBSNa asupra caracteristicilor conductive ale probelor obținute. Proprietățile țesăturilor au fost determinate prin măsurarea rezistivității electrice de suprafață. Structura şi morfologia acestora au fost analizate prin spectroscopie FT-IR, cu aparatul ATR, şi microscopie electronică de baleiaj. Morfologia materialelor acoperite a fost puternic influențată de dopantul utilizat – sare sau acid. S-a constatat că, în cazul dopantului în formă acidă, au rezultat particule de 10 de ori mai mari. De asemenea, testele efectuate au evidențiat faptul că, în cazul folosirii sării de sodiu ca dopant, materialele compozite posedă o conductivitate mai mare.

Cuvinte-cheie: polianilină dopată, polimerizare in situ, țesături, nailon 6.6, bumbac

Composite materials with conductive polymers content

In this paper we aimed to obtain textiles with electrically conductive properties improved by coating polyamide and cotton fabrics with doped polyaniline. Polymerization of aniline was performed in situ and by direct doping with DBSA and DBSNa. In this paper we aimed to influence the use of acid (DBSA) or salt (DBSNa) on conductive characteristics of the samples obtained. The fabrics performances were tested by surface electrical resistivity, while the structure and morphology were determined by FT-IR spectroscopy with ATR device and Scanning Electron Microscopy. The morphology of coated materials were strongly dependent of dopant (salt or acid) resulting grains size of 10 times bigger in case of acid dopant. Other tests also evidenced the differences between composite materials. Even if in the literature the acid was mostly used, in this study the composite materials with sodium salt as dopant were more conductive.

Key-words: doped polyaniline, in situ polymerization, fabric, nylon 6.6, cotton

Composite materials with intrinsically conducting polymers (ICP) attract much attention due to their applications as sensor, antistatic materials, electromagnetic interference shielding (EMI) and membrane materials [1–4]. Most used intrinsically conducting polymers (ICP) are polyaniline, polythiophen and polypirolle. Polyaniline (PANI) is known for it the advantages as low cost of monomer, good mechanical properties and thermal stability in conductive form, but it presented a low solubility in organic and inorganic solvents. The main methods of producing PANI-based composites are polymerization in solutions (chemical and electrochemical), adding different dopants, soluble polymers or thermoplastics [5–9].

The methods to increase the electrical properties of powders and thin films [10–11] were the doping with long chains compounds and/or emulsion route synthesis. The modifying properties of selected dopant make possible the obtaining of polyaniline in a form more conductive and soluble in standard solvents [12]. The doping can be realized direct or indirect (redoping). In the direct doping the dopant ion was added in initial reaction mass.

The studies of textile materials coated with polyaniline were made on polyester [13–15], wool [14, 15], cotton [14–16], Nylon 6 [14–17], and acrylics [14,15]. The aim of this paper was to obtain composite materials using polyaniline as intrinsically conducting polymers; dodecylbenzenesulphonic acid (DBSA) and sodium dodecylbenzene sulfonate (DBSNa) as dopants; and the cotton fabric with a mass of 107 g/m^2 and the polyamide fabric (type Nylon 6,6) with a mass of 112 g/m^2 as textile substrates. DBSA was choosing as dopant based on literature data that consider organic acids with long chain and sulfonic groups the best dopants for polyaniline films [18, 19].

Sodium dodecylbenzenesulfonate (DBSNa) is a well-known anionic surfactant exhibiting a recalcitrant molecular structure. Surfactants are the main ingredient of laundry detergents and they are also extensively used in cosmetics and dyeing of fabrics in textile industry [20].

DBSNa was used thinking that even after washing with detergents the obtained composites will keep their color and electrical properties. Poly (N-vinylpyrrolidone) (PVP) was added as steric stabilizer [21].

The “in situ” polymerization directly on textile materials were used for elimination of disadvantage given to the low solubility of polyaniline in solvents and to increase the electrical properties.

EXPERIMENTAL PART

Raw materials

For the preparation of composite textiles were used: aniline 99% (Sigma-Aldrich); poly(*N*-vinylpyrrolidone) (PVP; Merck); sodium dodecylbenzenesulfonate (DBSNa) of 80% purity from Fluka; dodecylbenzene-sulfonic acid (DBSA) of 90% purity from Fluka; ammonium persulphate (Merck); the cotton fabric with a mass of 107 g/m^2 and the polyamide fabric (type Nylon 6,6) with a mass of 112 g/m^2 (cotton and Nylon 6,6).

Synthesis procedure

The textile material previously washed with deionized distilled water was added into reactor. A solution obtained from 100 ml deionized distilled water, 7 g (0.028 mol) sodium dodecylbenzene-sulfonate (DBSNa) and 0.01 g poly (N-vinylpyrrolidone) (PVP) was added above. Reaction mass was intensively stirred. A solution formed by 200 ml water and 3.57 ml aniline was dropped above reaction mass. After few minutes of stirring an aqueous solution of 9 g ammonium persulfate in 100 ml water was dropped time to 15 minutes at 25°C. Reaction mass was uncolored but after stirring it was opaque yellow, brown and after 24 hours it was dark green. The textile material was removed from the reactor, washed with distilled water and dried. The molar ratio aniline: oxidant: DBSNa was 1:1.03:0.52.

The procedure was repeated for polyamide and cotton as textile materials. The powders were obtained after filtering the synthesis solutions remaining after removal of textile materials.

The same procedures were used for dodecylbenzen-sulfonic acid (DBSA). The quantity of acid used in reaction was 5 ml.

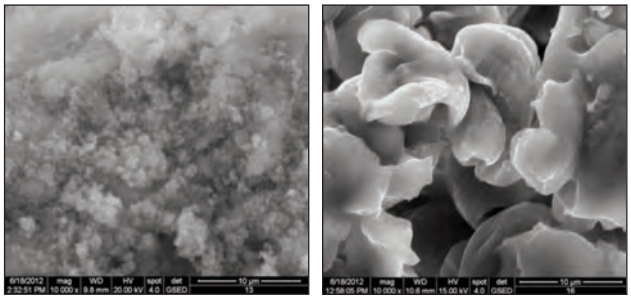
Obtained powders were noted PANI-DBSA and PANI-DBSNa while the covered cotton were noted C-PANI-DBSA and C-PANI-DBSNa and the coated polyamide were noted P-PANI-DBSA and P-PANI-DBSNa.

Characterization of composite materials

Infrared spectra were carried on a Cary 630 spectrometer at room temperature. ATR spectra on the textile materials were recorded with diamond crystal device between 650–1 800 cm^{-1} and 2 300–4 000 cm^{-1}. Surface morphology of textile material was observed using scanning electron microscope (SEM) type Quanta 200-FEI. The surface resistivity of the textile materials was measured according SR EN 1149-1: 2006 employing the 2 electrodes method, using a PROSTAT 800 meter.

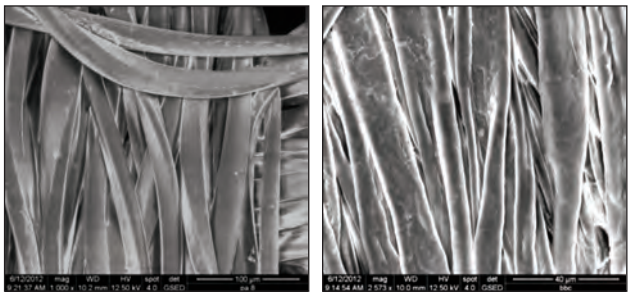
RESULTS AND DISCUSSIONS

The effect of acid or salt on the structure and morphology of obtained powders was evidenced with Scanning Electron Microscopy (SEM). The images of PANI-DBSNa and PANI-DBSA powders were given in figure 1.



a ***b***

Fig. 1. SEM images of obtained powders:
a – PANI-DBS Na; ***b*** – PANI-DBSA



a ***b***

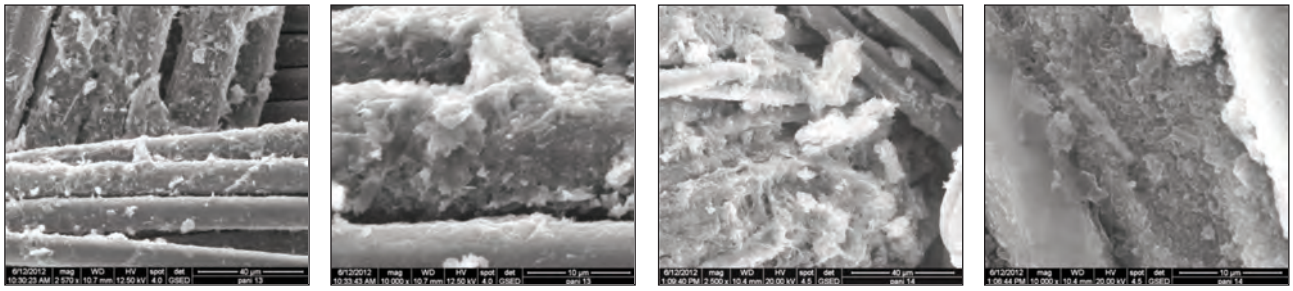
Fig. 2. SEM images of the used fabrics:
a – polyamide fabric (1 000 x); ***b*** – cotton fabric (2 500 x)

The PANI-DBSNa and PANI-DBSA powders showed completely different morphologies of grains. Aspect of PANI-DBSNa was as agglomerate of globular grains of few μm or less. The PANI-DBSA powder exhibits distinct peaks and valleys as those of PANI/DBSA reported by Pyo [33]. Morphology of textiles used as substrates for deposition was shown in figure 2. Each type of fiber has a unique morphology: cotton looks like a twisted ribbon; polyamide has tubular looks with smooth surface.

After coating of textile by procedure described in experimental part the composite materials were obtained. Figures 3 and 4 show the SEM images of composite materials at different magnifications. In the figure 5 the ATR spectra of composite materials obtained by “in situ” polymerization in emulsion were presented and in the table 1 are given the main frequencies and their assignations.

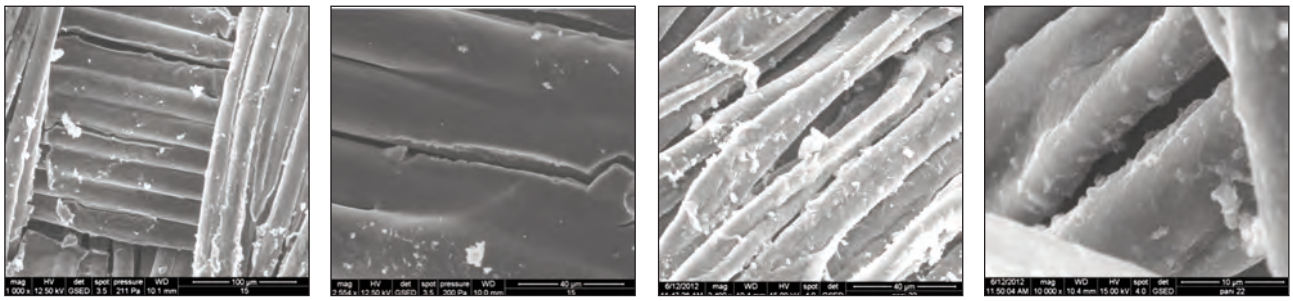
All major infrared bands of PANI [23] were observed: the out-of-plane bending of the benzene ring (650 – 900 cm^{-1}), the band of depronated PANI (1 158, 1 168 cm^{-1}), the benzenoid ring band (1 431, 1 424, 1 458, 1 470 cm^{-1}), the quinoid band (1 564, 1 534, 1 526 cm^{-1}), the C-H stretching band (2 904, 2 911, 2 923, 2 926 cm^{-1}) and the N-H stretching band (3 263 cm^{-1}).

The composites with cotton have the intensities and the positions of bands in infrared spectra almost the same that means the structure of doped polyaniline on substrates was the same. The transmittance values were different with 20% that show the cotton coated with DBSNa in composite C-PANI-DBS Na presented better optical properties.



a *b* *c* *d*

Fig. 3. SEM images of composite materials obtained by in situ polymerisation:
a – P-PANI-DBS Na at magnification of 2 500 x; ***b*** – P-PANI-DBSA at magnification of 10 000 x;
c – C-PANI-DBS Na at magnification of 2 500 x; ***d*** – C-PANI-DBSA at magnification of 10 000 x



a *b* *c* *d*

Fig. 4. SEM images of composite materials obtained by in situ polymerisation in emulsion:
a – P-PANI-DBS Na at magnification of 1 000 x; ***b*** – P-PANI-DBSA at magnification of 2 554 x;
c – C-PANI-DBS Na at magnification of 2 500 x; ***d*** – C-PANI-DBSA at magnification of 10 000 x

Table 1

MAIN FREQUENCIES CHARACTERISTIC TO PANI-DBSA AND PANI-DBSNA ON COTTON AND POLYAMIDE FABRICS

Assignment	C-PANI-DBSA	C-PANI-DBSNa	P-PANI-DBSA	P-PANI-DBSNa
C-N and N-H stretching	3 274; 3 334	3 274; 3 342	3 449; 3 291	3 420; 3 289
C-H stretching in benzene	-	-	3 050	3 057
C-H stretching	2 844; 2 911	2 858; 2 904	2 855; 2 923	2 855; 2 926
C=O stretching in amide	1 604	1 603	1 633	1 639
N=Q*=N	1 564	1 564	1 534	1 526
N−B**−N	1 431	1 424	1 458	1 470
C-N stretching in quinoide-benzenoide states	1 312; 1 158	1 311; 1158	1 370; 1 233	1 370; 1 233
C-H in plan bending	1 104	1 104	1 108	1 108
SO_3^- group of dopant	1 031	1 031	1 035	1 035
Methyl group attached by phenyl ring	991	998	995; 945	995; 945
Para di-substituted aromatic rings indicating polymer formation	824	824	826	826
C-H deformation out-of-plan	650	670	-	-

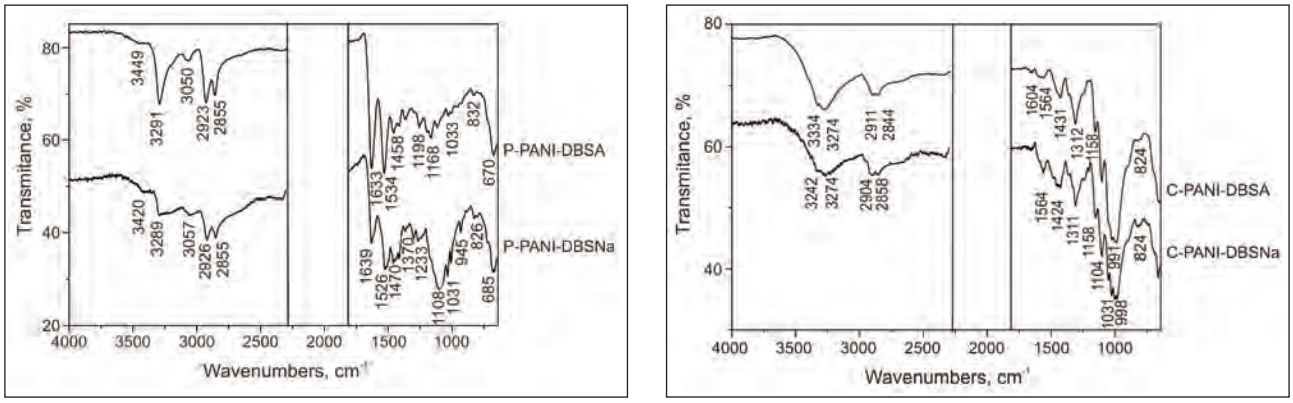
* *Q* is quinoide ring; ** *B* is benzenoid ring

In cases of composites with polyamide the position and the shape of bands were different.

This behavior can be correlated with formation of other types of bonds in P-PANI-DBSA then in P-PANI-DBS Na.

The transmittance values for these two composites with polyamide were presented a difference of 30% between them.

Comparing the four composites can be concluded that P-PANI-DBS Na has the best optical proprieties.



a *b*

Fig. 5. ATR Spectra of composite materials obtained by in situ polymerization in emulsion:
a – cotton fabric; ***b*** – polyamide fabric

Table 2

SURFACE REZISTIVITY OF INITIAL FABRICS USED FOR COMPOSITE FABRICATION	
Type of fabric	**Surface rezistivity**, Ωcm SR EN 1149-1:2006
Polyamide	$1.2 \cdot 10^{11}$
Cotton	$1.3 \cdot 10^{10}$

and sodium dodecylbenzene sulfonate (DBSNa). Method used was emulsion polymerization at 25°C, with a ratio of reactants aniline: oxidant: DBSNa or DBSA of 1:1.03:0.52. The inspection of fabrics showed obtaining of coatings formed by particles in case of DBSNa and coatings with smooth film aspect in case of DBSA.

What distinguishes the present procedure from the classical route are the following aspects:

Table 3

THE CHARACTERISTICS OF COMPOSITE MATERIALS				
Composite	**Polymer/Emulsion**	**Textile material**	**Surface rezistivity**, Ωcm SR EN 1149-1:2006	**Aspect/Color**
P-PANI – DBSA	PANI – DBSA water/PVP	Polyamide	$4.1 \cdot 10^{4}$	Uniform covered, light green
P-PANI – DBSNa	PANI – DBSNa water/PVP	Polyamide	$3.9 \cdot 10^{3}$	Uniform covered, green
C-PANI – DBSA	PANI – DBSA water/PVP	Cotton	$1.2 \cdot 10^{3}$	Uniform covered, dark green
C-PANI – DBSNa	PANI – DBSNa water/PVP	Cotton	$2.1 \cdot 10^{4}$	Uniform covered, dark green

The surface rezistivity of initial textiles and composite materials were measured according to SR EN 1149-1:2006. The surface rezistivity of initial textiles are given in table 2. The obtained results and other characterizations of composite materials are presented in table 3.

In conclusion from table can be seen that the textiles with PANI-DBS Na are more conductive then the textiles with PANI-DBSA.

CONCLUSIONS

In the present paper was used emulsion polymerization "in situ" to obtain of composite materials. The polymerizations were performed in the presence of two dopants dodecylbenzenesulphonic acid (DBSA)

- The polymerization occurs direct on the textile material;
- The doping is made in one-step reaction comparing to re-doping (two steps). This can decrease the production cost;
- The method enables the possibility of further improvements.

All synthesis lead to improving of electrical properties of coated materials of 10^{6}–10^{8} times compared with initial materials. Surface resistivity of cotton fabrics was better when using DBSA like dopant $1,2 \cdot 10^{3}$ Ωcm and for polyamide fabrics the better results was obtained when was used DBSNa as dopant $3,9 \cdot 10^{3}$ Ωcm.

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Evaluations of formaldehyde emissions in clothing textiles

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REZUMAT – ABSTRACT

Evaluări privind emisiile de formaldehidă de pe confecțiile textile

Lucrarea oferă informații privind evaluarea unor produse de îmbrăcăminte de pe piața românească, din punct de vedere al emisiilor de formaldehidă liberă şi parțial hidrolizabilă, testate în conformitate cu standardul european şi internațional SR EN ISO 14184-1:2002. Au fost investigate 161 de produse textile – confecții pentru copii, femei, bărbați, lenjerie – realizate din bumbac şi din bumbac în amestec cu alte fibre, care, în timpul utilizării, vin în contact direct cu pielea. Sunt prezentate rezultatele testelor cantitative privitoare la conținutul de formaldehidă de pe confecțiile textile pentru bărbați şi copii. De informațiile privitoare la efectele expunerii corpului uman la formaldehida existentă pe confecțiile textile pot beneficia atât organizațiile de supraveghere a pieței şi factorii de decizie privind sănătatea publică, cât şi firmele producătoare de materiale textile.

Cuvinte-cheie: produse textile, formaldehidă, etichetă ecologică

Evaluations of formaldehyde emissions in clothing textiles

This paper presents the evaluation of emissions of free and partially hydrolysable formaldehyde on clothes from Romanian market, tested in accordance with European and international standard SR EN ISO 14184-1: 2002. There were investigated 161 textile products – clothing for children, women, men, linen – primarily concern being cotton and its blends intended to come into contact with the skin. The quantitative formaldehyde assays in clothes for children and men are discussed here. The work brings information and data on human exposure to formaldehyde, from the clothing textiles. It is expected that the market surveillance bodies and the organizations which make decisions on public health as well as companies producing textiles will take advantage of it.

Key-words: textiles, formaldehyde, ecolabel

Competition advantages required for textile products on the market relate to quality and design, innovation and technology, high added value. Not only that, but the products have to be officially recognized by certification, ecolabels etc. These require additional effort and a slight increase in costs.

Present trends for the textile sector include also the marketing of textile products with low environmental impact and human health protection. In this respect one of the monitored substances is formaldehyde.

Formaldehyde is one of the most widely used chemicals in the world and it is present in very small quantities, usually less than 0.06 ppm, both indoors and outdoors [1].

When the air reaches the formaldehyde levels 0.1 ppm the following effects may appear: watery eyes, burning sensations in the eyes, nose and throat, cough, difficulty of breathing, skin irritation [2]. Similar effects to those produced by formaldehyde appear in case of allergies, cold, flu. People react different to formaldehyde: the sensitive one react at a concentration of 0.1 ppm. The World Health Organization recommends no more than 0.05 ppm exposure. In June 2004, the toxicity of this substance has been revalued upwards by the International Center for research on cancer (CIRC) and thus from "likely" carcinogen (Group 2A) it became "carcinogenic to humans" secure (Group 1). This has led to the multiplication of studies for assessment of formaldehyde emissions on different products and environments.

FORMALDEHYDE IN TEXTILE INDUSTRY

In the textile industry, formaldehyde is present in textile finishing processes to impart to products easy-care properties and other properties such as:

- resistance to wrinkling;
- good dimensional stability;
- compatibility with other finishing agents (waterproofing agents, emulsifiers, whitening);
- color resistance;
- the maintenance of fabric whiteness;
- environment protection in the process of the application of resins and other finishing operations for the final product;

These formaldehyde resins can chemically degrade under certain conditions of heat and humidity, with the release of formaldehyde. For this reason, many countries have introduced legal restrictions for the formaldehyde contained in products, including textiles.

EUROPEAN REGULATIONS ON FORMALDEHYDE AND TEXTILES

Harmonised European legislation does not contain rules on the restriction of free formaldehyde in textiles. But some countries have legal acts for the limits on the content of formaldehyde in the textile products, in order to reduce the risk of allergy and appearance of other adverse health effects on the population.

Such laws have been adopted by: Germany – Bedarfsgegenständeverordnung, April 1992; Austria – 194/Ordinance 1990; Finland – Decree 210/1988; Netherlands – Decree of 22 March 2001; Norwegian Government – Regulation no. 922/June 1, 2004.

EU eco-label

In the European legislation has been introduced (1993) by the European Commission the EU ecolabel for advertising of products with a high level of environmental performance. Through the Regulation (EC) no. 66/2010 rules were set for the establishment and implementation of the EU voluntary ecolabeling system. The EU ecolabel has as symbol a flower whose petals are 12 stars (fig. 1) [3]. The EU eco-label is awarded to 23 product groups including: "textiles" and "bed mattresses".

Fig. 1. EU ecolabel symbol

Commission decision 2009/567/EC establishing the ecological criteria for the award of the Community eco-label to textile products, includes the following specific criteria [4]:

- Formaldehyde shall not be used for stripping or depigmentation (art. 12);
- The amount of free and partly hydrolysable formaldehyde in the final fabric shall not exceed 20 ppm in products for babies and young children under 3 years old, 30 ppm for products that come into direct contact with the skin, and 75 ppm for all other products.

Formaldehyde testing is to be carried out in accordance with the method laid down in the standard SR EN ISO 14184-1. Filling materials consisting of fibrous material shall comply the requirements for the formaldehyde in textile products listed in article 26 (art. 31.2). By comparison, in EU GPP (Green Public Procurement) criteria for textiles [5] (http://ec.europe.eu/environment/gpp/pdf/criteria/textiles.pdf), the admissible amount of free and partially hydrolysable in the final product is much greater.

There are some studies presenting the results for the evaluation of free formaldehyde on textiles [6–7], but they focus on a specific market and are not so ample as to predict the market level. They give valuable data related to the human exposure to chemicals/formaldehyde for the consumers of textile products, for the market surveillance organizations and the organizations that make decisions on public health.

EXPERIMENTAL PART

In order to evaluate the free formaldehyde emissions in the textile products, in our work we tested 161 textile products from the Romanian market, originated in 12 countries, but most of them produced in Romania (table 1). The fibrous composition of the tested textile products is as follows (fig. 2): 51% of the samples are made up of cotton, 21% have in composition cotton mixed with other fibres, 8% represents products of wool and blended wool, 8% of products are from viscose, 12% from other fibers.

Table 1

COUNTRY OF ORIGIN FOR THE TESTED TEXTILE PRODUCTS

Country of origin	Tested products, no.	Share per country, %
Bangladesh	3	2
China	8	5
India	1	0,6
Italy	3	2
Poland	2	1,2
Portugal	1	0,6
Romania	122	76
Spain	3	2
USA	1	0,6
Sweden	2	1,2
Thailand	1	0,6
Turkey	2	1,2
Unknown	12	7,5

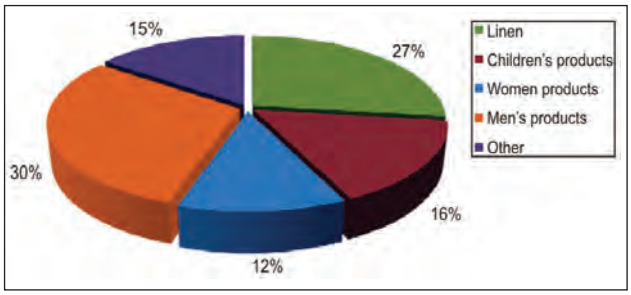

Fig. 2. The fibrous composition of the tested products

We classified the various types of tested textile products for each intended use, so as percentage of the total number of samples the classification is the following (fig. 3): textile products for children – 16%; textile products for women – 12%; textile products for men – 30%; linen – 27%; various – 15%. In this paper we present the results for men and children's textiles.

Free formaldehyde testing on children's textiles

When selecting products, particular importance has been given to testing of textiles for children who included products as: thick diaper, bonnet, T-shirt,

blouse, shirt, socks, stockings, panty, dress, plush toys. For these products, selection was made in order to have different linings and dyes, and printed motifs. The products being tested were mostly printed textiles (72%).

Results of testing formaldehyde content in textiles intended for children are shown in figure 4. The results indicate values for the formaldehyde emissions that comply with EU regulation for 78% of the total samples (fig. 5), 3 samples (fig. 6) that exceed the limit imposed that is maximum of 20 mg/kg (P 56 – t-shirt, P 67 – plush bear, P 62 – dress).

Two textile samples give high values for the formaldehyde emissions when compared with the admissible limit of 30 mg/kg (8%): P 13 – printed cotton, underside, 39.8 mg/kg compare to 30 mg/kg allowed; P 52 – printed shirt, phosphorescent 58.5 mg/kg (only 30 mg/kg allowed).

Free formaldehyde testing on men clothing

In this category the samples were: shirts, t-shirts, underlines, socks. The maximum admissible content on formaldehyde for these textiles is 75 mg/kg. In this category only 30% of determined values for the existing formaldehyde in the tested samples comply with European eco-label regulation. As an example we mention the shirt with an “non-iron" treatment which had 106 mg/kg formaldehyde.

Taking into consideration that the tested samples represent a very small part of the Romanian market, the conclusion for tests from the point of view of the consumers should indicate more precautious for textile clothing, especially it is recommended washing before use.

Summary

Statistics on non-compliance values determined in samples submitted for testing to evaluate the free formaldehyde content present the following:

- 1.2% of the total samples are over the acceptable limits in case of textile products for children;
- 2.5% of the total samples are over the acceptable limits for women textiles;
- 1.9% of all samples are over the acceptable limits for men textile products;
- 13% of the total samples are over the acceptable limits from textiles bedding.

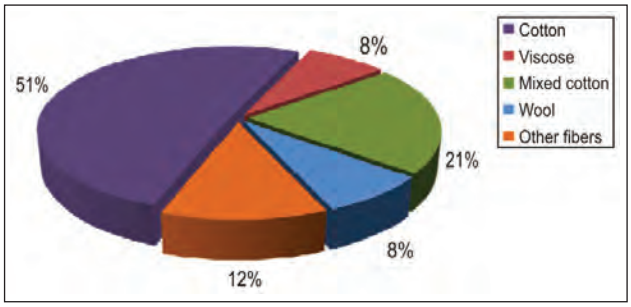

Fig. 3. Tested products per use category

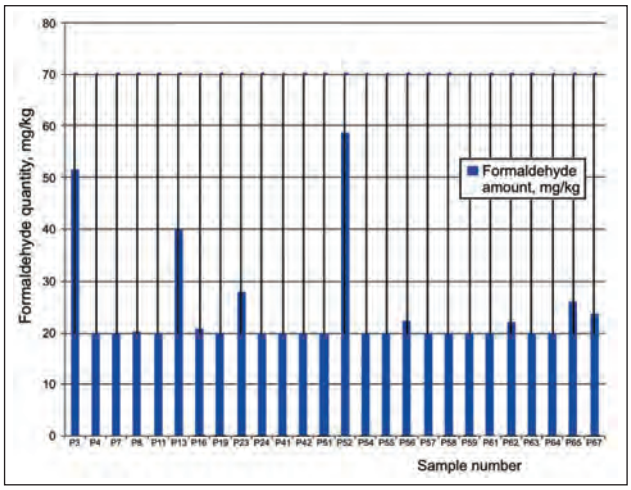

Fig. 4. Formaldehyde emissions in children clothes

Fig. 5. Textile samples

a *b* *c* *d*

Fig. 6. Noncompliant textile samples:
a – P 56; ***b*** – P 13; ***c*** – P 62; ***d*** – P 52

CONCLUSIONS

In today's society, the population is subject to a significant increase in the number of chemicals that the body comes into contact with. Among these is the formaldehyde, considered carcinogenic for humans.
In this context, this paper aimed to assess the emissions of formaldehyde of textile products which are distributed on the Romanian market, to establish their impact during wearing on children and adults.
The selection of 161 products was planned so as to cover as many types of textile fibres and products as were expected to present free formaldehyde. We could conclude that the textile products for children had adequate treatments so that they are within the limits of the strict requirements set out by the EU eco-label (probably due to the adoption of European eco-labeling legislation and to the more frequent checks of products on the market).
The men textile products present values for the free formaldehyde that exceeds the allowed limits, but a valid conclusion will require a more large investigation that the present one.

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The analyses of Turkish apparel industry by the five forces model

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REZUMAT – ABSTRACT

Analiza industriei de confecții din Turcia cu ajutorul modelului celor cinci forțe

Scopul acestui articol este de a analiza industria de confecții din Turcia, utilizând modelul celor cinci forțe al lui Porter. Studiul s-a bazat pe date din literatura de specialitate, referitoare la acest subiect, şi a cuprins 35 de producători de confecții din clasamentul Top and Next Top 500 Industrial Enterprises, realizat anual de Camera de Comerț şi Industrie din Istanbul. Rezultatele au fost evaluate pe baza unor tabele de frecvență şi comparații cu scala Likert. Conform rezultatelor obținute în urma acestei analize, s-a constatat faptul că concurența dintre companiile din industria confecțiilor din Turcia a fost intensă, din cauza existenței mai multor companii de dimensiuni comparabile şi a barierelor scăzute la ieşire. În plus, produsele alternative şi puterea de negociere a furnizorilor nu constituie o amenințare semnificativă. Din cauza situației economice globale, puterea de negociere a achizitorilor este în creştere. Conform datelor din literatura de specialitate şi a rezultatelor obținute, s-au făcut câteva recomandări, pentru industria de confecții din Turcia, privind adoptarea unor strategii competitive în sfera concurenței.

Cuvinte-cheie: industria de confecții, avantaj concurențial, modelul lui Porter

The analyses of Turkish apparel industry by the five forces

The purpose of this article is to analyze Turkish apparel industry by using Porter's Five Forces Model. A survey has been developed through the sources in literature to gather data for this purpose. Survey applied to the 35 apparel companies from the Top and Next Top 500 Industrial Enterprises ranking conducted by Istanbul Chamber of Industry each year. And the results were evaluated by using frequency tables, Likert scale of comparisons. According to the findings obtained from the analyses, that competition between the existing companies in Turkish apparel industry was dense, due to the many similar sized companies, low exit barriers. In addition to this, threat of substitute products and bargaining power of the suppliers are not very high. Bargaining power of buyers is increasing because of global economic situation. Depending on the literature and the findings, a number of strategies were recommended to Turkish apparel industry to adopt for the competition.

Key-words: apparel industry, competitive advantage, Michael Porter's model

The essence of strategy formulation is coping with competition. Yet it is easy to view competition too narrowly and too pessimistically. Competition in industry is rooted in its underlying economics and existing competitive forces that go well beyond the established combatants in a particular industry. Customers, suppliers, potential entrants and substitute products are all competitors that may be more or less prominent or active depending on the industry. The collective strength of these forces determines the ultimate potential profit of an industry [1].

When Micheal Porter conceived the five competitive forces model, it propelled strategic management to the very heart of the management agenda. The framework became a center-piece of texts on business strategy and strategic management, and essential examination material on MBA and similar courses globally [2].

Due to the process of globalization, rivalry on the world's apparel industry is getting tougher. Considering the effects of employment and export operations on economy, Turkish apparel industry is regarded as an essential branch of Turkish industry. The purpose of this study is to analyze Turkish apparel industry structurally utilizing Porter's Five Forces Model. Within the scope of this purpose, the structure of Turkish apparel industry was analyzed with the ranking of Top and Next Top 500 Industrial Enterprises, conducted by Istanbul Chamber of Industry annually.

LITERATURE REVIEW

As different from each other as industries might appear on the surface, the underlying drivers of probability are the same [3]. The five forces model is a framework that defines the rules of competition in the industry and highlights what is important in order to have a long-term competitive advantage [4]. To analyze the competitive environment, the model applies some concepts of industrial organization theory and Porters Five Forces Model can be handled as a logical extension of Structure – Conduct – Performance (SCP) model [5, 6].

According to the model, the industry's competitiveness is influenced by five forces and the collective strength of these forces determines the ultimate profit potential of that industry [4]. Therefore, to understand the rivalry and profitability in industry, five forces model – new entrants, suppliers, customers, substitute products and rivalry among existing firms- should be analyzed with the basic structure of the industry [3] (fig.1). This model is a frame that defines the rules of rivalry in industry and underlines what is important to obtain a long-term competitive advantage [7].

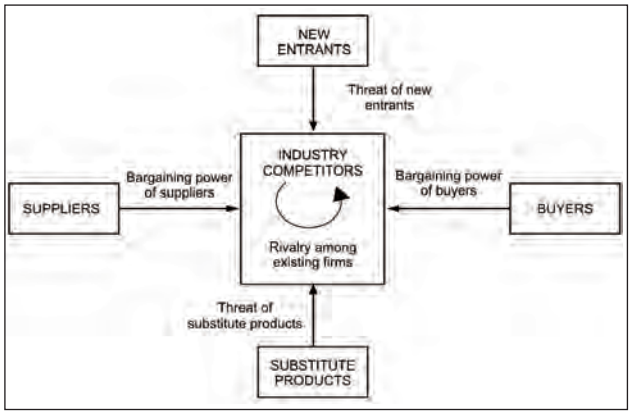

Fig. 1. Forces driving industry competition

Threat of new entry

The threat of new markets entrants refers to the prospect of new competitors entering the industry. The most common barriers to entry are economies of scale, brand equity, product differentiation, capital requirements, switching costs, access to distribution channels, cost advantages independence of scale and government policy [8].

The bargaining power of buyers

Buyer power is the impact that purchasers have on the industry. Where there is only one purchaser in the industry, the buyer has the greatest power [9]. The bargaining power of buyers determines their influence on the selling industry's profitability. Traditional economics tells us that customers have the greatest bargaining power when they are large, few in number and able to switch easily to alternate suppliers [10].

The bargaining power of suppliers

Supplier power is the mirror image of buyer power. As a result, the analysis of supplier power typically focuses first on the relative size and concentration of suppliers relative to industry participants and second on the degree of differentiation in the inputs supplied. The ability to charge customers different prices in line with differences in the value created for each of those buyers usually indicates that the market is characterized by high supplier power and at the same time by low power [8], [11].

Substitute products

All firms in the industry are competing, in a broad sense, with industries producing substitute products. Substitutes limit the potential returns of an industry by placing a ceiling on the prices firms in the industry can profitably charge. The more attractive the price-performance alternative offered by substitutes, the firmer the lid on industry profits [4].

Rivalry among existing firms

The intensity of rivalry, which is the most obvious of the five forces in an industry, helps determine the extent to which the value created by an industry will be dissipated head-to-head competition [12]. Intense rivalry is the result of a number of interacting structural factors: numerous or equally balanced competitors, slow industry growth, high fixed or storage costs, lack of differentiation or switching costs, capacity augmented in large increments and diverse competitors [13], [8].

RESEARCH METHODOLOGY

Data collection method and questionnaire development

In this research, survey method was used as a data collecting method. It was used to figure out the agreements of participants on the structural analyze of industry (1 – absolutely disagreement, 5 – absolutely agreement) by using Five-point Likert-type scale as basis. There are 26 statements in the survey. The questions, which are used to analyze the structure of sector, according to five forces model, are developed by utilizing the books of such writers as Eren (2010), M. Porter (2008), Dinçer (2007), Dess ve Miller (1996), Grant (2002). Last part of the survey includes statements of executives, who participated in the survey, about characteristics of business organization.

The sample for the study

The sample frame for the study was derived from the database of the Istanbul Chamber of Industry's Top and Next Top 500 Industrial Enterprises 2009. From the Top 500 Industrial Entreprise 13 apparel companies and 48 apparel companies from the Next Top 500 Industrial Entreprises were determined. 11 apparel companies out of 13 from the Top 500 list and 24 out of 48 from the Next Top 500 have answered. A total of 172 surveys were collected with 59 from the Top 500 and 113 from Next Top 500. In total the survey was sent to 61 apparel companies and 35 have answered, which corresponds to 57.4% participation rate.

RESULTS AND DISCUSSIONS

Profile of sample firms

Table 1 lists the characteristics of the apparel companies that participated in the survey. The table reveals that 34.3% are from Top 500 Industrial Enterprises while 65.7% are from Next Top 500 industrial enterprises. 48.9% of the companies employ less than 1200 employees. 54.8% of the companies are operating for more than 15 years. This shows that these large corporations are also old.

Barriers of entry and exit, current competition, suppliers and substitute products

Barriers of entry consist of factors such as, economies of scale, capital requirements, difficulties in forming distribution channels, learning curve and experience and difficulties in accessing raw materials (table 2). Considering the answers of participants on threat of entry to the industry, it is observed that a company which will enter the apparel industry, will not have difficulties to access raw materials and will not have to start working with high production capacity (avg. = 2.51; avg. = 3.8).

Table 1

CHARACTERISTICS OF THE COMPANIES THAT PARTICIPATED THE SURVEY		
Size/No. of companies	**Company count**	**Percentage**
1 – 599	43	25.1
600 – 1 199	41	23.8
1 200 – 1 799	37	21.5
1 800 – 2 399	24	13.9
2 400 – 2 999	5	2.9
3 000 – 3 599	8	4.7
3600 +	10	5.8
Years of operation		
5 – 14	28	16.4
15 – 24	48	28
25 – 34	46	26.8
35 – 44	16	9.2
45 – 54	9	5.2
55 – 64	17	9.8
65+	4	2.3
Foreign partnership situation		
Yes	13	7.6
No	156	90.7

Table 2

THREAT OF ENTRY TO INDUSTRY			
Statements	**N**	**Avg.**	**Std. dev.**
Economies of scale	172	2.51	1.05
Capital requirements	172	3.40	0.977
Difficulties in forming distribution channels	172	3.97	0.875
Relationships between the customers and the existing companies	172	3.66	0.880
Necessity of technical knowledge	172	4.28	0.703
Necessity of experience	172	4.15	0.773
Difficulties in accessing to the raw materials	172	3.80	0.799

Moreover, there is no requirement for high capital (avg. = 3.4). Although it is observed that a company will have difficulties in forming distribution channels once entered into the apparel industry, it will need high level of technical knowledge and experience (avg. = 4.28; avg. = 4.15).

It can be said that the factors which effect the customers' power of bargain are as follows: the size of customers, being informed about the price of products in the market, costs of changing firm, their ability of reverse integration, their profits and benefits. When the participants' responses to the statements about the bargaining power are analyzed, it is observed that their ability of producing the products which they buy from the firm, is low (avg. = 2.56). Furthermore,

Table 3

THE BARGAINING POWER OF CUSTOMERS			
Statements	**N**	**Avg.**	**Std. dev.**
Switching costs	172	2.99	1.032
Detailed information on the product prices	172	4.12	0.811
The number of buyers is small	172	3.45	1.156
Threat of backward integration by buyers	172	2.56	1.166
Price sensitivity of buyers	172	2.78	1.167

Table 4

THE BARGAINING POWER OF CUSTOMERS			
Statements	**N**	**Avg.**	**Std. dev.**
Concentration of suppliers relative to buyer is high	172	2.84	1.084
The quality of products that we supply effects the quality of our firm's products directly	172	4.38	0.695
The suppliers' maturity date has direct effect on our maturity date directly	172	4.41	0.708
Switching costs	172	3.52	0.868
Threat of forward integration by the suppliers	172	2.34	0.867
Our business enterprise buys high quantity of raw materials from our suppliers	172	4.12	0.740

it is observed that they do not use the number of product order as an element of bargain (avg. = 2.78), in return, it is revealed that the number of customers is low (avg. = 3.45) and customers have detailed information about the prices in the market (avg. = 4.12). The elements that provide bargaining power to the suppliers are similar to the elements that provide bargaining power to customers. The elements that provide bargaining power to the suppliers are these: the numbers of suppliers in the market, the importance of suppliers' product in terms of business organization, the integration ability, the scale of product obtained from suppliers. When the supplier participants' responses to the statements about the bargaining power are analyzed, it is observed that the number of firms that business organizations can obtain products is not low (avg. = 2.84), they can also change their suppliers without an extra payment (avg. = 3.52) and they buy high quantity of raw material from their suppliers (avg. = 4.12). Conversely, it is seen that suppliers' products are quite important in terms of both maturity date and quality of the firm.

When participants' responses to the statements about the replacement product treatment are analyzed, it can be stated that there is no replacement product threat for Turkish ready-made clothing sector (avg. = 3.52).

Table 5

THREAT OF SUBSTITUTE PRODUCTS			
Statements	**N**	**Avg.**	**Std. dev.**
In our industry there are products that can replace our firm's products	172	3.52	0.834
Developments in technology create the threat of replacement product for our industry	172	2.62	0.854

Table 6

THE BARGAINING POWER OF CUSTOMERS			
Statements	**N**	**Avg.**	**Std. dev.**
Competing firms that are the same size and have the same influence	172	4.37	0.659
Slow industry growth	172	3.30	1.048
In the sector we operate there is excess supply	172	3.20	1.012
There is no cost to our firm when the products our firm produced are kept in stock, *R*	172	4.35	0.747
We should follow different strategies to compete with our competitors	172	3.77	0.819
Exit barriers are high	172	3.33	0.884

The elements that determine the rivalry among existing firms are as follows: presence of many same sized firms, the capacity increasing, and high cost of stocking, high exit barriers. When the top and mid-level manager participants' responses to the statements about competition between existing competitors, it can be said for the apparel industry that the competition between existing competitors is high. Presence of small and medium sized firms in the industry can be seen as an element that increases the competition most (avg. = 4.37). Low growth rate of the industry (avg. = 3.3) and excess supply are other elements that increase the competition. When responses to the statements about competition between existing competitors are analyzed, it can be said that for Turkish apparel industry, the competition between competitors is high.

CONCLUSIONS

The aim of this article was to analyze Turkish apparel industry within the frame of Porter's five forces model. In the light of the findings above, Turkish apparel industry is dominated by small-medium sized firms. Due to this, rivalry among competitive companies is high. Additionally, the global developments - competition in the apparel industry has increased with the joining of China to the World Trade Organization. Economies of scale in apparel industry and the capital requirements are not very high in apparel industry. However, access to distribution channels, technical knowledge necessity and experience are barriers that hinder entry.

Bargaining power of customers has been increasing since the 2008 economic crises in the world. Customers are very strict about the product prices and they are all well-informed about the product prices. In addition to this, the number of the buyer company is not very high. This situation increases customer's power. However, customers do not have ability to produce items.

Due to the low switching costs, number of sourcing company and getting high amount of raw materials bargaining of power suppliers are not very high. In addition to this, the raw material quality has a significant effect on the company's product quality. And the lead times of raw materials are very important for the company's lead time. These items are increasing the buyers' bargaining power in the Turkish apparel industry.

Threat of substitute products has not been experienced throughout the industry yet. And substitute product threat is not high for apparel industry at the moment. But the improvements at the technology can create substitute products for the apparel products.

As a general conclusion, it is possible to say that the globalization and the global economic developments affect Turkish apparel companies. In this article the industry environment of the Turkish apparel companies was analyzed. Turkish apparel companies were using cost leadership until 2 000, but after 2 000 the world started to change and Asia countries were the cost leaders of the world's production area. It is not possible for Turkish companies to fight with Asian countries in the cost leadership. Due to this and the results of the analyses Turkish apparel companies should follow the differentiation strategy for the competitive advantage.

Future study: What are the resources of companies to get competitive advantage in apparel companies?

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DOCUMENTARE

Confecții textile

LYCRA® SPORT – UN MATERIAL TEXTIL CU NOI NIVELURI DE PERFORMANȚĂ

Având în vedere faptul că susținerea muşchilor, libertatea de mişcare şi confortul sunt cerințe esențiale pentru articolele de îmbrăcăminte destinate sportului de înaltă performanță, firma ***INVISTA*** a creat un nou material textil *Lycra® sport*. Certificarea acestui material s-a făcut cu trei ani în urmă. Actualele standarde de performanță permit materialelor textile *Lycra® sport* să-şi păstreze proprietățile inițiale. Ele oferă libertate de mişcare, elasticitate bidirecțională, confort şi o mulare pe corp perfectă şi de lungă durată.

În prezent, INVISTA a introdus încă două niveluri de performanță pentru acest material. Unul dintre noile standarde de performanță a fost dezvoltat pentru textilele de compresie, utilizate în sporturile de performanță, cu un consum mare de energie. Materialul textil *Lycra® sport energy* asigură un echilibru perfect între forța de compresie, libertatea de mişcare şi maximum de confort, făcând posibilă realizarea unor articole de îmbrăcăminte cu caracteristici optime de compresie.

Aceleaşi standarde noi de performanță se aplică şi în cadrul articolelor de îmbrăcăminte sport, la care accentul cade pe frumusețe şi modă. Materialul textil

Lycra® sport beauty asigură un efect de modelare îmbunătățit, susținând în acelaşi timp libertatea de mişcare şi confortul necesar activităților sportive. Materialul Lycra® sport beauty a fost lansat sub motoul: *"Să arătăm în formă, în timp ce ne menținem în formă".*

Pe materialul textil Lycra® sport este ataşată o etichetă detaşabilă, care-l încadrează într-un anumit sortiment şi care indică faptul că acesta îndeplineşte standardele categoriei specifice. Întregul proces de clasificare se bazează pe cunoştințe de specialitate.

Legat de aceasta, David Capdevila – reprezentant, la nivel global, al segmentului de articole de îmbrăcăminte activă, declara: "*Standardele de performanță a materialelor textile Lycra sport sunt expresia ştiinței care stă la baza succesului multor activități sportive, în care compresia, libertatea de mişcare şi confortul sunt factori-cheie pentru sportivi*".

În concluzie, se poate afirma că toate materialele textile Lycra® sport posedă o suficientă capacitate de revenire elastică pentru a realiza etapele de compresie necesare. Datorită reducerii forței dintre întinderea materialului textil şi solicitarea elastică, compresia este mai uniformă. În plus, se asigură un înalt nivel de confort, în timpul activităților sportive.

Kettenwirk Praxis, 2012, nr. 4, p. 7

Noi tehnologii

AVANTAJELE UTILIZĂRII CELULOZEI PENTRU COMPOZITE

Compozitele termoplastice *Thrive,* care folosesc, ca aditiv pentru consolidarea acestora, fibre celulozice provenite din surse sustenabile au fost lansate de către compania ***Weyerhaeuser,*** cu sediul în Federal Way, Washington.

Aceste compozite, în curs de brevetare, vor fi utilizate inițial în domeniul bunurilor de uz casnic şi al pieselor auto, deoarece oferă o serie de avantaje, comparativ cu materialele consolidate cu fibre scurte de sticlă sau cu fibre naturale, cum ar fi sisalul, cânepa şi kenaful. Materialele alternative Thrive sunt disponibile sub formă de pigmenți concentrați pentru procesatori şi paleți termoplastici.

Compozitele Thrive, disponibile pe scară largă, sunt economice, au o greutate redusă şi posedă excelente proprietăți de rezistență la tracțiune şi flexiune. "*Aceste compozite pot îmbunătăți durata ciclului de modelare cu până la 40%. Produsele Thrive necesită un consum de energie redus şi pot reduce uzura echipamentelor de prelucrare, în comparație cu cele care conțin fibre scurte de sticlă, cu efecte abrazive. Toate acestea creează beneficii semnificative pentru companiile care doresc să-şi reducă amprenta de carbon, iar performanța şi productivitatea cresc*" – a declarat Don Atkinson, vicepreşedinte al Departamentului de marketing şi produse inovative al companiei producătoare de fibre celulozice Weyerhaeuser.

În prezent, compozitele Thrive sunt disponibile sub formă de celuloză în amestec cu polipropilenă, având indici de curgere cu valori ridicate sau joase. Deoarece fibrele celulozice sunt compatibile cu diverşi polimeri de bază, compania intenționează să extindă linia de produse în afara polipropilenei, la o serie de polimeri din hidrocarburi şi nonhidrocarburi.

Compozitele Thrive absorb uşor coloranții şi oferă o excelentă fluiditate şi capacitate de umplere a pereților subțiri, oferind producătorilor o mai mare flexibilitate în proiectare. Ele sunt create printr-un proces brevetat, care permite controlul dispersiei de fibre celulozice în matricea polimerică. Acest lucru are ca rezultat un finisaj neted de suprafață, care deschide noi oportunități de utilizare a fibrelor naturale în materiale plastice compozite. De asemenea, dacă producătorii doresc ca fibrele să fie vizibile, această opțiune este realizabilă.

Pe lângă aspectul îmbunătățit, diferit de al celorlalte fibre naturale, compozitele Thrive posedă caracteristici de performanță care sporesc de la un lot la altul. Acest lucru a fost confirmat şi de dr. Ellen Lee, expert tehnic în cercetarea materialelor plastice, din cadrul companiei Ford Motor, care a afirmat: "*Utilizarea compozitelor pe bază de fibre celulozice este o opțiune benefică. Stabilitatea lor termică excelentă permite extinderea gamei de aplicații auto ale materialelor din fibre naturale. Odată cu utilizarea sporită a acestor materiale provenite din surse regenerabile, se poate reduce în mod semnificativ amprenta de mediu a produselor realizate, odată cu acumularea mai multor beneficii în întregul lanț de aprovizionare*".

Compania Weyerhaeuser deține 20 de milioane de acri de pădure, care asigură o aprovizionare globală de la o sursă de încredere, iar o parte din fibra celulozică provine din aceste păduri.

Weyerhaeuser va folosi unitățile sale de producție a celulozei şi canalele sale globale de logistică pentru fabricarea şi livrarea de produsele în întreaga lume.

Smart*textiles and nanotechnology, ianuarie 2013, p. 7*