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Information about 6th Central European Conference 2010 "FIBRE-GRADE POLYMERS, CHEMICAL FIBRES AND SPECIAL TEXTILES"

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The 6th Central European Conference „Fibre-Grade Polymers, Chemical Fibres and Special Textiles" – CEC 2010, held in Bratislava, Slovakia, was organized by Department of Fibres and Textile Chemistry, Institute of Polymer Material, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, at the occasion of 70th anniversary of the beginning of education. It was another one succeeding highly successful previous CEC conferences. The first CEC conference was held in Lodz, Poland (1999) and next ones were organized in Bratislava (2001), Portorož (2003), Liberec (2005) and Krakow (2007).

The conference provides an effective possibility to exchange experience of participants from all areas of fibre and textile science, technology and business.

On 6th CEC 2010 participated members from many countries: Czech Republic, Poland, Germany, Slovenia, Croatia, Spain, Italy, Ukraine, USA and Slovak Republic.

At the Conference 22 oral and 25 poster contribution were presented.

THERMOMECHANICAL AND MECHANICAL PROPERTIES OF MODIFIED POLYPROPYLENE FIBERS

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Abstract: *This work was aimed to study the properties of polypropylene (PP) fibers modified by inorganic additives, assigned for improve the end-used properties of construction composites based on silica. Modification of fibers by addition of sufficient additive insure more intense anchoring of polypropylene fibers in cement matrix, what leads to expressive improve of functional of PP fibers in relation to transmission and absorption of deformation energy at mould and load silica composites. Impact of inorganic additives on the thermomechanical and mechanical properties of fibers, and the compatibility of individual components are investigated.*
Thermomechanical properties of modified polypropylene fibers were evaluated by thermomechanical analysis (TMA). From obtained dependences, temperature of fiber shrinkage and total shrinkage of fibers containing inorganic additives were found to be lower than at specimens of standard fiber.
Mechanical properties of fibers were study by investigation of characteristics as strength and Young's module of fibers with and without stabilization.
Keywords: *polypropylene, thermomechanical and mechanical properties, modification, inorganic additive*

1. INTRODUCTION

Polypropylene fibers are used in construction applications as a reinforcing agent extensively for many years [1]. Reinforced concrete is worldwide most commonly used civil engineering material. The term fiber-reinforced concrete (FRC) is defined as concrete containing dispersed randomly oriented fibers [2, 3]. Fibers are providing three-dimensional reinforcement of the concrete, and thereby concrete becomes more tough and durable. From a constructional point of view the practical function of fibers is to protect composite against sudden failure at the crack initiation in matrix. Dispersed fibers are transferring the tension influencing on the concrete until the ultimate strength of fibers is reached [3, 4].

The character and properties of fiber reinforced cement depend on the type of material and on geometry, distribution, orientation and concentration of fibers. There are four main categories of fibers used as reinforce in concrete. For a consideration of used material type it can be used steel fiber, glass fiber, synthetic fiber including carbon fibers, and natural fiber [3].

Polypropylene fibers utilization alters the characteristics of concrete in a very beneficial way. Concrete's flexural strength, bonding strength, compressive strength and dynamic performance are effectively improved as a result of its production with PP fibers. Also the water penetration and mass loss due to abrasion is reduced and the fatigue life of concrete is also prolonged [1, 5-10]. By physical and chemical modification is reached more intense anchoring of polypropylene fibers in cement matrix. Insurance of consistently fixed fibers in matrix is assured by addition of sufficient additive. Functional of PP fibers in relation to transmission and absorption of deformation energy is expressive improved, what leads to ability at mould and load silica composites.

The thermomechanical and mechanical properties of polypropylene fibers modified

by inorganic additives are studied in this work.

2. EXPERIMENTAL

2.1 Material used
In this study PP fibers were used in a form of standard fiber (PP/S) and composite fibers. PP used for preparation of concentrates and fibers modified by inorganic additives was PP TATREN HT 1810 with MFI = 20.9 g/min, produced by Slovnaft a.s., Bratislava (SR). The PP with different content of inorganic additive has been mechanically mixtured and melted using the two screw extruder. The obtained PP/nanoadditive concentrates have been used at the preparation of PP composite fibers by continual technology. Content of inorganic additive in composite fibers was 2 wt.% (PP/K2), 4 wt.% (PP/K4), 6 wt.% (PP/K6), 8 wt.% (PP/K8), 10 wt.% (PP/K10), 12 wt.% (PP/K12), 14 wt.% (PP/K14) and 16 wt.% (PP/K16). Fibers were also stabilized 1 minute at 95°C.

2.2 Methods used
Thermomechanical properties
TMA experiments were performed using Shimadzu Thermomechanical Analyzer TMA-50. Temperature at which the fibers are deformed at a constant load and total deflection of fiber at 90°C were determined using the TMA. Conditions of measurement were following: heat from room temperature to 90°C at the heating rate 5°C/min, and fiber length 9.8 mm.

Mechanical properties
Tensile test was done in order to measure the tension of fiber to tensile stress until the interruption of fiber. Fibers are straining continuously. Maximum tensile strength and corresponding extension is measured at the rupture of fiber. Mechanical properties were measured by Instron 3343 device and evaluated using Instron program. Measuring conditions:
- fixture length of fiber 125 mm,
- rate of clamp shifting 500 mm/min,

Tenacity (σ) is the strength that is necessary for the breakage of fiber per unit weight, expressed in cN/dtex. Determined is from the measured force F and the fineness of the fiber:

$$\sigma = \frac{F_{max}}{T_d} * 100 \qquad (1)$$

where F_{max} is the maximum force at breakage [cN] and T_d is fineness of fibers [tex].
Young's modulus is constant defined by Hook's low as dependence of tension on deformation in the area of low stress, expressed in cN/dtex. Experimentally is determined from the linear area of the tensile diagram stress-strain dependence.

3. RESULTS AND DISCUSSION

Dimensional stability of PP standard and composite fibers in dependence on temperature growth from room temperature to 90°C at rate 5°C/min were measured using TMA. From experimental dependencies were obtained the shrinkage temperatures of PP samples and total shrinkage of samples at 90°C. The results are shown in Table 1.

Table 1 Deformation temperature (T) and shrinkage (l) of standard and composite PP fibers with content of inorganic additives

Sample	T [°C]	l [%]
PP/S	55.40	-2.20
PP/K2	53.42	-2.38
PP/K4	55.13	-1.93
PP/K6	55.54	-0.97
PP/K8	56.18	-1.32
PP/K10	53.60	-2.21
PP/K12	55.06	-1.73
PP/K14	56.51	-1.62
PP/K16	54.05	-1.13

Shrinkage was detected at all measured samples. The behavior of standard PP fibers is comparable to composite PP fibers. In dependence on increasing concentration the shrinkage of PP composite fibers containing inorganic additives is decreasing.

Table 2 Tenacity (σ) and Young's module (E) of standard and composite PP fibers with different concentration of inorganic additives stabilized at 95°C during 1 minute and without stabilization

Sample	σ [cN/tex]		E [N/tex]	
	Without stabilization	After stabilization	Without stabilization	After stabilization
PP/S	28.86	27.06	2.80	2.30
PP/K2	26.11	23.25	2.76	2.40
PP/K4	24.48	24.95	2.74	2.49
PP/K6	27.29	25.81	2.67	2.58
PP/K8	26.43	26.00	2.76	2.65
PP/K10	25.81	25.22	2.84	2.60
PP/K12	25.21	23.83	2.69	2.46
PP/K14	22.46	23.50	2.54	2.51
PP/K16	21.55	22.47	2.54	2.37

Modification of fibers by inorganic additives improves dimensional stability of PP fibers. Temperature of fiber deformation was found to be comparable in standard and composite fibers.

In this part mechanical properties of standard and composite PP fibers were evaluated. Tenacity (σ) and Young's module (E) of standard and composite PP fibers were measured without and after stabilization (at 95°C for 1 minute, Table 2).

Tenacity of composite PP fibers without stabilization is decreasing with rising content of inorganic additives and in compare to standard fiber. After the stabilization tenacities were found to be lower than it was at fibers without stabilization, although at higher percentage of additives the tenacity was approaching to samples without stabilization.

By measuring Young's module it was detected, that attributes are higher at samples of standard fibers than it was at composite fibers without stabilization. After the stabilization PP fibers with addition of inorganic additives reached higher Young's module approaching to values of samples without stabilization

4. CONCLUSION

- Modification by inorganic additive improves dimensional stability of PP fibers

- The stabilization of PP fibers with higher content of inorganic additives improve mechanical properties
- By this modification PP fiber improving end-used properties of reinforced concrete can be prepared.

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SUPERABSORBING FIBRES IN NONWOVENS

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Abstract: *We would like to introduce in this paper performance characteristics of superabsorbing polymeric materials and possibilities of their usage in the field of preparation of textile materials. The paper focuses on nonwovens, evaluation of application of the superabsorbing fibres in an assortment of nonwovens and study of their performance characteristics. Application of superabsorbing fibres in the assortment of nonwovens enables to produce textile materials with a high added value and new performance characteristics. Combination of superabsorbning fibres with other kinds of fibres allows to prepare materials with higher absorptive and insulation properties designed mainly for applications e.g. in building, automotive and textile industry, agriculture, medicine etc.*
Keywords: *superabsorbent, superabsorbing fibre, nonwoven, special applications*

1. INTRODUCTION

Nonwovens belong due to their rather simple preparation and low price to often required materials in various application fields. Their properties depend not only on technological conditions of manufacture but mainly on properties of the used fibre types.

Rather quick development in the field of preparation of textile fibres in the last few years corresponding to the increasing requirements of the market has brought a number of new, advanced fibre types which fulfil even the most demanding requirements for quality and performance of the textiles. Application of the advanced fibre types offers new possibilities of preparation of nonwovens with new performance characteristics which increase qualitative parameters of the so-called standard nonwovens. The novel fibre types include also superabsorbing fibres whose preparation and evaluation in the assortment of nonwovens in the industrial scale is only in the beginning. They are destined for use in various applications due to their specific properties mainly from a viewpoint of increased absorption of water and aqueous solutions as well as insulation properties.

2. INFORMATION

2.1 Superabsorbing polymers

Superabsorbing polymers, so-called superabsorbents (SAP), are special materials whose hydrophilic network is able to abosorb large amounts of water and aqueous solutions. Particular molecules of the superabsorbing polymer link with molecules of other compounds to spatial (three-dimensional) networks by means of so-called „cross-linkers" in which liquid is fixed by strong hydrogen bonds and it is impossible to release it even under pressure. Amount of liquid absorbed by a superabsorbent is considerably dependent on content of ions and pH of particular absorbed solution. Some superabsorbents exhibit absorption of deionized water as much as 2000 times their weight, absorption of distilled water 800 times their weight and absorption of potable water 300 times their weight. Figure No. 2 (a, b, c) shows absorptivity of a superabsorbing fibre using distilled water coloured with a blue pigment for better visual assessment.
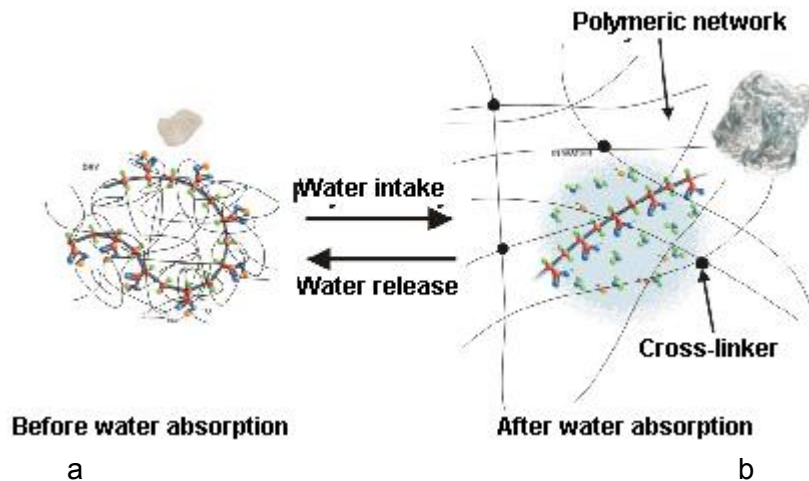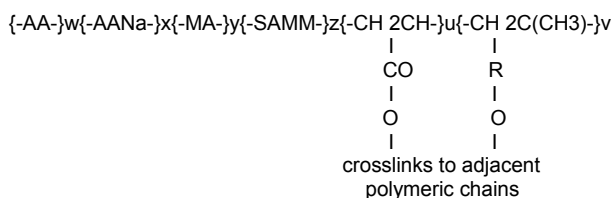
Figure 1 Structure of a superabsorbent: a) before water absorption; b) after water absorption

Figure 2 Proof of absorptivity of superabsorbing fibres: a) left: 100% superabsorbing fibre, right: distilled water; b) gradual addition of distilled water to the superabsorbing fibre; c) superabsorbing fibre after absorption of distilled water

2.2   Superabsorbing fibres

Superabsorbing fibres (SAF) are cross-linked acrylate polymers consisting of three different monomers: acrylic acid (AA), methacrylate (MA) and a small amount of special acryl/methacrylate monomer (SAMM) is which acrylic acid is partly neutralized by sodium salt of acrylic acid (AANa).

{-AA-}w{-AANa-}x{-MA-}y{-SAMM-}z{-CH 2CH-}u{-CH 2C(CH3)-}v
                                              | |
                                             CO   R
                                              | |
                                              O   O
                                              | |
                                    crosslinks to adjacent
                                       polymeric chains

Figure 3 Chemical structure of a super-absorbing fibre

Superabsorbing fibres are water insoluble, they are able to absorb water and aqueous solutions more quickly than superabsorbing powders because they have small diameter and a large surface area. They do not lose their fibrous structure on swelling, do not melt and start to decompose very slowly at temperatures > 200°C.

3.   PROCESSING OF SUPER-ABSORBING FIBRES INTO NONWOVENS

Smooth, undrawn staple fibres (SAF) 0.1 dtex with 52 mm staple length were used to evaluate workability and application of superabsorbing fibres in construction of a nonwoven. The nonwoven contained 10 – 50 wt.% of superabsorbing fibres, remaining 90 – 50 wt.% were standard staple polypropylene fibres. This fibre blend of superabsorbing and polypropylene (PP)

fibres was used to prepare needlepunched nonwovens under the same technological conditions. One side of a nonowoven (sample No. 8) prepared from a fibre blend containing 50 wt.% SAF and 50% PP was finished thermally using infra radiator with 3.9 m/min. fusion rate for the purpose of evaluation influence of the physical treatment on a change of functional parameters of the nonwoven. All prepared samples of blended nonwovens were subsequently evaluated from a viewpoint of their performance characteristics using methods for determination of swell capacity.

Two international methods were used to evaluate absorptivity of the prepared samples of blended nonwovens by means of swell capacity.

− *ISO 17190-5:2001 „Gravimetric determination of free swell capacity (FSC) in saline solution".* This method is based on determination of weight of a nonwoven sample before and after absorption of a liquid. Demineralized water was used as a test liquid. Test procedure includes preparation of test samples measuring 10 x 10 cm, which are conditioned in a desiccator for 24 hours and then they are weighted, immersed in horzontal position in demineralized water for 30 min. and after 30 min. of draining they are weighted again. Result of the measurement is W_f – amount of bonded absorbed liquid in grams to a gram of the sorbent.
− *ISO 17190-6:2001 Gravimetric determination of fluid retention capacity (FRC) in saline solution after centrifugation.* A modified method was used for mesurement. Demineralized water was used as absorbed liquid instead of 0.9% saline solution. The method is based on determination of weight of a nonwoven sample before and after absorption of a liquid (demineralized water) and after centrifugation. Measuring process is the same as in the first method, but the wetted samples are weighted only after centrifugation. A centrifuge with 1400 rotations/min. was used for centrifugation. Result of the measurement is W_g – amount of bonded absorbed liquid in grams to a gram of the sorbent.

4. RESULTS FROM MEASUREMENT OF SWELL CAPACITY OF THE NONWOVENS

Results from measurement of swell capacity of blended nonwovens containing superabsorbing fibres are given in Table 1. Sample No. 1, a nonwoven made of 100% polypropylene is a reference sample. Samples No. 2 – 7 are nonwovens made from a blend of superabsorbing fibres and polypropylene fibres with various percentage of the components. Sample No. 8 is a nonwoven with the same material composition as sample No. 7 with the difference that surface of one side of the sample No. 8 is also thermally finished by fusing. Graphic representation of swell capacity of the prepared nonwoven samples is shown in Figure 4.

Table 1 Swell capacity of the nonwovens.

Sample No.	Sample description	W_f [g/g]	W_g [g/g]
1.	100% PP	10.8	1.3
2.	10% SAF / 90% PP	18.0	7.4
3.	15% SAF / 85% PP	18.2	7.6
4.	20% SAF / 80% PP	18.3	8.9
5.	30% SAF / 70% PP	22.1	9.1
6.	40% SAF / 60% PP	27.8	12.7
7.	50% SAF / 50% PP	29.6	15.2
8.	50% SAF / 50% PP nonwoven with a surface thermal tretment	11.2	9.7

Comparison of swell capacity of the nonwoven reference sample (sample No. 1) and nonwovens based on a blend of superabsorbing and standard polypropylene fibres (samples No 2-7) shows that with increasing share of superabsorbing fibres absorbing capacity of the nonwovens increases. Amounts of bonded absorbed liquid in blended nonwovens are higher in comparison with the reference sample not only after spontaneous draining of excess liquid, as proven by value of the W_f parameter, but also after centrifugation, as defined by the W_g parameter.
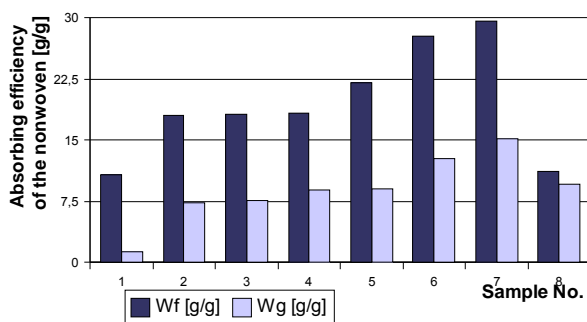

Figure 4 Swell capacity of the nonwovens.

Weight of the nonwoven containing 50% SAF is in comparison with the reference sample about 3 times higher before centrifugation and even 11, 5 times higher after centrifugation. This remarkable difference is caused by amount of water bonded by the superabsorbing fibre. Increase in weight of the nonwovens is influenced by structure of the superabsorbing fibre due to which the fibre is able to retain rather large amout of bonded distilled water even after centrifugation without its spontaneous or mechanical centrifugation. On the contrary in the case of centrifugation of the reference sample almost all amount of distilled water is centrifugated.

From a viewpoint of study of influence of the surface tratment of the nonwoven by fusing on change of its performance characteristics we can say on the base of the achieved results that swell capacity of the blended nonwoven sample (sample No. 8) decreases due to surface fusing in comparison with the unfused sample with the same material composition (sample No. 7). Difference in swell capacity of the fused nonwoven sample before and after centrifugation is minimal. On comparison of the sample No. 8 with the reference sample (sample No. 1) we can see that swell capacity of these samples is on a comparable level. A significant difference between these samples was observed only in amount of liquid after centrifugation W_g when amount of absorbed liquid of the blended nonwoven before and after centrifugation did not change considerably, which is a proof of absorbing capacity of the used superabsorbing fibres.

Visual evidence of absorbing capacity of superabsorbing fibres in the nonwovens is shown in Figure 5. A reference sample made of 100% PP (sample No. 1 – right) and a nonwoven containing 10 wt.% SAF (sample No. 2 – left) were used for the test.
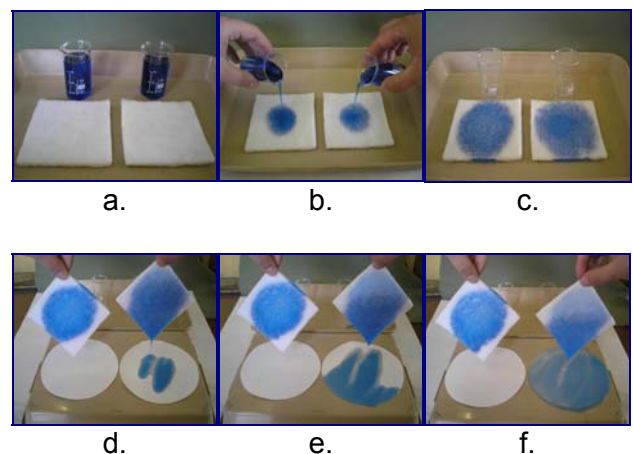
Figure 5 Absorbing capacity of a nonwoven containing 10 wt.% SAF in the nonwoven: a) left – nonwoven containing 10 wt.% SAF / 90% polypropylene, right – nonwoven made of 100% polypropylene; b) application of 50 ml distilled water containing colour pigment on the nonwovens; c) nonwovens with distilled water; d) and f) distilled water flowing down the nonwoven

5. CONCLUSION

Combination of superabsorbing fibres with standard PP fibres and/or other fibre kinds enables to prepare materials with new, advanced multifunctional properties. Application of superabsorbing fibres in nonwovens enhances their swell parameters and performance characteristics. Swell capacity of such materials depends on quantity of superabsorbing fibres in textile construction. It is possible to say on the base of results of the measured swell efficiency that absorbing capacity of the nonwovens increases with increasing share of superabsorbing fibres. Thermal surface finish of the nonwovens based on a mixture of superabsorbing and standard fibres decreases its swell properties as compared with an unfused nonowoven with the same material composition.

Enhancement of functional parameters and performance characteristics of the nonwovens via application of superabsorbing fibres increases their added value and extends application possibilities in various fields of the economy. They find considerable application in geotextiles (protective barrier on slopes preventing soil slip on floods, substratum of dumping sites, construction of roads, railways etc.), building industry (water fixation in construction of water canals, tunnels, protection on laying electrical and optical cables, filtration materials in air condition systems, drying wet areas etc.), agriculture, horticulture, forestry (textile carriers with seeds, sheets for young plants etc.), human and veterinary medicine (materials designed for absorption of body fluids, hygienic products for women, disposable diapers, incontinence products, ambulatory pads for animals etc.), automotive industry (fuel filters – trapping of water from fuels, filling of automotive seats etc.), clothing and shoe industry (filling materials with enhanced sorptive and insulation properties, inside sorption layer in shoes ensuring dry climatic environment etc.), household applications (sorptive filling materials used in production of furniture, cleaning materials – cloths for fluid absorption, industrial cleaning of machines etc.).

MECHANICAL PROPERTIES, RELAXATION BEHAVIOUR AND THERMAL CHARACTERIZATION OF FALSE-TWIST TEXTURED POLYLACTIDE MULTIFILAMENT

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1. INTRODUCTION

Polylactide (PLA) is a biodegradable hydrolysable aliphatic polyester which can be completely obtained from renewable resources. A partially oriented melt-extruded PLA multifilament 167dtex/68 yarn was false-twist textured under different conditions to further stabilize its structure. Tensile strength in straight, knot and loop form was measured in order to assess the influence of texturing conditions on tensile, bending and lateral compression of the multifilaments. Relaxation tests were performed to estimate different bonding levels in the polymer. The simultaneous observation of the thermal transitions detected by DSC and TMA enabled us to evaluate the thermal stability of the multifilaments and the evolution of primary and secondary transitions induced by texturing conditions. Relationship between thermal characterization and mechanical properties of the multi-filaments were studied to determine the influence of the texturing variables on the mechanical behaviour of the PLA textured yarns and to predict the best manufacturing conditions to produce PLA multifilaments.

2. MATERIALS

Table 1 describes the different PLA textured yarns according to texturing conditions (pre-texturing draw ratio and temperature), sample reference, linear density and cross-section. Sample C3 was lost and values assigned to it were estimated by statistical modelling using predictive models based on the other experimental results.

3. METHODS

Tensile properties

Specimens with gauge length of 100 mm were tested in straight (20 trials), looped (10 trials) and knotted (10 trials) forms, after conditioning in a standard atmosphere for 48 h. Specimens were subjected to tensile testing at 60%/min according to the ASTM D2101 Standard.

Using the Stress/Extension curve (Figure 1) the following parameters were determined:

- At yield point Y: Stress σ_Y [MPa] and Extension ε_Y [%].
- At minimum yield stress point S: σ_S [MPa].
- At breaking point B: Stress σ_B [MPa] and Extension ε_B [%]. Results of stress in loop ρ_{LP} and knot ρ_{KT} forms were expressed in efficiencies calculated as the ratio between the stress in these forms and the stress in the straight form in %.

Table 1 Texturing conditions (draw ratio and temperature) of PLA 167 dtex/68 multifilament, sample reference, and estimated cross-section using PLA density (1.25 g/cm³)

Draw Rat v_1/v_0	1.30			1.35			1.40		
Temp [°C]	135	150	165	135	150	165	135	150	165
Reference	*A1*	*A2*	*A3*	*B1*	*B2*	*B3*	*C1*	*C2*	*C3*
C sec/mm²×10³	17.93	17.69	17.44	17.30	17.11	17.09	16.87	16.55	16.43
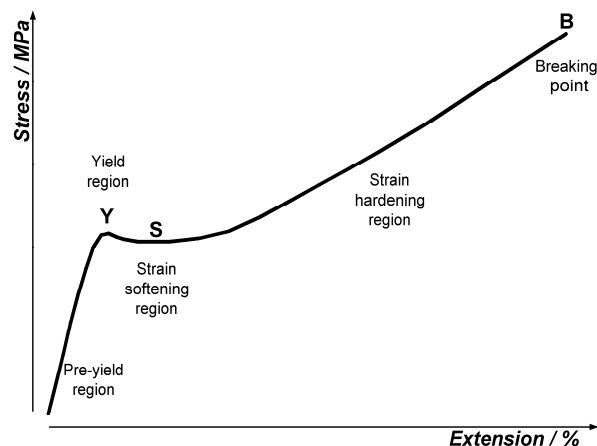
Figure 1 Stress/extension curve of the PLA multifilaments up to breakage, where the pre-yield (elastic), yield and post-yield (strain-softening and strain-hardening) regions can be observed

Relaxation experiments
Five specimens with gauge length of 100 mm were stretched at 10, 20 and 30% at a rate of 30%/min to determine the initial stress and the relaxation of stress up to 180 seconds. Using the methodology explained elsewhere [1] based on the application of the Nutting's law relating stress σ, stretching ε and time t ($\sigma = \psi\, \varepsilon^\beta\, t^{-\kappa}$), the stress relaxation rate κ was determined, and the mean values of the initial stress σ_0 and the final non-relaxed stress σ_f as % of the initial stress were estimated according to the method used by the authors [2].

Thermomechanical analysis
Two samples of each reference (Table 1) 12.8 mm in length were tested in a TMA/SDTA 840 Mettler Toledo under the following conditions: Initial temperature 25°C, final temperature 165°C, heating rate 10°C/min, nitrogen purging gas 35 mL/min under a periodic load between 0.025 and 0.05 N at 1/12Hz. Variations in sample length resembled the curve in Figure 2 (right). The deformation amplitude is inversely related to Young's modulus. The analysis of E-storage and E-loss curves [3] gave the following parameters:

- E_{min} *[MPa]*: E-storage modulus after glass transition (minimum) and
- T_φ *[°C]*: Temperature of maximum phase lag between E-storage and E-loss modulus.

Differential Scanning Calorimetry
Glass transition, relaxation, cold crystallisation and melting events were determined by a Mettler Toledo DSC-823 apparatus. Textured filaments were cut in very short lengths and duplicated samples of approximately 6 mg were sealed in 40 µl aluminium punched pans to guarantee good contact of the sample with the DSC sensor. DSC curves were obtained under the following operating conditions: Initial temperature 30°C, final temperature 200°C, heating rate 10°C/min and nitrogen purging gas 35 ml/min. Using the DSC curve (Figure

2 left) the areas below and above the base line yield the following parameters:
- ΔH_r [J/g]: Relaxation enthalpy.
- ΔH_{cc} [J/g]: Cold crystallisation enthalpy.
- ΔH_m [J/g]: Melting enthalpy.

Crystallinity X in % was calculated through the relationship $100 \times (\Delta H_m - \Delta H_{cc})/93.7$ [3].

4. RESULTS AND DISCUSSION

Results of the tensile properties, relaxation and thermomechanical analysis are given in Table 2 and those of enthalpies yielded by the DSC are given in Table 3. Abbreviations of the physical properties are those defined under the description of the methods.

Yield stress and extension are highly influenced by texturing. There is a relevant effect of the pre-texturing draw ratio on both stress and extension (Figure 3). The higher the draw ratio the greater both yield stress and extension. Texturing temperature appears to exert a slight influence on yield parameters. Yield stress increases with texturing temperature from 135 to 150°C and the effect on yield extension increases with the pre-texturing draw ratio.
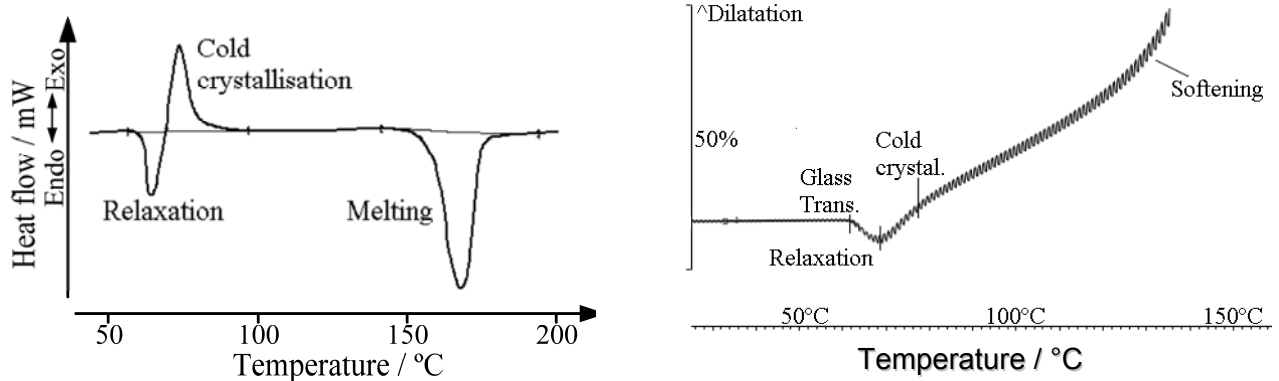
Figure 2 (left) DSC curve of PLA false-twist textured multifilament from 30 to 200°C and (right) TMA curve multifilaments 12.8 mm in length under a periodic load from 25 to 165°C at 10°C/min.

Table 2 Stress σ_Y and extension ε_Y at yield, minimum yield stress σ_S, stress σ_B and extension ε_B at break, loop ρ_{LP} and knot ρ_{KT} strength efficiencies. Mean values of the initial stress σ_o, relaxation rate κ and final non-relaxed stress σ_f, when stretched at 10, 20 & 30%. Minimum E-storage modulus after glass transition E_{min} and temperature of maximum phase lag between E-storage and E-loss modulus T_φ

REF	σ_Y [MPa]	ε_Y [%]	σ_S [MPa]	σ_B [MPa]	ε_B [%]	ρ_{LP} [%]	ρ_{KT} [%]	σ_o [MPa]	κ rate ×10³	σ_f [%]	E_{min} [MPa]	T_φ [°C]
A1	122.2	3.54	116.9	236.8	33.90	99.64	90.00	174.64	62.42	64.03	25.9	67.5
A2	126.9	3.66	122.0	238.3	32.99	99.28	85.63	168.29	61.26	64.65	34.1	67.8
A3	125.6	3.64	122.7	242.8	33.16	96.42	85.66	163.32	60.77	64.79	75.0	68.5
B1	127.5	3.75	123.6	249.4	31.27	99.95	87.84	179.00	58.39	65.66	34.1	68.1
B2	129.9	4.02	127.6	252.5	30.10	94.80	84.85	178.80	58.84	65.92	61.6	68.5
B3	127.9	4.13	125.7	254.4	31.27	96.34	83.93	176.05	58.57	65.92	119.3	68.7
C1	128.4	4.15	126.7	225.3	24.56	98.26	96.25	184.81	57.26	66.53	61.0	68.7
C2	132.3	4.48	132.2	250.4	26.85	95.54	88.80	188.36	56.90	66.73	105.2	69.0
C3	130.3	4.72	131.4	260.9	27.86	94.06	90.24	193.48	57.96	66.59	167.1	70.0

Table 3 Enthalpies of relaxation ΔH_r, cold crystallization ΔH_{cc} and melting ΔH_m of the PLA textured multifilaments measured by differential scanning calorimetry

Reference	A1	A2	A3	B1	B2	B3	C1	C2	C3
ΔH_r [J.g^{-1}]	7.74	7.65	5.43	7.89	6.51	4.06	5.81	5.05	1.73
ΔH_{cc} [J.g^{-1}]	14.35	13.92	10.29	13.89	11.55	9.07	11.68	10.11	7.32
ΔH_m [J.g^{-1}]	43.29	45.35	44.21	42.48	44.56	43.17	44.23	44.13	43.47
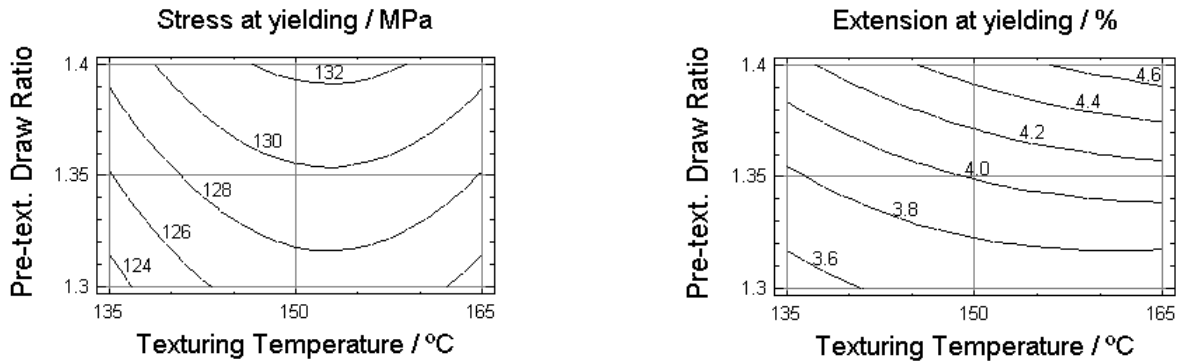
Figure 3 Influence of texturing variables (pre-texturing draw ratio and temperature) on yield stress (R² = 94.0%) and on yield extension (R² = 99.9%) of textured PLA multifilaments

Both DSC and TMA curves revealed a relaxation when the glass transition occurs. On tensile testing, stress relaxation was observed at yielding by a decrease in stress when extension proceeds.

The depletion in stress is given by σ_Y-σ_S and Figure 4 (left) shows the influence of the texturing variables on it. The depletion decreases as texturing effect increases (higher draw ratios and temperatures). Figure 4 (right) shows its relationship with the maximum phase lag temperature between E-storage and E-loss. The phase lag temperature increases with cross-linking in the fibre through stronger binding in the amorphous phase, which results in lower relaxation at the glass transition.

As regards breaking stress, there is a marked interaction between texturing temperature and draw ratio: Texturing temperature does not affect breaking stress when draw ratio is 1.3 but it shows a progressively increasing effect as draw ratio ascends (Figure 5 left). Breaking extension decreases with draw ratio although the intensity of the effect decreases as texturing temperature increases (Figure 5 right). Loop and knot strength efficiencies decreased with fibre brittleness. The lowest texturing temperatures yielded the highest efficiencies. The highest efficiency in loop form was at 1.3 draw ratio whereas in knot form was at 1.4 draw ratio. Loop and knot strength efficiencies depended on the effect of orientation: Low orientation favoured bending (loop) resistance because yarns showed the highest breaking extension (34%) while high orientation favoured a better resistance to a combined effect of lateral compression and bending (knot effect) because of its lowest breaking extension (26%). Texturing temperature decreased efficiencies in both tests owing to its effect on crystallinity.

Texturing increases crystallinity. Figure 6 shows the effect of the increase on crystallinity induced by the texturing temperature on breaking stress according to the three levels of orientation induced by the pre-texturing draw ratio. The higher the orientation, the stronger the effect of the increase of crystallinity on breaking stress. The same trends can be observed when the minimum E-storage modulus mainly attributed to the crystalline phase of the fibre is considered.
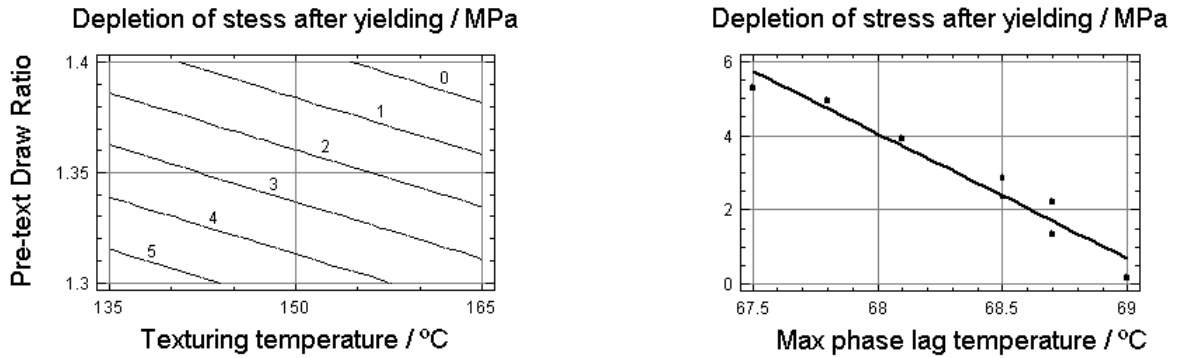
Figure 4 Influence of texturing variables on stress depletion after yielding (R² = 95.4%) and its relationship with the maximum phase lag temperature between E-storage and E-loss (R² = 94.6%)
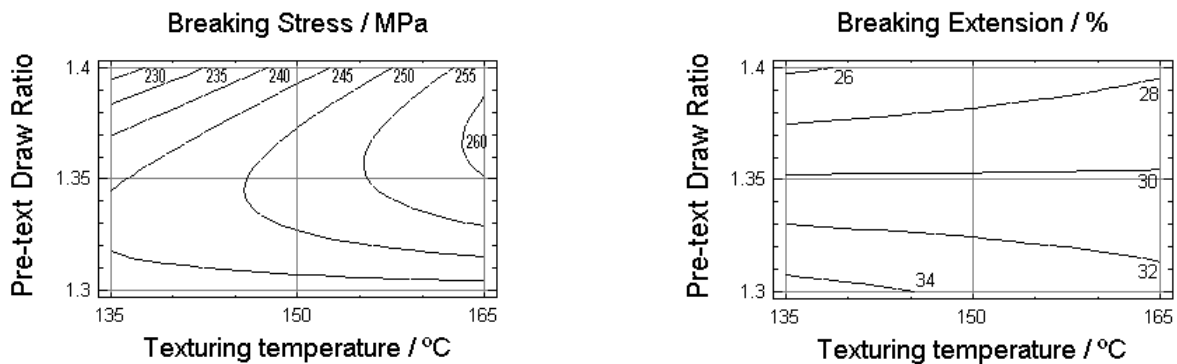
Figure 5 Influence of texturing variables (pre-texturing draw ratio and temperature) on breaking stress (R² = 81.2%) and extension (R² = 93.8%) of textured PLA multifilaments
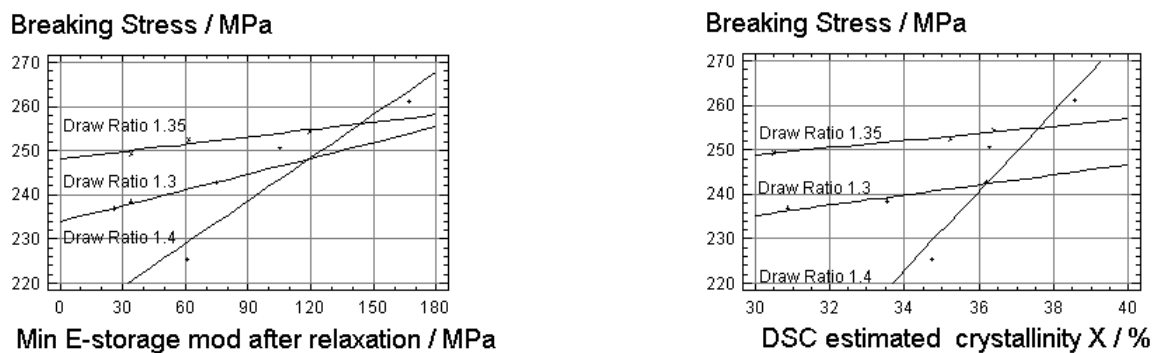
Figure 6 Relationship between breaking stress and E-storage modulus due to crystalline phase of PLA and with the DSC estimated crystallinity according to texturing draw ratio
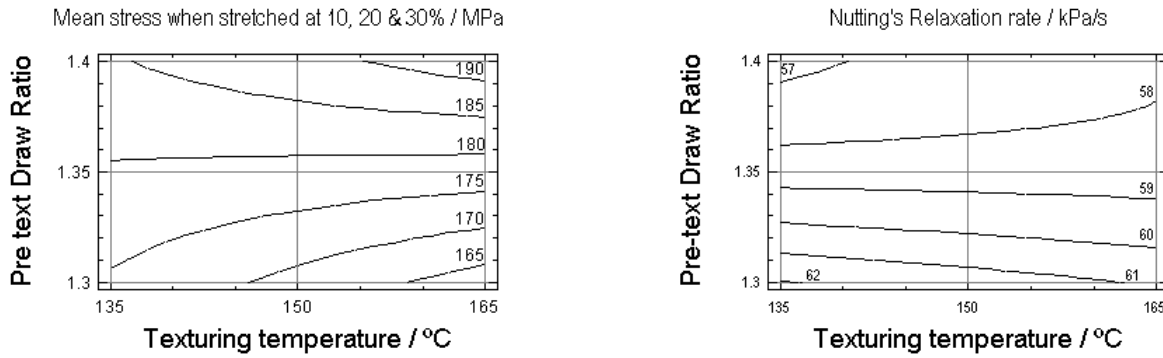
Figure 7 Influence of the texturing variables (pre texturing draw ratio and texturing temperature) on the mean initial stress induced when stretched 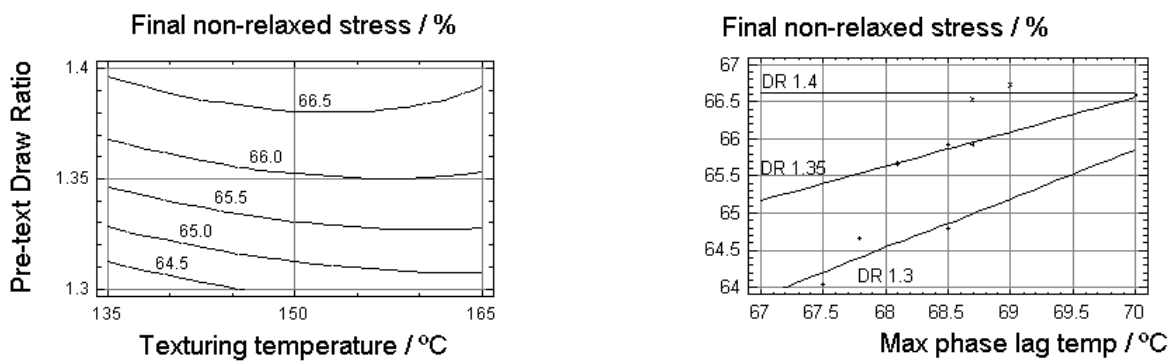at 10, 20 & 30% for relaxation (R^2 = 99.4%) and on the relaxation rate (R^2 = 97.44%) estimated by the application of the Nutting's model

Figure 8 Influence of the texturing variables (pre texturing draw ratio and texturing temperature) on the mean final non-relaxed stress when stretched at 10, 20 & 30% (R^2 = 99.9%) and its relationship with the maximum phase lag temperature between E-storage and E-loss

As regards the relaxation, Figure 7 shows the prominent effect of the orientation on both the initial stress induced by stretching and the rate of relaxation. It is evident that the draw ratio leads to an increase in the alignment of the macromolecules within the fibre becoming more compact and, consequently, increasing the initial stress when stretched, and decreasing the relaxation rate. The slight effect of the temperature interacts with the effect of the draw ratio. At high orientation, the increase in temperature makes the initial stress to ascend. As regards the final non-relaxed stress (Figure 8 left), the effect of draw ratio on this is also noteworthy and only a slight effect of temperature is observed. Figure 8 (right) shows its relationship with the maximum phase lag temperature. The stronger the binding in the amorphous phase, the higher the non-relaxed stress.

5. CONCLUSIONS

The orientation in the fibre exerts a marked influence on yield stress and extension. Texturing temperature slightly decreased the yield parameters. The internal relaxation detected by thermal techniques is related with yield stress depletion after yielding. Thermal treatments and orientation increases binding in the fibre, leading to an increase in the phase lag temperature. When highly oriented, cross-link increases breaking stress of the filaments while no variation in the final non-relaxed stress is observed.

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INFLUENCE OF CONSTRUCTIONAL PARAMETERS ON END-USE PROPERTIES OF FINE COTTON SHIRTING MADE OF COMPACT YARN

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Abstract: *The influence of constructional parameters on end-use properties of finished fine cotton fabrics made from fine compact yarn was investigated. Compact yarn was made from Extra Long Staple Egyptian cotton. Floating has important influence on lower tensile stress and lower creasability. Yarn smoothness has influence on better softness and air permeability. Yarn fineness influences the softness of fabrics. The best results relating to the durability and comfort of shirting were obtained with unwashed and 10-times washed fabrics with minimal floating yarns and with gassed compact yarn in warp.*
Key words: *Egyptian cotton, compact yarn, fine yarn, shirting fabrics, washed fabrics*

1.   INTRODUCTION

Among shirting materials, which are commercially available, cotton is still most popular for manufacturing men's business shirts [1]. The results of the survey conducted in December 2008 among fifty businessmen of age 27 to 40 years in Ljubljana show that customers, when buying men's shirts, make decision mostly on the basis of a proper fashion model (25%), quality of material (24%) and price (20%); less important criteria are the care (17%) and brand name (14%). Approximately 62% of questioned persons wear shirts two years maximally, and even 90% of them care of their shirts at home.

One of the most important factors, which characterize a qualitative men's business shirt, is the quality of shirting material. The quality depends above all on durability, softness, breathability, sorption and creasability of material. The construction and finish in addition to the type of yarn have the most important influence on end-use properties of a fabric. Each washing and ironing contributes to the material wear and tear as well as to the deterioration of its mechanical and aesthetic properties and its touch [2, 3].

In comparison with conventional spinning yarn compact spinning yarn provide more efficient utilization of substantial strength of fibres, which makes compact yarn stronger by even 25% and imparts them higher breaking elongation. Due to low surface hairiness the fabrics made of compact yarn are more resistant to abrasion and pilling, have higher lustre, higher elasticity and softer touch than the fabrics made of conventional spinning yarn [4]

The purpose of the research was to estimate the influence of constructional parameters on end-use properties of fine cotton fabrics made of compact yarns spun from the Giza 87 and Giza 70 Extra Long Staple cotton.

2.   EXPERIMENTAL PART

Four cotton fabrics (Figure 1) industrially produced by Tekstina d.d. Ajdovščina were included in the research. Fabrics were made from double twisted compact yarns of fineness Nm 140/2 and Nm 100/2. Fabrics designated SY, SM and SL were made in lengthwise stripe combination weaves; a fabric designated SX had a ground motif (in ground weave there are motifs produced by floating threads) (Figure 2). Fabrics designated SM and SX had high yarn floating (up to five floating threads in fabric SM and up to nine floating threads in fabric SX).

All fabrics were finished in the same way: dry singed, mercerized, finished, softened and

sanforized. The finishing bath was composed of a cross-linking agent DMDHEU, catalyst $MgCl_2$, softening agent (emulsion of polydimethylsiloxane) and fatty acid amide, emulsion of amino modified polydimethysiloxane), swelling agent (ethoxylated fatty alcohol) and polyethylene emulsion additive.

The changes in the quality of fabrics were assessed after 10 washing cycles. A laboratory washing procedure took place at 60°C with 50 grams of Ariel Auto washing agent per 4-5 kilograms of fabric for each washing cycle. After each washing cycle, the fabrics were dried in a drying machine on the programme for cotton fabrics, and hand ironed with an electric iron in accordance with the fabric producer's instructions at temperature near 220°C

3. RESULTS AND DISCUSSION

Fabric samples were made from a high quality Extra Long Staple Egyptian cotton Giza 70 and Giza 87. Giza 87 is a top quality variety among Egyptian cottons due to its superior fiber fineness in comparison to a newer cotton variety Giza 70 [5]. The yarn Nm 140/2 made from Giza 87 had almost 2-times higher specific breaking stress than the yarn Nm 100/2, made from Giza 70 (Table 1) also because of higher twist. Yarn irregularity, thick and thin places and nep values of the yarn Nm 100/2 were better than those of the yarn Nm 140/2. Gassing process diminished hairiness of the yarn Nm 140/2 to the very low value.

| SY | SM | SL | SX |
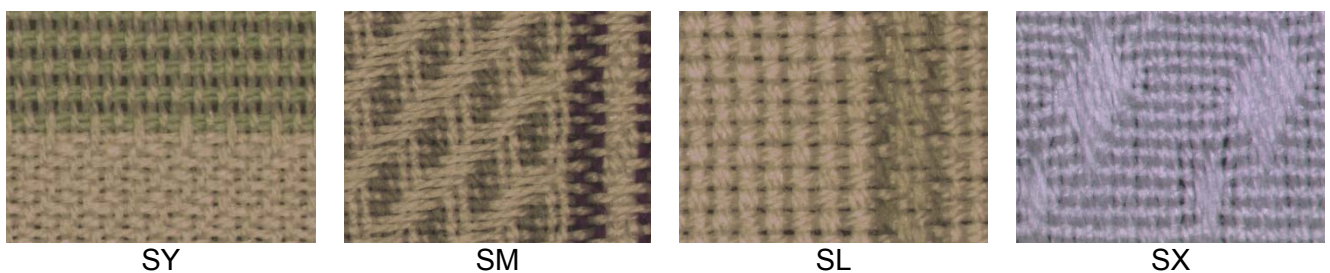
Figure 1 Fabric samples (magnification 20-x)
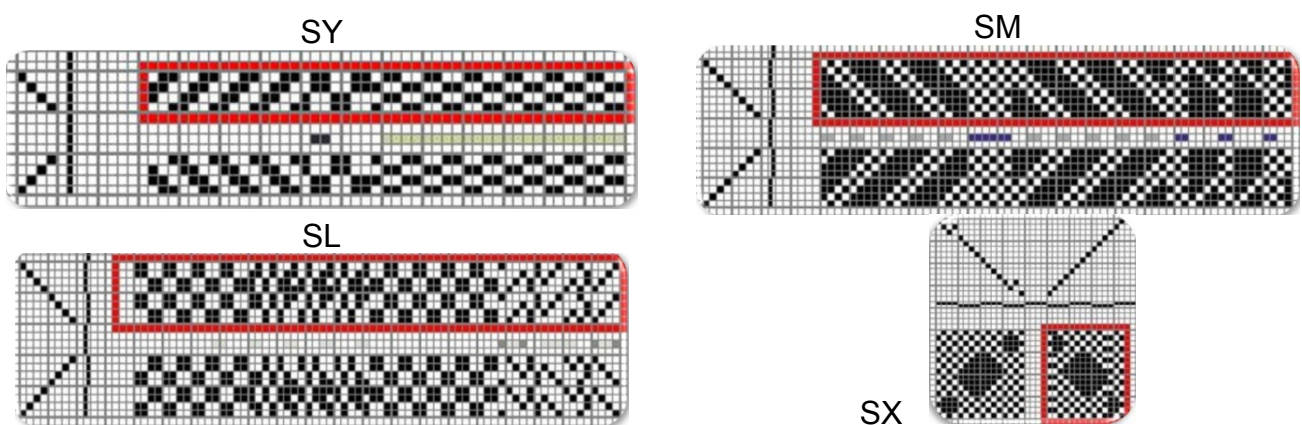
Figure 2 Weave patterns of analyzed fabrics

Table 1 Properties of compact yarns

Properties	Yarn Nm 100/2, Compact	Yarn Nm 140/2, Compact gassed
Cotton type	Giza 70	Giza 87
Used as warp in fabric samples	SX, SL	SY, SM
Used as weft in fabric samples	SX, SL, SY, SM	-
Linear density (Average /CV)	11.98 tex /3.94%	8.26 tex / 2.50%
Twist (Average /St. dev./CV)	1100.48 m^{-1}/ 4.63%	1408.96 m^{-1} / 3.04%
Breaking force (Average /St. dev./CV)	2.14 N / 10.14%	2.76 N / 5.78%
Breaking stress	17.83 cNtex^{-1}	33.45 cNtex^{-1}
Breaking elongation (Average /St. dev./CV)	3.92% / 12.38%	4.11% / 8.33%
Uster	8.40%	9.50%
CV	10.5 m	11.9 m
Thin (-50%)	0	1
Thick (+50%)	4	11
Neps (+200%)	24	24
Hairiness	3.60	1.70

Table 2 Constructional and physical characteristics of fabrics samples

Sample	Density warp/weft (ends/picks Per 10 cm)	Fabric crimp (%)		Mass per unit area (g/m^2)	Thickness (μm)	Density (g/cm^3)
		Warp direction	Weft direction			
SY	548/498	10.2	3.9	105.68	72	1.47
SM	556/463	8.6	5.9	103.09	86	1.20
SL	553/407	7.5	3.9	111.00	108	1.03
SX	544/327	9.2	3.9	104.81	149	0.70

The basic constructional parameters of finished fabrics are presented in Table 2. Fabrics SY and SM with finer yarn in warp direction, have lower thickness, mass per unit area and much higher density than fabrics SX and SL with coarser yarn in warp direction. Fabric density depends on warp/weft density, woven structure and fabric crimp. Number of flotations influences on increasing fabric thickness because flotating thread is lifted above fabric surface.

The durability of fabrics was assessed on the basis of specific breaking stress (Figure 2, a) and pilling. All fabrics surpassed the demanded breaking force of 200 N/100 yarns in warp/weft directions: SX: 511/402 N/100 yarns; SL: 360/362 N/100 yarns; SY: 280/365 N/100 yarns and SM: 248/347 N/100 yarns.

After washing the fabrics 10 times, only the breaking force of fabric SM in warp direction decreased under 200 N/100 yarns (to 170 N/100 yarns).

The highest specific breaking stress has fabric SY in weft direction. Weave structure defines number of interlacing points and thus friction surfaces between threads, which affect strongly the specific breaking stress. In our case fabric SY has higher specific breaking stress in warp direction comparing to fabric SM, due to more compact structure. Specific breaking stress was in high correlation with the density of fabrics in weft direction (r = 0.995); in warp direction it was lower (r = 0.914) (Figure 2, a).

All fabrics had excellent pilling after 7000 cycles (grade 5 after ISO 12945-2). 10-times washing of the fabrics had only a minimal influence on deterioration of pilling (grade 5). Higher breaking elongation of fabrics enables better body movement comfort. Fabric SX

had the highest breaking elongation (Figure 2, b) in warp direction. Breaking elongation increased with washing.

The softness of fabrics was assessed from the stiffness (Figure 3, a), which was low, i.e. under 100 mg/cm. Fineness and smoothness have strong influence on stiffness. This was confirmed with fabrics SY and SM in warp direction, where the finest yarn Nm 140/2 was used. Washing deteriorated the softness of all fabrics in both directions.

The creasability, assessed from a recovery angle (Figure 3, b), was over 50° only in fabrics SY and SM in warp direction, which we explained with the smoothness of the yarn Nm 140/2. In warp direction, fabric SM had higher recovery angle than fabric SY because of higher yarn floating. Creasability increased with washing due to partly removed finish.

The smoothness of yarn also influences air permeability (Figure 4, a), which was the highest in fabrics SY and SM.   Air permeability of all fabrics deteriorated with laundering by 10 to 30% after 10-times washing because fibres protruding from the yarns increased the number of pores in fabrics.

The wettability of fabrics was assessed according to AATCC 22 standard method. It was zero, completely wetted, for all fabrics (unwashed and washed 10-times). The velocity of water absorption (Figure 4, b) of unwashed samples achieved the value under 1 mm/s. After 10 washing cycles, it increased even to 13 mm/s as a result of partly removed finishes, which were unstable in water.

At the end the quality of all fabrics together was evaluated on the basis of the set criteria, which were the highest possible strength and breaking elongation, highest crease recovery angles, lowest stiffness, highest air permeability and quickest sorption of fabrics. By using the statistical method of the Spearman's rank correlation, we estimated the fabrics with grades from 1 (the worst) to 5 (the best). Among the unwashed samples fabric SY was the best (3.63) and fabric SL the worst (2.30). After 10 washing cycles, fabric SY kept the first place (3.71) and was followed by fabrics SL (3.00), SM (2.50) and SX (2.43).

The relative changes of properties between unwashed fabrics samples and washed 10-x are shown in Table 3.
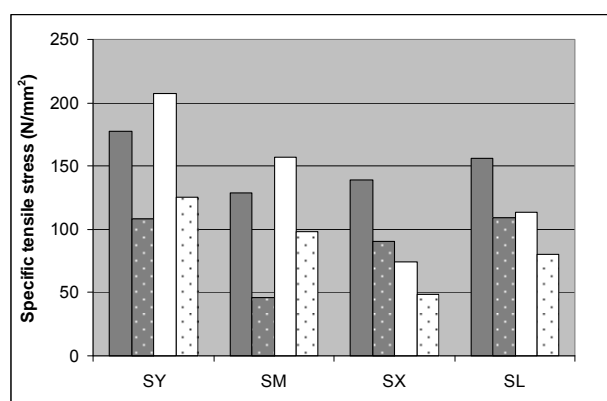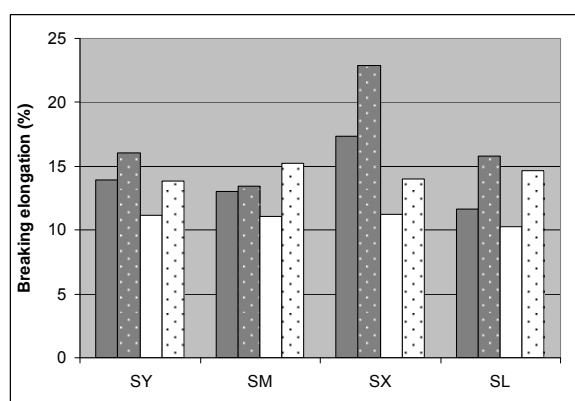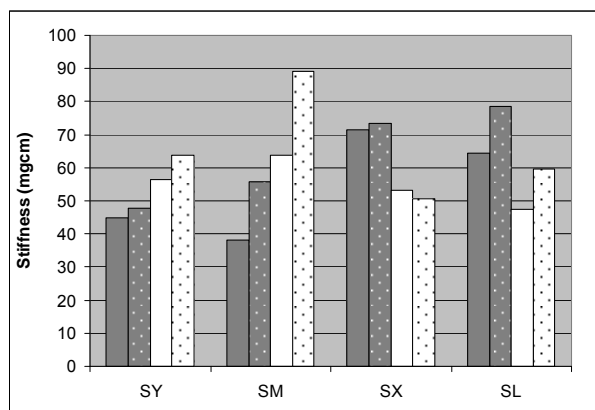

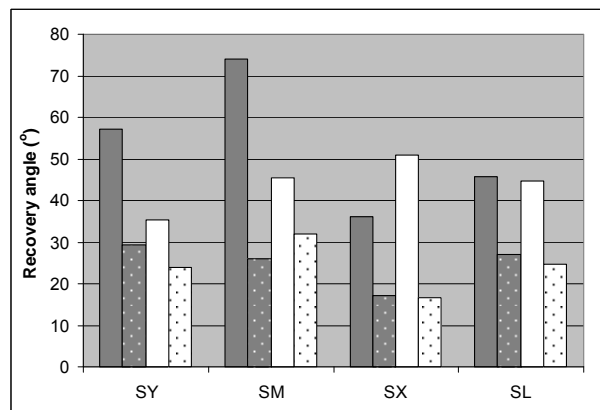(a)   (b)

Figure 2 Specific breaking stress (a) and breaking elongation (b) of fabrics in warp (grey) and in weft direction (white). Washed fabrics 10-times are marked with dots.
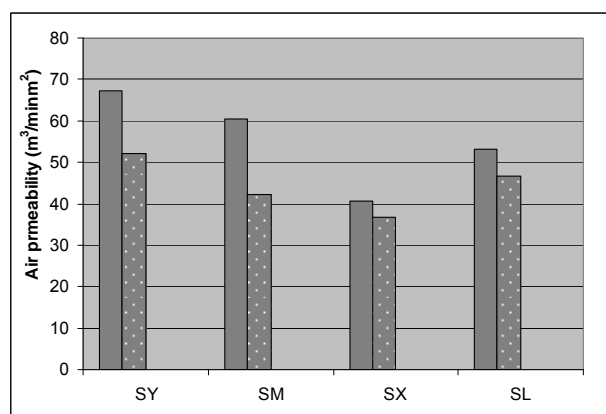
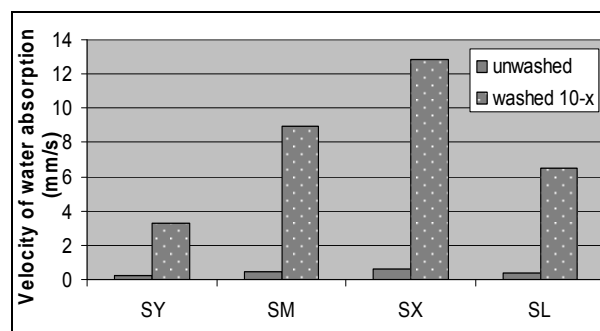(a)   (b)

Figure 3 Stiffness (a) and recovery angle (b) of fabrics in warp (grey) and in weft direction (white). Washed fabrics 10-times are marked with dots.

(a)   (b)

Figure 4 Air permeability (a) and velocity of water absorption (b) of fabrics of unwashed fabrics (grey) and washed fabrics 10-times (marked with dots).

Table 3 Relative changes of properties between unwashed fabrics samples and washed 10x

Sample	Thickness (%)	Mass per u.a. (%)	Density (%)	Specific tensile stress (%)		Breaking elongation (%)	
				warp	weft	warp	weft
SY	+76.2	+1.6	+72.2	-39.0	-39.5	+2.1	+2.7
SM	+98.7	+1.75	+94.3	-64.2	-37.5	+0.4	+4.2
SX	+61.8	+0.9	+59.7	-35.3	-34.6	+5.5	+2.8
SL	+59.5	+1.8	+56.4	-30.0	-29.2	+4.1	+4.4

4. CONCLUSIONS

The best results of the durability and comfort of shirting were obtained with unwashed and 10-times washed fabrics with minimal floating yarns and with gassed compact yarn in the warp. 10-times washing cycles affected the properties of fabrics, which partly deteriorated, particularly breathability (lower air permeability); as a result of removal of the finishes, which are unstable in water, water sorptivity of fabrics increased. Yarn

smoothness had influence on better softness and air permeability of fabrics. Yarn fineness influenced the softness of fabrics.

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EXTRACTION OF CHROMIUM FROM DYED TEXTILES BY MEANS OF ARTIFICIAL SKIN SURFACE FILM LIQUID

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Abstract: The growing interest about the possible interaction of the textile materials with the human skin lead to test analytical methods for toxicological and eco-toxicological quality determination of the textile manufactures.
Actually the analysis of heavy metals is based on a method adopted by some private textile eco-labels, where the metals are extracted from the textiles materials by means of an artificial saline solution prepared according to the ISO 105 E-04 standard, which is specific for testing color fastness to perspiration.
In this work we have tested an alternative method to extract chromium from textile materials, using an artificial skin surface film liquid which should better mimic the human sweat. The results were compared to those obtained using the ISO standard solution.
Moreover, the metal extraction yield was derived by the determination of total chromium in the ashes.
Keywords: Chromium extraction, artificial skin surface film liquid, textiles.

1. INTRODUCTION

Chromium compounds are widely used in various industrial processes, as metal finishing, leather tanning, inorganic chemicals production, wood preserving and metallurgical industrial processes.

Chromium often is also used in different textile processes, as dyeing and printing [1], and it is present above all in metal complex dyes. In particular the fast black dyeing on wool and nylon is carried out using chromium based dye, in fact one of the most widely used dyes in the world is the chromium dye C.I. Mordant Black 11 [2]. This kind of dyes guarantees high fastness to wet and light treatment, so they are preferred to acid dyes in wool dyeing.

Therefore it is possible to find chromium in textiles dyeing wastewaters as free ionic metal or complex metals, where it contributes to the environmental concerns [3].

Chromium exists in nature in several oxidation states, but trivalent and the hexavalent forms are the most interesting because of their properties and very different toxicity [4]. The trivalent chromium has low mobility, with solubility minimal at pH above

5.5. It is necessary for normal protein, fat and glucose metabolism, for proper insulin function and it is used as micronutrients and dietary supplements [5].

On the contrary, the hexavalent chromium compounds (CrO_4^{2-}, $Cr_2O_7^{2-}$) are more toxic than the trivalent chromium ones, because of their higher solubility in water, rapid permeability through biological membranes and subsequent interaction with intracellular proteins and nucleic acids [6]. A large number of studies demonstrate that the hexavalent form is genotoxic and carcinogenic, causes allergic dermatitis, induces oxidative stress, DNA damages, apoptotic cell death and altered gene expression [7-12]. Finally, Cr(VI) is a well known lung carcinogen [13] and also a human reproductive concern [14-19]. Moreover, negative effects also on environment are reported. In fact, chromium interferes with several metabolic processes of vegetable and animal organisms [20-21] and it is highly toxic to plants which results in reduced roots, phytomass and photosynthetic pigments [22-24].

Because of negative effects of chromium on human health [25], international authorities

and organizations are developing strategies and regulations to protect the consumers and the workers exposed during the production process. Actually some private eco-labelling voluntary schemes impose Cr requirements based on the extraction of the metal by means of a saline solution simulating the human acid perspiration [26], but there aren't national or European standards about restriction on presence of chromium in textiles, except for some REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) regulations that limit the quantity of residual sodium dichromate also in textile materials.

Moreover, there are some technical problems regarding the availability of laboratory methodologies that are sufficiently sensitive, specific and reproducible for testing chemicals safety on textile materials.

Nowadays the analysis of heavy metals in textile materials, like copper, nickel and chromium, is based on a method adopted by some private textile eco-labels, which requires a metal extraction from the textile materials by means of an artificial acid saline solution prepared according to the ISO 105 E-04 standard. The method is specific for testing color fastness to perspiration. In previous studies, it was investigated in depth and best operative conditions were identified [27].

Nevertheless the dissolution of chemical constituents from jewelry, textiles, cosmetics, drugs, industrial chemicals and particles in direct and prolonged contact with human skin is often assessed *in vitro* using artificial skin surface film liquids (SSFL) as surrogates of human sweat. In literature 45 different formulations of artificial SSFL are reported [28].

In this work we applied the best conditions based on ISO 105 E-04 standard to thetrivalent and hexavalent chromium extraction using an artificial skin surface film liquid solution, which should better mimic the human sweat. The extractions are carried out at two pH values (5.5 and 8). Cr(tot) and Cr(VI) content in textile material was determined by means of AAS (atomic absorption spectroscopy) and UV-visible spectroscopy respectively, and the results were compared to those obtained using the ISO standard solution.

Finally, the metal extraction yield was derived by the determination of total chromium in the ashes.

The aim of this research was to propose an alternative extraction method based on extraction solutions as similar as possible to human sweat, to evaluate chromium content in textile materials.

2. EXPERIMENTAL

2.1 Sample and extraction procedure

A 100% wool top dyed with a chrome-dye was extracted by means of a SSFL solution (Table 1) in reproducible conditions of time and temperature and at two pH values (5.5 and 8). The same sample was extracted at the same extraction conditions by means of artificial saline solutions, prepared according to the ISO 105 E-04 standard [29].

The textile sample (1.00 ± 0.01 g) was dried in oven at 105 ± 2°C for 4 hours, introduced into 100 ml of extraction solution and shook at 40°C for 2 hours. After the extraction, the solutions were filtered under vacuum with a 0.45 μm membrane. Cr(tot) in the extraction solution was determined using electro-thermal atomic absorption spectroscopy GFAAS (Perkin Elmer 4100 ZL with THGA graphite furnace) using argon as inert gas. In Table 2 are reported the instrumental parameters and operating conditions. The determination of the Cr(VI) content in the solution was carried out using ultraviolet-visible spectroscopy (UV-Vis), and it was determined as a colored complex with 1,5-diphenylcarbazide, using appropriate reference solutions.

Table 1 ISO solution composition [29] and SSFL composition according to Gudewill [30]

Substance	SSFL SOLUTION		ISO SOLUTION	
	Sweat as caused by exercise (pH 5.5) [g/l]	Sweat as caused by heat (pH 8) [g/l]	Substance	pH 5.5 [g/l]
NaCl	3.51	5.8	NaCl	5
KCl	0.75	0.67	L-istidine monohydrate	0.5
CaCl2	0.14	0.14	$NaH_2PO_4 \cdot 2H_2O$	2.2
NH4Cl	1.59	1.59		
Urea	0.58	0.52		
Lactic Acid	3	0.35		

Table 2 Instrumental parameters and operating conditions

PARAMETER	Cr
Wavelength [nm]	357.9
Slit width [nm]	0.7
Lamp current [mA]	30
Gas flow [ml/min]	250
Sample volume [μl]	20
HEATING PROGRAM TEMPERATURE [°C] (ramp time [s], hold time [s])	
Drying 1	110 (1, 20)
Drying 2	130 (5, 30)
Ashing	1500 (10, 20)
Atomization	2300 (0, 5)
Cleaning	2400 (1, 2)

2.2 Ashing procedure for the verification of the method efficiency

The ashing method based on UNI 8047 [31] was applied to extract chromium from the textile material. The ashes were dissolved in nitric acid and distilled water (1:50) and filtered on filter paper to obtain a clear solution. The chromium content in the solution was determined by GFAAS spectroscopy. The metal content extracted into the eluate was compared with the metal content extracted from the textile material by the ashing and the total efficiency of the SSFL solution extraction method was verified.

3. RESULTS AND DISCUSSION

3.1 Cr(tot) and Cr(VI) determination

The operational development of the research consisted in the determination of the quantity of the metal extracted from the wool top by SSFL solution. Each extraction was performed in triplicate. The analytical results were expressed as mean of three lectures with their standard deviation and they were compared to those obtained using the ISO standard solutions (Table 3). Cr(III) concentration is obtained from the difference between total and hexavalent chromium.

Table 3 Mean value of total and hexavalent chromium concentration

Solution	Concentration [mg/kg]		
	Cr(tot)	Cr(VI)	Cr(III)
SSFL pH 5.5	7.8 ± 0.7	n.d.	7.8 ± 0.7
SSFL pH 8	5.1 ± 1.2	1.8 ± 0.6	3.3 ± 1.3
ISO pH 5.5	10.0 ± 0.3	2.0 ± 0.1	8.0 ± 0.2

n.d. = not detectable

The quantity of metal extracted and the relative ionic form is closely related to the pH of the saline solution simulating the sweat and to the capacity of the solution to oxidize the metal. Also the balance of ionic couple Cr(III)/Cr(VI) is affected by pH conditions of the solution. At lower pH values Cr(VI) tends to reduce to the more stable Cr(III) ionic form, otherwise at higher pH values the hexavalent form is more stable.

The ionic strength of the extracting solution, besides pH, is also one of the important factors that influence the aqueous equilibrium uptake of chromium species from textile materials.

Generally speaking, the Cr(III) and Cr(VI) removal decrease with increasing ionic strength and the effect could be significant at ionic strength lower than 0.5 M [32].

Aqueous chemistry of Cr(III) is well understood. At relatively higher pH conditions, chromium(III) displays a tendency to aggregate and form hydroxy bridged oligomers of relatively lower solubility [33].

Comparing SSFL and ISO solutions at the same pH, it is evident that the standard ISO solution is more efficient to extract total chromium from textiles rather than SSFL. In fact, at pH 5.5 the ISO solution extracts about 21% more than the SSFL solution.

The ionic strength of the ISO solution is lower compared to the SSFL solution and this could explain the different solution absorption of the total chromium ions.

Moreover, the extraction by SSFL solution is more efficient and reproducible at acid rather than at basic pH values. In fact, the acid SSFL solution extracts about 35% total chromium more than basic one. This probably occurs because the higher pH conditions of the aqueous solution favour the aggregation of Cr(III) in a less soluble form, the ionic strength being similar.

A significant fraction of the total metal extracted by means of the SSFL solution at pH 8 is constituted by hexavalent chromium that, in this pH condition, is more stable and tends to remain in the oxidized form. On the contrary, the hexavalent chromium is not detectable in SSFL solution at pH 5.5. In this last solution at lower pH value, all the chromium is present in the more stable trivalent form. Also the SSFL solution contains lactic acid which can reduce the hexavalent chromium at lower pH values in aqueous acidic medium [34].

The ISO solution at pH 5.5 is able to extract a significant amount of Cr(VI), with respect to the SSFL solution at the same pH value. The different Cr(VI) absorption of the ISO solution can't be explained only in terms of pH values. However the chemical composition of the two extracting solutions is slightly different in terms of ionic strength. The ionic strength of the ISO solution is lower compared to the SSFL solution and this could explain the different solution absorption of the Cr(VI) ions.

The ISO solution at pH 5.5 extracts the higher quantity of Cr(VI) in absolute, but the ratio Cr(VI)/Cr(tot) is lower with respect to the SSFL solution at pH 8.

3.2 Analysis of total chromium in the ashes

The metal extraction yields were derived comparing the metal content extracted into the SSFL and ISO solutions with the metal content extracted from the textile material by ashing. The total chromium content in the textile material dyed with chromium dyestuff was of 21.66 mg/kg. The results of efficiency of the extraction solutions are reported in Table 4.

Table 4 Percentage of metal extraction yield

Solution	Yield [%]	
	pH 5.5	pH 8
SSFL	36	23.5
ISO	45.7	/

The chromium extraction behavior of the ISO and SSFL solutions is not the same at pH 5.5 that is the pH value normally applied by the textile eco-labels standards as Oeko-Tex Standard 100 and others. In fact, the percentage of metal extraction yield varies according to the pH conditions and extraction solution composition, from 23% to 46%. So the extraction yields confirm the better extraction efficiency of ISO standard solution. At pH 5.5, the ISO solution extracts more total chromium and a significant part of this in a hexavalent form. The SSFL solution, at the same pH value, is less aggressive and extracts a lower amount of total chromium only in the trivalent form.

4. CONCLUSIONS

In last years, the possible interaction of the textile materials with the human skin lead to develop test analytical methods to determine the toxicological and eco-toxicological quality of the textile manufactures.

Actually, because of negative effects of chromium on human health, some private eco-labelling voluntary schemes impose Cr requirements based on the extraction of the metal by means of a saline solution simulating the human acid perspiration prepared according to the ISO 105 E-04 standard, but this method is affected by a low reproducibility.

In this work the specific conditions of extraction identified in previous studies were applied to thetrivalent and hexavalent chromium extraction using an artificial skin surface film liquid solution (SSFL), at two pH values (5.5, 8). The SSFL solution proposed in this work is an example of a real surrogate of human sweat on a biological base.

The results obtained show that the ISO standard solution is more efficient to extract total Cr from textiles rather than SSFL. Moreover, as we expected, the extraction of total chromium by SSFL solution is more efficient and reproducible at acid rather than at basic pH values. The SSFL solution at pH 5.5 extracts total chromium only in the trivalent form, but at pH 8 is present also the hexavalent form. The ISO solution at pH 5.5 extracts the higher quantity of Cr(VI) in absolute, but the ratio Cr(VI)/Cr(III) is lower with respect to the SSFL solution at pH 8.

Finally, the results show that at pH 5.5 the metal extraction yield of SSFL solution is lower, if compared to the ISO one.

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