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SYSTEMIC ANALYZE BY LIFE CYCLE INVENTORY OF THE HYDROPHOBIZATION UNIT PROCESSES FOR TEXTILES

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Abstract: *This paper presents aspects regarding life cycle inventory (LCI) of the classical hydrophobization process used in textiles finishing. According to the ISO 14040-14044 stardards used for determine the framework for conducting an LCA (life cycle assessment), there are 4 steps for obtaining an LCA – scope definition, LCI, LCA impact, LC (life cycle) interpretation. In our work, we analized warming impact generated by gases, water footprint and energy impact. For analyzed sample (bbc 100%), treated with NUVATTC (based on fluorocarbon) for obtaining hydrophobic effect, was analyzed the LCI and the process tree. The goal was to obtain the environment impact level for classical hydrophobization based on fluorocarbon. The research methodology consisted in collecting technical input and output data and using the SimaPro software for generating the LCI. We obtained the input data (raw material, energy, chemical substances and water consumption) by direct measurements on machinery, device logs and specifications of the equipment (technical books) and processes. The output data (waste energy, water and chemicals were obtained using statistics, internet databases and SimaPro software. The environmental impact categories identification (carginogenic, inorganic compounds upon the breath, climate change, radiation, ozone layer, Eco-toxicity, land use, minerals and fossil fuels) was done by using the method ECO indicator 99. This study shows that the process of classic hydrophobization has a negative impact on significantly on climate change, fossil fuels, ozone layer and effects of inorganic compounds upon the respiration, and all this is the consequence of the chemicals, based on fluorocarbon, use.*

Key words: *life cycle inventory, textiles, hydrophobic, impact, environment.*

1. INTRODUCTION

The analysis of life cycle inventory involves procedures for collection and calculation of data on the system-product for hydrophobic textile that will be included in the life cycle inventory, for quantifying inputs of materials, energy or chemical substances and the materials output such as energy, products, the discharges into the air, water, soil - which are relevant to the system-product [1].

The analysis of the life cycle inventory (LCI) for a system - textile hydrophobic product represents the collection of inputs and outputs during the life cycle. To generate the LCI are necessary a large amount of data about the process or the production of the hydrophobic textile materials. The inputs (raw materials, energy, ratio between the main product and co-products and production rate) and output (discharged waste into the ambient environment). There are numerous

methods for the generation of LCI and among the most used but cost expensive is the use of commercial software applications (commercial off the shelf –COTS) such as GABI or SimaPro, which reward allow quick access to data online updated. Another possibility is to achieve the study LCI directly from the source data (technical books of machinery or equipment, national statistics, technical journals, direct measurements on machinery, logs, and reports of the specific data from textile industry, the results of laboratory tests, governmental documents, reports, databases, scientific articles, books and patent, the specifications of the equipment or processes) [1].

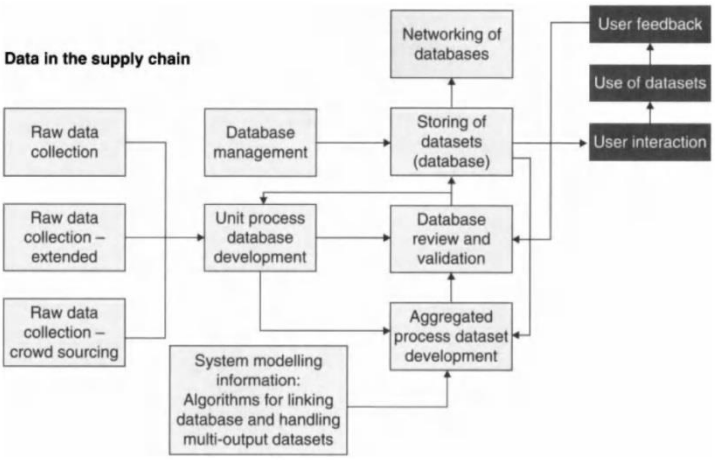

Fig. 1: *Raw data stream – LCI with feeback [2]*

2. EXPERIMENTAL PART

The experimental part consisted in LCI for data collected from classical textile hydrophobization process. Data, collected from industrial technological process and from indirect sources such as internet database and speciality scientific literature, were used for establish the LCI [3, 4].

The study is one type of Cradle-to Gate that approaches the production phase (after the collection of the raw materials to the development of the product). By using the method Eco-Indicator 99 was identified the following categories of environmental impact : carcinogenic, organic compounds and inorganic upon the breath, climate change, radiation, the ozone layer, Eco-toxicity, acidification /eutrophication, land use, minerals and fossil fuels. The impact types obtained by SimaPro are presented in the following diagrams:

-Specification diagram (Fig. 2);

-Normal diagram (Fig. 3);

-Weighted diagram (Fig. 4);

-Single Score diagram (fig. 5).

In Fig. 2 can be identified the resources with the most significant environmental impacts, such as heat supplied by natural gas, the consumption of fluorocarbon dioxide (of the substance for hydrophobization NUVA TTC) and consumption of electrical energy for the operation of the hydrophobic coating. We can remark that the volume of water (74 l) consumed in the classical hydrophobization process for 100 kg BBC material, has a minor impact on the environment. The same thing can be said about the consumption of acetic acid (37 ml/ 100 kg BBC). The program

SimaPro7 has the possibility of the evaluation of the impact on the environment through diagrams of the following approaches: normalization and weighting.

The normalisation is a procedure required to show the extent to which a category of impact has a significant contribution to the general problem of the environment, and is done by means of the division of the category indicator of impact by a value of "Normal". There is a procedure whereby each category of impact is related to the relative importance of these [5, 6, 7].

The weighting method has as its objective the quantitative aggregation of the results of using the weighting factors. This kind of approach has impact on categories reported between these categories. Each category of impact is multiplied by a weight, the date of seminificatia that category the impact of general [7, 8].

It is also noted that the natural gas (14%), tetrafluoretilene (78%) and the electrical energy used (6%) have a negative effect on climate change (Fig.3). The procedure for the classic hydrophobization contributes to global warming through the greenhouse effect caused by fluorocarbons presence. Natural gas used in the process (10%), tetrafluoretilena (43%) and the electrical energy consumed (47%) have a negative effect on the environment, in the form of radiation emitted into the atmosphere. In Fig. 4 it is presented the semnificativ impact of fossil fuels, climate change and inorganic upon the respiration. In Fig. 3 and 4 is presented the signifiant impact of the finishing based on fluorocarbon (tetrafluorethilene) and heat necessary in this process, for fossil fluel, ozone layer and climate change.

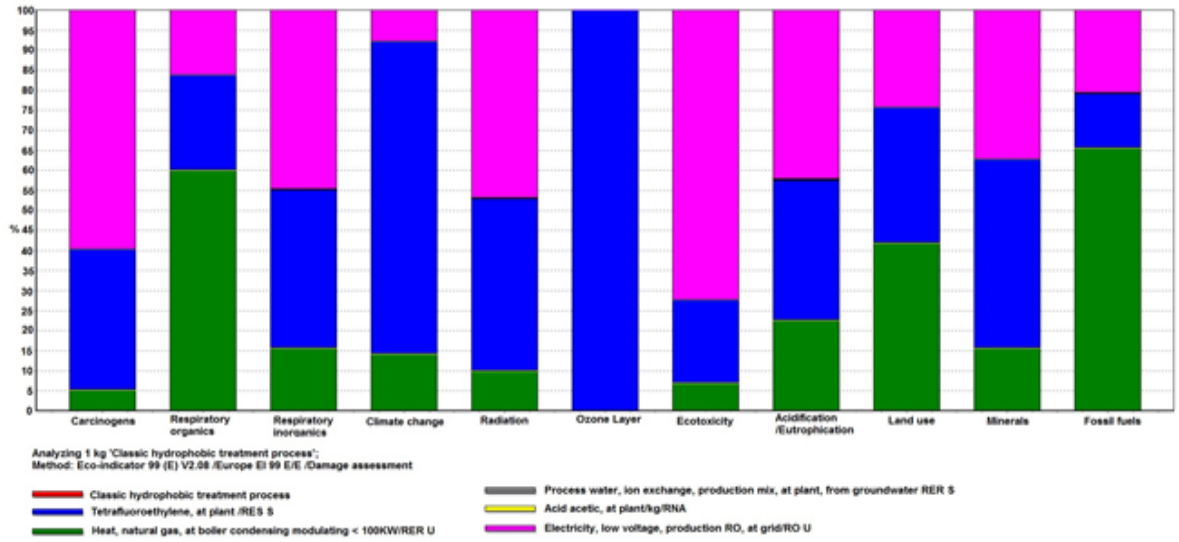

Fig. 2: *Specification diagram for 100% bbc sample hydrophobizated by classical process*

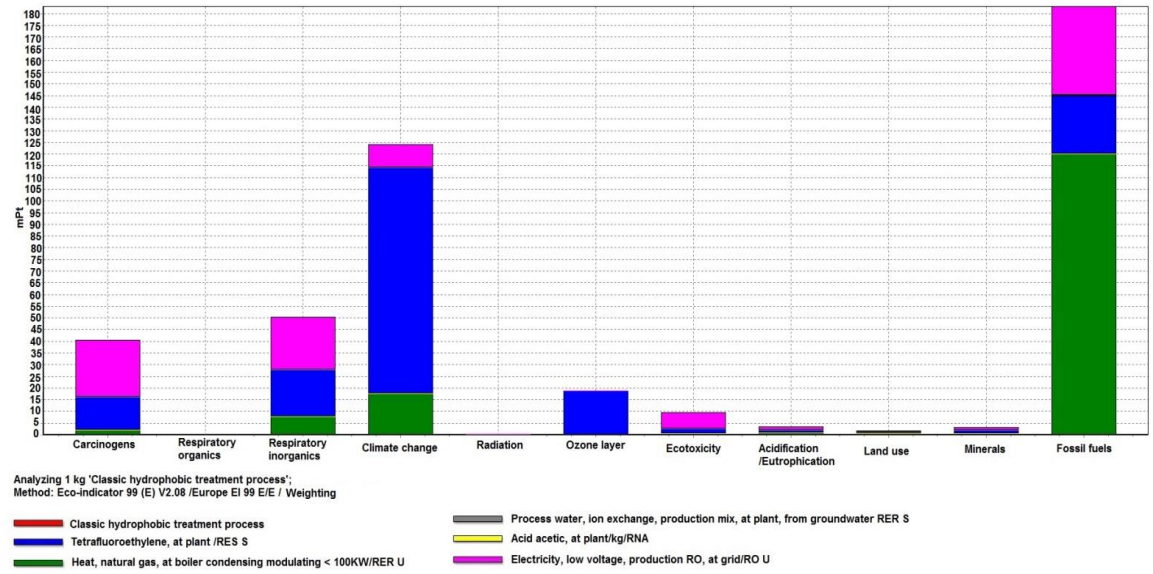

Fig. 3:*LCI evaluation by normalized method*

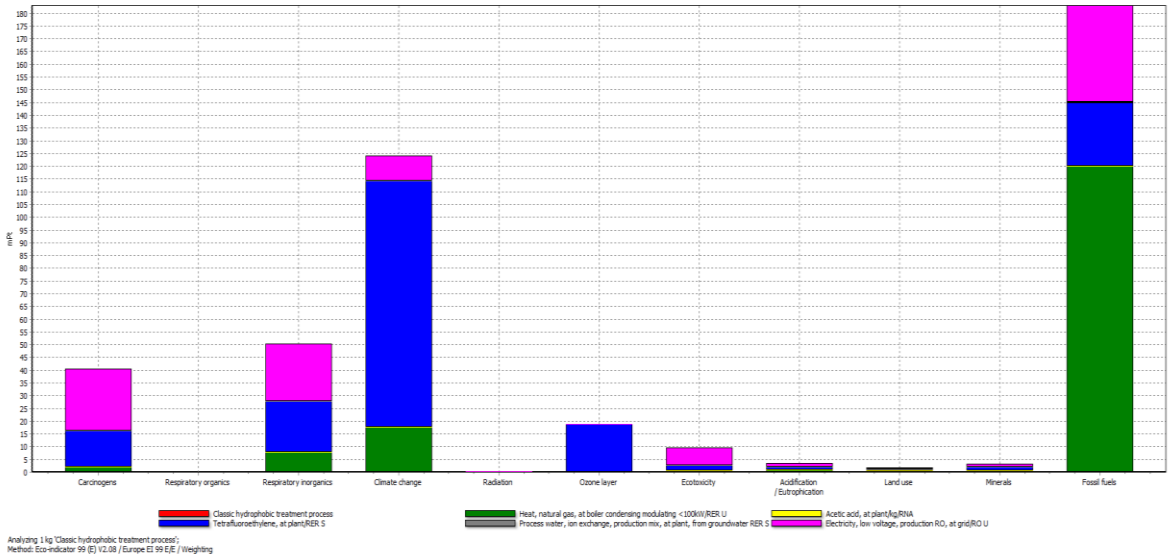

Fig. 4: *LCI evaluation by weighting method*

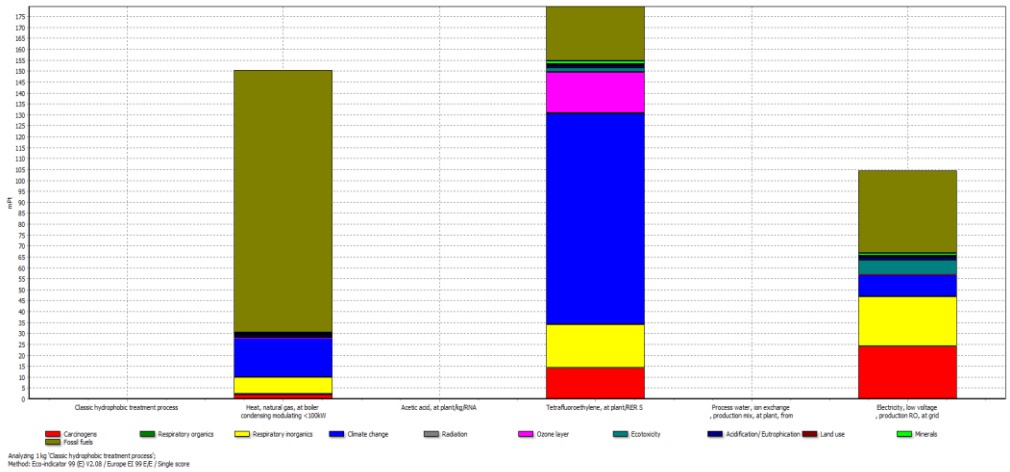

Fig. 5: *LCI evaluation by single score method*

3. DISCUSSIONS

For textile sample treated with NUVATTC, was carried out the inventory of the life cycle (ICV) using the software SimaPro and have determined the process tree for classical hydrophobisation (Fig. 6) and the effect on the environment on the impact categories. In the program was used ECO-Indicator 99 [9], which provides for the quantification of the following categories of impact : carcinogenic substances, organic compounds and inorganic with negative effect on the respiration, climate change, radiation, the ozone layer, Eco-toxicity, acidification /eutrophication, land use, minerals and fossil fuels.

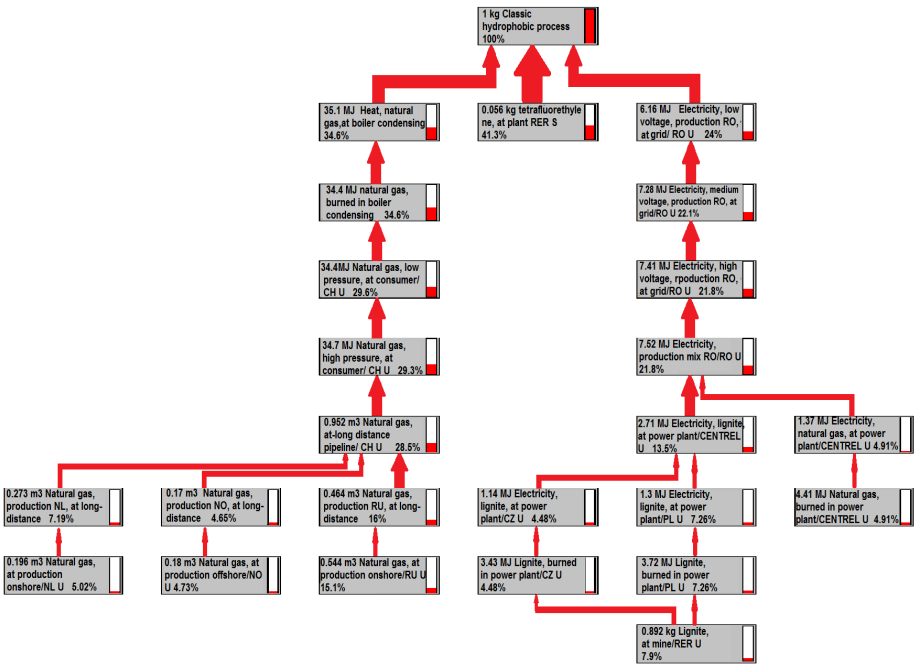

Fig. 6: *Process tree for classical hydrophobization*

5. CONCLUSIONS

The investigation of the process and the diagram for environment impact on different categories (Eco-Indicator Method 99) were prepared by weighting method. From all diagrams used in evaluation, we observed a significant impact of the classic hidrophobization on fossil fuels, climate change, ozone layer and effects of inorganic compounds upon the respiration, given in the main by fluorocarbon use.

6. ACKNOWLEDGMENTS

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STIFFNESS MODIFICATION OF COTTON IN CHITOSAN TREATMENT

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Abstract: *Chitosan is a biopolymer obtained from chitin, and among their most important aspects highlights its applications in a lot of industrial sectors due to its intrinsic properties, especially in the textile sector. In the last years, chitosan is widely used in the cotton and wool finishing processes due to its bond between them and its properties as an antifungical and antimicrobial properties. In this paper three different molecular weight chitosan are used in the finishing process of cotton to evaluate its influence in the surface properties modification. In order to evaluate the effect of the treatment with chitosan, flexural stiffness test is performed in warp and weft direction, and then the total value is calculated. The cotton fabric is treated with 5 g/L of different types of chitosan in an impregnation bath. This study shows the extent of surface properties modification of the cotton provided by three types of chitosan treatment. The results show that all types of chitosan modify the cotton flexural rigidity properties but the one which modifies it in a relevant manner is chitosan originated from shrimps.*

Key words: *Chitosan, textile, flexural stiffnes, chitin, cotton.*

1. INTRODUCTION

Chitosan is known well known for its use in wound dressing [1, 2] but it has however a lot of other uses and can be used as artificial skin, colour removal in textile mills, paper finishing, or textile finishing due to its antibacterial properties [3]. Recently other different use is developed as pre-mordant in cotton and wool dyeing [4]. Chitin can be easily acquired from crab or shrimp shells but has to be deacetylated in 40% sodium hydroxide at 120°C for 1-3h. to produce 70% deacetylated chitosan [5].

The bond between chitosan and cotton is a difficult bond because of the likeness of the two polymers and it has to be dissolved in an acid to improve it. This is only possible as result of the highly basic nature of chitosan. Then bonding of chitosan with cotton happens after the cotton is oxidised [6]. Figure 1 shows how the cotton (I) is oxidized (II). Once the cotton is oxidized it is able to react with the chitosan molecules.

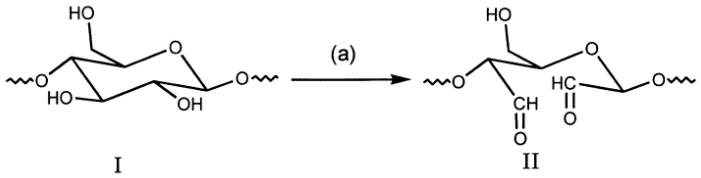

Fig. 1: *Oxizidation of cotton (a)* ***[6]***

2. OBJECTIVE

The main objective of this work is to study the influence of the chitosan molecular weight in pre-tratment of the cotton treated with three different molecular mass chitosan, low, medium and originated from shrimps.

3. MATERIALS AND METHODS

Chitosan is used as a natural mordent at the present paper. All chitosan used, low molecular weight (XL), medium molecular weight (XM) and chitosan originated from shrimps were commercial products, supplied by Sigma-Aldrich. As that paper's purpose is evaluate the influence of chitosan as bio-mordant the concentration used is 5 g/L for all tipes of chitosan.

The fabric used is a cotton twill fabric with 210 g/m^2 which has been chemically bleached in an industrial process. The treatment with chitosan was performed in an impregnation bath adding 6 ml of acetic acid to have a slightly acid solution, in order to dissolve the chitosan better. To be sure the solution is completely dissolved the solution stirred for 24h hours. After the chitosan treatments, cotton samples were dryed at 80°C in a screen printing engineering TD-20 and cured at a temperature of 80°C in a WTC Binder 030.

The influence of cotton pre-treatment with chitosan was performed by flexural rigidity test as described in the standard UNE-40-392-79.

4. RESULTS AND DISCUSSION

The flexural rigidity test is used in order to verify the degree of modification of the cotton properties treated with different types of chitosan. As chitosan is used in most of applications as a pre-treatment it is very important that the cotton properties remain regular. In the present paper the cotton fabric is treated with three types of chitosan to evaluate flexural stiffness, obtaining the following results.

It has been evaluated, as indicated in the standard, in the weft and warp direction by both sides of the fabric. The results show higher values of flexural rigidity in the warp direction than in the weft direction for the three types of chitosan, and also for the untreated sample due to the fabric structure. As can be seen in figure 3, whilst the flexural stiffness values in warp direction are higher than 2000 mg/cm, in weft direction the values are lower than 1800 mg/cm.

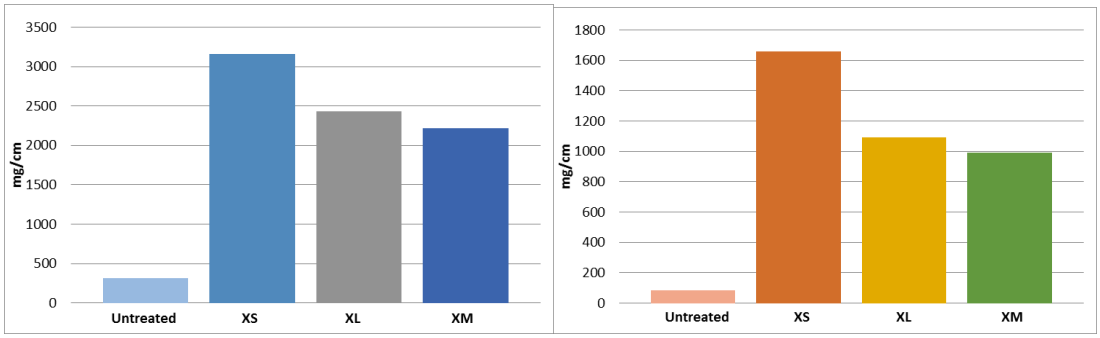

Fig. 2: *Flexural stiffness in warp and weft direction of the cotton treated with different types of chitosan*

Comparing the results of flexural rigidity of the fabric treated with the three types of bio-mordants, the chitosan that present the highest flexural rigidity is the chitosan from the shell of shrimps, followed by the low molecular weight chitosan. The medium molecular weight chitosan is the one which modify in a less extent the cotton properties in both warp and weft directions. Must be said that the difference between the medium and low molecular weight chitosan is very small.

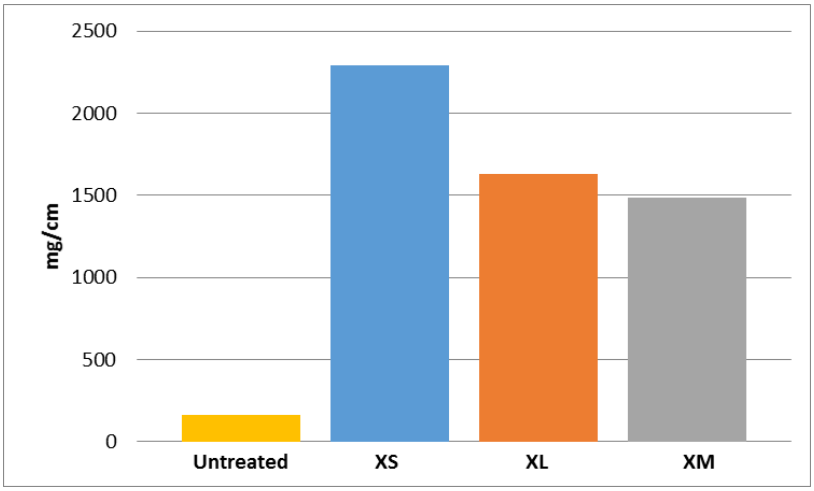

Fig. 3: *Total flexural stiffness of the cotton treated with different types of chitosan*

The total flexural rigidity of the treated fabric with different types of chitosan reinforces the flexural rigidity values obtained in the weft and warp direction. The chitosan originated from shrimp shells is the one that gives the most rigidity to the cotton, with a great difference from the low and medium molecular weight chitosan. The chitosan of medium and low molecular weight hardly offers significant differences, and as can be seen in figure 4, both values are around 1500 mg/cm.

5. CONCLUSIONS

The next conclusions can be extracted:

- Medium and low molecular weight chitosan have similar flexural stiffness values.
- In comparison to the untreated cotton with those treated with different types of chitosan, a remarkable increase in flexural stiffness in the weft, warp and total stiffness was observed.
- Chitosan originated from shrimp shells is discarded because it modifies the properties of cotton in a high manner.

- Based on the flexural stiffness test the best chitosan is medium molecular weight because it doesn't modify the cotton properties as other types of chitosan does.

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STUDY OF CHITOSAN MICROCAPSULES DEGRADATION WITH APPLICATION IN THE DEVELOPMENT OF NEW MEDICAL TEXTILES

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Abstract: *Chitosan is a polysaccharide derived from chitin; chitin is the second most abundant polysaccharide in the world, after cellulose. Several remarkable properties of chitosan offered unique opportunities to the development of biomedical and agriculture applications. In addition, chitosan allows obtaining microcapsules with diferrent functionalities according to the core material, but his characteristic allows achieving a control release of the active material. Chitosan microcapsules can be obtained by different encapsulation methods; in this case the extrusion-gelling method has been selected and two kinds of nozzles have been used. The simple nozzle produce a matrix, it can be described as a solid polymer system in wich the core material is distributed more or less uniformly throughout the polymer matrix. The concentric nozzle is a standard nozzle configuration to produce core-shell capsules.*
This study analyses the biodregradability of chitosan microcapsules obtained by co-extrusion/gelling using a single and concentric nozzle, with the aim of defining possible applications in the field of medical textiles.So the weight loss (%) has been calculated in diferent times, in order to compare the weight loss (%) in each type of microcapsules. The difference in degradation time is due to the quantity of chitosan in the microcapsules. The microcapsules obtained by simple coextrusion contain a greater quantity of polymer than those obtained by concentric extrusion

Key words: *Chitosan, biodegradability, microcapsules, co-extrusion and gelling.*

1. INTRODUCTION

Chitosan is a polysaccharide derived from chitin; chitin is the second most abundant polysaccharide in the world, after cellulose. The presence of amino groups in the chitosan structure might be protonated-providing solubility in diluted acidic aqueous solutions, several remarkable properties of chitosan offered unique opportunities to the development of biomedical applications. [1], [2]

In addition, chitosan is applied to crops with the aim of reducing or replacing more costly and environmentally damaging chemical bactericides. With reduced input costs and the potential for increased yields, farmers could gain substantial benefits from these applications of chitosan and its oligosaccharides to crops. [3]

Chitosan has a wide variety of applications in agricultural and biotechnological industries [4], [5], all of them with a direct relationship with the textile sector. So, chitosan allows obtaining microcapsules with diferrent functionalities according to the core material, but his characteristicas allows achieving a control release.

Encapsulation is defined as a process in which an active agent (core) is enveloped by a polymeric membrane (shell) to confer small capsules many useful properties [6].

We can say that encapsulation is a way to protect the substance to be encapsulated, determining its controlled release. Therefore, encapsulation confers added value to a commercial substance. It allows the generation of new application of products for properties that could not be applied so far. Encapsulation can be used to protect the active agents from oxidation caused by heat, light, moisture and contact with other substances and to prevent the evaporation of volatile compounds. An example of very sensitive compounds, to these factors are essential oils, substances responsible for taste, aroma and many functional properties [7],[8].

The obtention of chitosan capsules is realized by means of ionotropic gelation method. In acid solution, the chitosan $-NH_2$ is protonated to be $-NH^{3+}$. This molecule interacts with the Thymidine 5'-triphosphate sodium salt solution (TTP) by ionic interaction to result capsules.

The objective of this research is study the degradation of two kinds of microcapsules using chitosan as a wall material, in order to define new medical applications.The microcapsules were obtained by co-extrusion / gelling using a simple and a concentric nozzle.

2. EXPERIMENTAL

2.1. Materials

Medium molecular weight chitosan with a deacetylation degree of 75-85% (Sigma Aldrich, Spain) was used as shell material. The core material was an essential oil (Ensencias Lozano, Spain). Sodium triphosphate pentabasic (STP) (Sigma Aldrich, Spain) was used as a cross-linker material.

2.2. Microcapsules obtention

Capsules were obtained by BUCHI B-390 encapsulator at room temperature (Fig 1). Two kinds of nozzle were used to obtain different kind of microcapsules (Fig 2). Concentric nozzle configuration produces core-shell microcapsules and single nozzle configuration produces solid microcapsules.

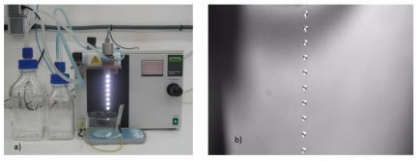

Fig. 1: *(a) Encapsulator BUCHI B-390. (b) Formation string of beads with the chitosan (shell) and core material*

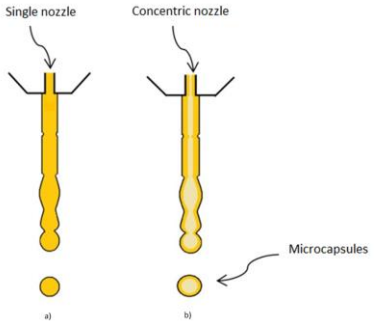

Fig. 2 *(a) single nozzle. (b) concentric nozzle*

Equipment variables are potential (V) and frequency (Hz). These variables were modified until it was perfectly observed the formation of the string of beads. The obtained capsules were filtered and washed three times with distilled water in order to remove any solution of crosslinking agent that could be remaining in the capsule wall. [9, 10]

The following table shows the optimum conditions under which the two types of microcapsules are obtained:

Table 1: *Encapsulation conditions*

	Microcapsules by single nozzle	**Microcapsules by concentric nozzle**
Chitosan Shell material (%)	1	1
Crsolinker agent (g/l)	8	8
Frecuency (Hz)	40	40
Potential (V)	250	250
External nozzle (mm)	0.9	0.9
Internal nozzle (mm)	-	0.45

2.3. Techniques of characterisation

2.3.1. Degradability Test

In order to obtain the samples for the degradability test, the microcapsules were filtered out from the suspensión and were then left exposed to ambient conditions for twenty minutes before being weighed.

The degradability test was performed on each of the two sample types:

- Sample A: microcapsule samples obtained by concentric coextrusion.
- Sample B: microcapsule samples obtained by simple coextrusion.

The degradability test was performed with different samples for each time interval, taken from an initial total of 20.0 g of microcapsules for sample A and 17.3 g microspheres for sample B.

This quantity was used to obtain independent samples for measurement times. Samples were tested in triplicate for each time interval. Thus, degradability tests were performed with an approximate quantity of 0.5 g of microspheres for sample A and 0.4 g of microspheres for sample B for each point of measurement.

The degradability test was performed by immersing the quoted microsphere samples in 10 ml of phosphate buffer solution (PBS, at pH = 7.4), at 37ºC. The degradability tests were performed in the absence of light.

Weight loss for each of the ten time intervals was calculated (t): at 1 day, 3 days, 7 days, 9 days, 11 days, 15 days, 18 days, 21 days, 30 days, 42 days. All tests were performed in triplicate.

The results are presented as averages of the three measurements taken at each point with associated standard deviation, according to the following formula:

$$\% \text{ weight loss} = ((\text{final weight} - \text{initial weight})/\text{initial weight}) * 100 \quad \textbf{(1)}$$

Where: final weight is the weight of the sample at each time interval t, and initial weight is the weight of each sample at the commencement of the experiment (t=0).

3. RESULTS

The following table (**Error! Reference source not found.**) shows the weight-loss results, expressed as a percentage, obtained for both types of chitosan microcapsules. The values obtained correspond to the average weight loss of each of the triplicated samples for each time interval, calculated with standard deviation. The degradability tests were performed under the following physiological conditions (PBS, pH=7.4, 37ºC, in the absence of light).

***Table* 2:** *Degradability of the two types of chitosan microspheres, expressed as a %of the weight loss*

		SAMPLE A	SAMPLE B
$t_{degradation}$ (days)	**$t_{degradation}$ (h)**	**Weight loss (%)**	**Weight loss (%)**
0	0	0	0
1	24	66.85±0.53	33.96±5.15
3	72	69.17±1.96	32.24±2.50
7	168	89.57±0.99	42.37±1.52
9	216	88.90±7.61	49.60±6.41
11	264	96.11±1.91	47.30±5.15
15	360	92.53±11.46	57.98±4.23
18	432	96.65±1.33	59.64±12.49
21	504	98.91±1.78	82.18±2.87
30	720	99.31±0.66	93.64±2.25
42	1008	100±0.00	90.73±5.16

As can be appreciated from Table 2, weight loss during the first 24 hours is considerable, particularly in sample A, and in both cases, the time that the microspheres spend in incubation in the buffer solution at body temperature leads to their progressive degradation: sample A breaks down completely, and sample B practically (90%).

The photographs which appear below were taken of the appearance of the chitosan microcapsules at each degradation time interval. The images show the turbidity present in the solution containing samples from the first stage: this turbidity is due to the breakdown of the chitosan itself coupled with the presence of micelles of oil deriving from the release of the functional oil from within the microcapsule. This study does not include trials to determine whether or not the micelles observed derive only from the functional oils released during degradation or if a percentage may derive from diffusion of the oil through the membrane.

The following images compare the appearance of the microcapsule suspension with the appearance once filtered at the different time intervals used for analysis.

Fig 3: *Appearance of the microcapsules at rest for SAMPLE A after 24 h at 37ºC.*


Fig 4: *Appearance of the microcapsules at rest for SAMPLE B after 24 h at 37ºC.*


Fig 5: *Appearance of the microcapsules at rest for SAMPLE A after 15 days at 37ºC.*


Fig 6: *Appearance of the microcapsules at rest for SAMPLE B after 15 days at 37ºC.*


Fig 7: *Appearance of the microcapsules at rest for SAMPLE A after 42 days at 37ºC.*


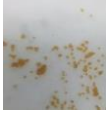

Fig 8: *Appearance of the microcapsules at rest for SAMPLE B after 42 days at 37ºC.*

As can be seen in the above images, the type B samples maintained in the buffer solution for 15 days at 37ºC gradually darken, which may be an additional indication of the degradation process acting upon the biopolymer. Plotting a graph for the values obtained in Table 1 clearly shows that type A samples present faster degradation than type B (Figure 9).

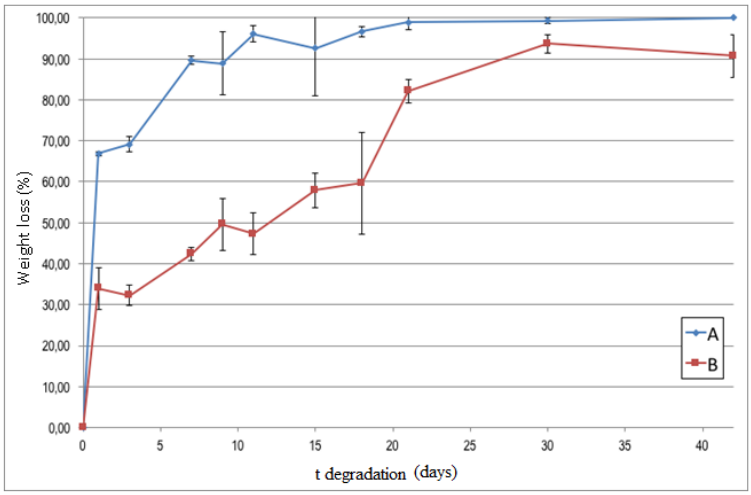

Fig 9: *A comparison of the degradation of the two samples analyased´*

5. CONCLUSIONS

The chitosan microcapsules analysed display a progressive rate of degradation under physiological conditions. The chitosan samples obtained by concentric extrusion (reference A) display a faster degradation rate at shorter time intervals and achieve almost total degradation at 21 days.

However, the samples obtained by simple extrusion are much more resilient to degradtion under the test conditions and display a linear rate of degradation to 30 days at which point degradation stabilises at around 90% weight loss.

This difference in degradation time is predictable as the quantity of chitosan differs: the microcapsules obtained by simple coextrusion contain a greater quantity of polymer than those obtained by concentric extrusion, as can be seen in figure 10:

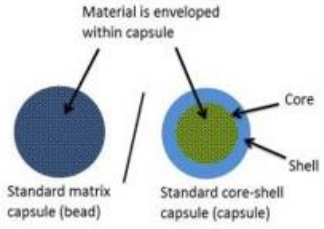

Fig 10: *a) Micropaculas por co-extrusión simple; b) microcápsulas por co-extrusión concéntrica.*

The release time for the core material can be defined based upon the results of the study, and the results can then be applied to the development of medical textiles which have been functionalised with microcapsules for use in the treatment of a range of conditions and pathologies.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

STUDY ON THE INFLUENCE OF ULTRASOUND IN BIOSCOURING TREATMENT OF 50 % OF FLAX + 50 % OF COTTON FABRICS

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Abstract: *Study on the influence of ultrasound in Bioscouring treatment of 50 % of flax + 50 % of cotton fabric was made. The role of the Bioscouring treatment was the removing of natural cellulose attendants such as: pectin, hemicelluloses, waxes, extractable substances, etc.*
The cleaning treatment was carried out with a commercial enzymatic product called Beisol PRO (which consists of a mixture of enzymes pectinases), in water at a 20:1 liquid to fabric ratio and a temperature of 55 ^{0}C, in the precence of a complexing agent (2 g/L EDTA) and a washing agent (0.5 % Denimcol Wash RGN).
The effect of the enzyme mixture was intensified by ultrasound at a frequency of 45 kHz in an ultrasonic bath Elmasonic X-tra basic 2500 from Elma Company, Germany, leading to the improvement of the process and better properties for treated material.
The experiments were conducted after a central, rotatable second order compound program with two independent variables: enzyme concentration (concentrations between 1-3% o.w.f) and treatment time (15-55 minutes).
Treated samples were analyzed for weight loss, hydrophilicity, whiteness index, yellowness index, crystallinity, tensile strength, elongation at break, scanning electron microscopy analysis (SEM), CIELAB color system analysis of the samples dyed with alizarin and ruthenium red dyes.
The results showed that the bioscouring process performed in the presence of ultrasound has been effective at a lower enzyme concentration and a lower duration of the treatment, thereby reducing the costs and the possibility of degradation of the treated material.

Key words: *cotton/flax fabric, bioscouring treatment with ultrasound, weight loss, whiteness index, K/S color strength, crystallinity*

1. INTRODUCTION

Ultrasounds are elastic waves with frequencies between 16-106 kHz which can be used in the form of longitudinal waves to improve the mass and heat transfer. This intensification increases

with the increasing of frequency and power transmitter, having the effect of reducing treatment duration and the temperature below the usual ones. Also, by using ultrasound, the following effects are obtained: changing of layer and substrate limit of the interface material-solution with the increasing of rate diffusion; degassing of the solutions and materials occurs and a temporary fiber deformation, which ensures a deep penetration of chemical agents in the treated textile materials [1].

Flax and cotton fibers contain besides cellulose, other morphological impurities like: hemicelluloses, pectins, extractable substances, waxes, etc., which have to be removed to get a good wettability and a good whiteness degree of the fabrics. These impurities can be removed by classical scouring treatment where NaOH is used or enzymatic scouring process where specific enzymes like pectinases are involved. In addition, for both type of treatment, a complexing agent and a washing product are utilized. EDTA (Ethylenediaminetetraacetic acid) is the complexing agent most used because complexes with the majority of the metal ions and has a good stability in an alkaline medium. The washing product is used to emulsify the unsaponifiable materials. Nonionic surfactants are preferred because of their high emulsification capacity [2].

These treatments must be conducted in order to increase the percentage of the crystalline zone with the reducing of amorphous one, so that the treated material to have appropriate mechanical properties [3].

During chemical or biochemical treatments of textiles, various cellulose degradations may occur by conversion of alcohol groups into carbonyl or carboxyl groups by oxidation or hydrolysis reactions. These degradations can be expressed by: microscopic, chemical and viscosimetric methods, etc. [4].

The efficiency of the bioscouring process can be determined by the following analyses: weight loss, hydrophilicity, whiteness index, yellowness index, crystallinity, tensile strength and elongation at break, scanning electron microscopy analysis (SEM), CIELAB color system analysis of the samples dyed with alizarin and ruthenium red dyes.

2. EXPERIMANTAL PART

For conventional alkaline scouring and enzymatic treatments, samples of 50 % of flax + 50 % of cotton material with the following characteristics were used: 120 ± 3 cm width, 220 ± 10 g/m^2, for warp direction 100 % of cotton yarn with Nm 14 and 50 % of flax + 50 % of cotton yarn with Nm 14 for weft direction.

Prior to the alkaline and bioscouring treatments, the samples were washed at 100 °C using a AATCC standardized Lander-Ömeter, model M228-AA from SDL Atlas Company - USA, followed by: drying, conditioning and weighing [5].

All enzymatic experiments were carried out with a commercial enzymatic product called Beisol PRO (which consists of a mixture of enzymes pectinases), in water at a 20:1 liquid to fabric ratio and a temperature of 55 ^{0}C, in the precence of 2 g/L EDTA as a complexing agent and 0.5 % Denimcol Wash RGN as a surfactant. A central, rotatable second order compound program with two independent variables: enzyme concentration (concentrations between 1-3 % o.w.f) and treatment time (15-55 minutes) was used. The effect of the enzyme mixture was intensified by ultrasound at a frequency of 45 kHz in an ultrasonic bath Elmasonic X-tra basic 2500 from Elma Company, Germany. After bioscouring treatment, the samples were washed with hot water at 70°C, cold water and dried at room temperature [6]. For comparison a classic alkaline treatment was done with 10 g/L sodium hydroxide, 5 g/L sodium carbonate, 1 g/L sodium bisulfite, 2 g/L sodium silicate and 2 g/L Sulfolen 148 (S-148, alkyl polyglicol ether) as a wetting agent.

After drying and conditioning of the treated samples till constant weight, the following analyses were done: weight loss, hydrophilicity, crystallinity, tensile strength and elongation at

break, whiteness index, yellowness index, CIELAB color system analysis of the samples dyed with alizarin and ruthenium red dyes and scanning electron microscopy analysis (SEM).

The weight loss was determined by gravimetric method. The samples were dried at 105 °C in an oven from Caloris Group, Romania till constant weight. The weight loss was calculated using the following equation:

$$\% \text{ weight loss} = (W1-W2)\ x100/W1 \quad (1)$$

where, W1 and W2 are the weights of dried samples fabric before and after the treatments.

The hydrophilicity of the treated samples was determined according to AATTCC Test Method 79-2007.

Because during the treatment, fibers degradation may appear by oxidation or hydrolysis reactions, XRD analysis and tensile strength of the material were made.

The cellulose crystallinity procent of the samples was determined by X-ray diffraction with a MiniFlex 600 diffractometer (Rigaku Corporation, Japan), operating at 40 kV, 15 mA, with CuKα monochromatic radiation, and using SC-70 detector and the automatic 6 position sample changer, ASC-6. The scan range was 5°-45°, with step width 0.05°, scan speed 1.2° / min. at room temperature and humidity. The PDXL2 Version 2.4.2.0 containing powder diffraction analysis package, PDXL Comprehensive Analysis, was used to analyze and calculate the cristallinity procent based on the diffraction intensity of the crystalline and amorphous phases.

The tensile strength and elongation at break was determined by using a testing machine 5KT from Tinius Olsen – United States with an interface running on a connected PC by Horizon software. The ASTM D 5035 – 06 "*Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method)*" was used [7].

Whiteness and yellowness degree were determined on a Datacolor 500 spectrophotometer. For an opaque view each sample was folded twice to give four plies and the whiteness was measured four times at different points. The Hunter Whiteness Index and DIN 6170 Yellowness Index were calculated automatically by Datacolor Tools 2.0 software.

The degree of pectins removal was determined by ruthenium red dyeing method. The reflectance (R %) at 540 nm was measured on Datacolor 500 spectrophotometer and K/S values were calculated. The dyeing method with alizarin dye was used to determine the amount of calcium removed from the treated fabric.

The surface morphologyies of the cotton/flax fabrics were explored by scanning electron microscopy (SEM). The samples were placed on a specimen support, then coated with Au using an auto fine coater (JFC-1200, JEOL Co., Japan). Observations were conducted using a SEM (LYRA 3, Tescan, Czech Republic) at 2 or 10 kV, respectively.

3. RESULTS AND DISCUSSIONS

Table 1 presents the results obtained for the samples subjected to the alkaline and bioscouring treatments for different conditions.

Table 1: *The results obtained for the samples subjected to the alkaline and bioscouring treatments for different conditions*

No.	Enzyme [% o.w.f]	Time [min]	Weight loss [%]	Hydrophilicity [s]	Crystallinity	Tensile strength [N]	Elongation at break [%]	Whiteness index	Yellowness index	k/s Ruthenium red	k/s Alizarin
1	1.30	21.00	1.26	0.68	67	965	9	57.25	16.12	1.06	0.65
2	2.70	21.00	1.02	0.79	67	960	9	57.11	16.34	1.02	0.64
3	1.30	49.00	0.34	0.85	63	949	9	56.52	16.78	1.03	0.64
4	2.70	49.00	1.31	0.74	70	1035	8	57.02	16.17	1.06	0.65
5	1.00	35.00	0.36	0.76	66	975	8	55.97	16.79	1.07	0.66
6	3.00	35.00	0.90	0.82	65	957	9	57.55	16.09	1.05	0.65
7	2.00	15.00	0.26	0.79	64	950	9	56.18	16.82	1.11	0.67
8	2.00	55.00	0.80	0.74	67	980	9	57.52	15.94	1.02	0.65
9	2.00	35.00	1.28	0.79	73	1057	8	56.58	16.48	0.91	0.62
10	2.00	35.00	1.37	0.79	68	987	9	55.85	17.02	0.91	0.61
11	2.00	35.00	1.06	0.73	71	1048	8	56.33	16.83	0.88	0.60
12	2.00	35.00	1.38	0.77	72	1053	8	56.17	16.86	0.96	0.63
13	2.00	35.00	1.26	0.73	71	1050	8	56.28	16.64	0.97	0.64
AT	Alkaline	60.00	4.71	0.41	68	962	8	58.21	16.11	0.79	0.63
M	Control	-	-	-	62	874	9	48.00	18.42	1.31	0.72

Enzymatic treated samples present a weight loss lower than alkaline treated sample because the bioscouring treatment is less aggressive. It can be noticed that in the case of the enzymatic treatments the smallest weight loss occurs in the sample 7 at 2 % (o.w.f.) enzyme concentration and a treatment time of 15 min. The higher weight losses occur especially for samples 9 to13 where enzyme concentration was 2 % (o.w.f.) and treatment time 35 minutes.

Hydrophilicity values obtained from enzymatic treated samples are similar with the hydrophilicity of alkaline treated sample, which shows a good and effective treatment without significant weight loss. For all treatments, the weight loss values are in agreement with data from the literature which mentions values between 5-10 % for alkaline treatment and below 5 % for enzymatical ones [8]. Also, a hydrophilicity lower than 1 second is cosidered very good.

The crystallinity (Cr) value was obtained from the ratio between the peak area of the crystalline plane located for 2θ in the range of 22.46° and 22.86° and the total area. X-ray diffractograms for untreated flax/cotton fabric (1), enzymatically treated sample - 2 % o.w.f. and 35 minutes (2) and alkaline treated sample (3) are presented in Fig. 1.

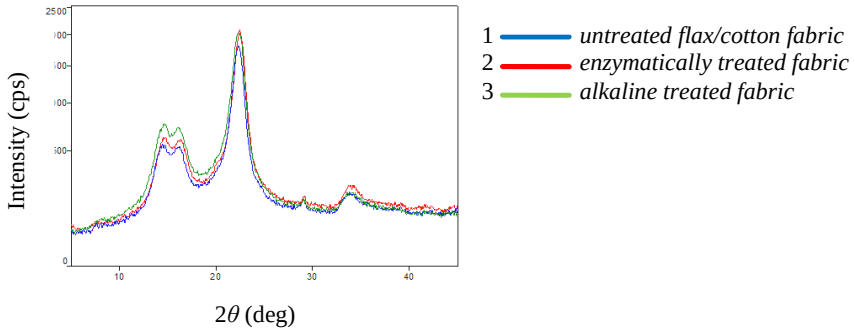


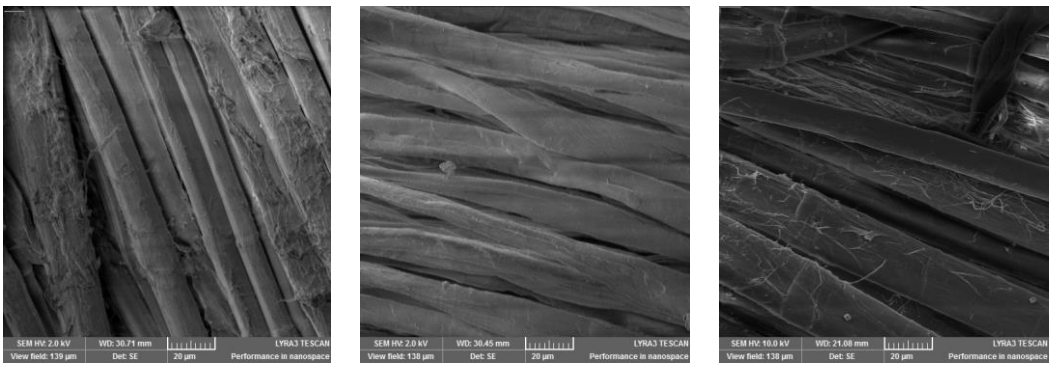
Fig. 1*: X-ray diffractograms for untreated flax/cotton fabric (1), enzymatically treated fabric- 2 % o.w.f. and 35 minutes (2) and alkaline treated fabric (3)*

As it can be seen from Table 1, for all treatments there was an increase in crystallinity compared to the control. With the increasing of crystallinity, the tensile strength of the fabric also increased. From figure 1 which presents a comparison between diffractograms obtained for the control, the best enzymatic treatment and alkaline treatment, it can be observed that enzymatic sample has the higher degree of crystallinity (73) followed by alkaline one (68) which means that the treatment was effective for removing of the non-cellulosic impurities.

A slightly whitening of the material appeared after the cleaning treatments. Small variations of Whiteness Index are oberved compared with the control. The whiteness index was increased with 17 % for the best enzymatic treatment and 21 % for classic alkaline treatment. Regarding the Yellowness Index this was decreasing by a percentage between 7 % and 13 %.

For the case of Ruthenium red dyeing method, the values obtained for color strength K/S of enzymatically treated samples compared to the control, a decrease between 15 % - 33 % is observed. For alkaline treatment a 40 % decreasing was registered. For alizarin dyeing method the K/S values present a decreasing between 7 -17 % for enzymatically treated samples and 12.5 % for alkaline treated sample.

The morphological changes of the treated samples were studied by scanning electron microscopy (SEM). Figure 2 presents the SEM micrograph of grey flax/cotton fabric (a), enzymatically treated sample at 2 % enzyme concentration and 35 minutes (b) and alkaline treated sample (c).



(a) (b) (c)

Fig. 2*: SEM micrographs for untreated fabric (a), sample treated with 2 % enzyme for 35 minutes (b), alkaline treated sample (c).*

The micrograph (a) shows some amounts of impurities and flaking compounds on the fiber surface for untreated sample. These represent the non-cellulosic materials binding the fiber bundles together and making the fiber surface highly hydrophobic. The enzymatic treatment (b) removed the impurities from the fiber surface leading to a smooth and clean surface. For the classical alkaline treatment (c) some peeling effect is observed due to the fibers degradation.

5. CONCLUSIONS

During the studies carried out it was found that:

- Enzymatic treated samples presented a weight loss lower than alkaline treated sample because the bioscouring treatment is less aggressive.
- Hydrophilicity values obtained for samples enzymatically treated are similar to that obtained for alkaline one, which showed a good and effective treatment without significant weight loss.

- It was noticed that in the case of the enzymatic treatments the smallest weight loss occurs in the sample 7 at 2 % (o.w.f.) enzyme concentration and a treatment time of 15 min. The higher weight losses occur especially for samples 9 to13 where enzyme concentration was 2 % (o.w.f.) and treatment time 35min. For all treatments, the weight loss values are in agreement with data from the literature which mentions weight loss values between 5-10 % for alkaline treatment and below 5 % for enzymatical ones. Also, all hydrophilicity values are lower than 1 second which demonstrates a very effective treatment.
- For all treatments was an increase in crystallinity compared to the control. With the increasing of crystallinity, the tensile strength of the fabric also increased.
- The whiteness index was increased with 17 % for the best enzymatic treatment and 21 % for classic alkaline treatment. Regarding the Yellowness Index this was decreasing by a percentage between 7 % and 13 %.
- For the case of Ruthenium red dyeing method, the values obtained for color strength K/S of enzymatically treated samples compared to the control, a decrease between 15 % - 33 % is observed. For alkaline treatment a 40 % decreasing was registered.
- For alizarin dyeing method the K/S values presented a decreasing between 7 -17 % for enzymatically treated samples and 12.5 % for alkaline treated sample.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE APPLICATION AND CHARACTERIZATION OF GRAPHENE DECORATED WITH TiO2 –Fe (1%)-N ON COTTON FABRICS

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Abstract: *Doped TiO2/graphene nanocomposites are studied due to their capacity to absorb the visible rays and large applicability in photo-catalytic applications. In this paper, we summarize our experiments on the development of photocatalytic fabrics based on deposition of doped TiO2/graphene nanocomposites by ultrasound method. We have investigated the surface morphology by scanning electron microscopy (SEM) and elemental composition was determinate through EDX. Other information were obtained from electrical resistivity analysis measured on Prostat PRS-801 instrument, evaluation of the cotton fabrics wettability by measuring the contact angle on a VCA Optima instrument and evaluation of the photo-catalytic properties of the treated fabrics under solar and visible light (Xenotest) by measuring the trichromatic coordinates of the treated and untreated textile materials. The results demonstrated that the ultrasound is an effective method to deposit nanoparticles on textile materials and that the uniform dispersion of TiO2- graphene composites depends on sonication parameters. Also, the treatment used on textile materials doesn't improve the electrical properties of the knit. The results obtain after evaluation of the photo-catalytic activity by photo degradation of methylene blue under visible and solar light show the performance of the developed fabrics and also that the photo-catalytic activity is high under visible light and solar light.*

Key words: *graphene-doped TiO2, photocatalyst, composite, nanoparticles, methylene blue.*

1. INTRODUCTION

Recent efforts to enhance the photocatalytic activity of TiO2 and develop self-cleaning[1], antibacterial[2] and antifungal cotton fabrics[3] are focused on the preparation of TiO2 composites with MWCNT[4], graphene[5] reduced graphene[6] or graphene oxide[7]. These composites increase the wavelength absorption across the entire visible light spectrum due to the graphene highly conjugated structure, and to the band gap reduction of carbon doped TiO2 [8]. Consequently, graphene-TiO2 show a high photocatalytic activity under visible light towards degradation of different contaminants [9,10]. The present research evaluated the potential photocatalytic activity of cotton fabrics coated with graphene decorated with TiO2 –Fe (1%)-N.

2. EXPERIMENTAL PART

2.1 Materials

Textile material: knitted cotton 188g/m2 weight; 0.927 mm thickness.

Chemical reagents:

- TiO2 doped with 1% iron and nitrogen and 2% graphene [TiO2 –Fe(1%)-N +2%GO, abbreviated GO] prepared by hydrothermal synthesis by National Institute of Materials Physics, Bucharest, Romania;
- Sodium dodecyl hydrogen sulphate (SDS) (Sigma-Aldrich),
- Distillate water.

2.2 Method

The cotton knit was treated with 0.16g/L GO prepared by dispersing the GO powder in 0.04g / L SDS for 180 minutes at 30^0C on ultrasound bath.

The fabric was immersed three times in above prepared dispersion and maintained 30 minutes at 60^0C on an ultrasonic bath.

After each immersion, the fabric was dried for 15 minutes under an IR lamp.

2.3 Characterization of knits treated with TiO_2

The morphology and presence of composites particles were evidenced by scanning electron microscopy and energy dispersive spectra (SEM/EDX, Quanta 200, FEI).

The hydrophily was determined by measuring the contact angles with a 5µl distilled water droplet on a VCA Optima (AST Products Inc., USA) instrument. The results are the average of ten measurements in different points on the samples surface.

The electrical resistivity of the textile materials was measured on Prostat PRS-801instrument (Prostat Corporation, USA) according standard SR EN 1149-1: 2006, at 20.70C and relative humidity of 28.8%.

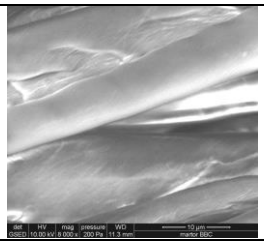
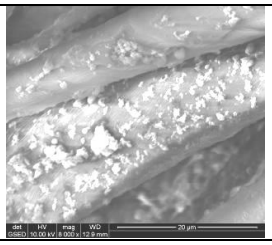
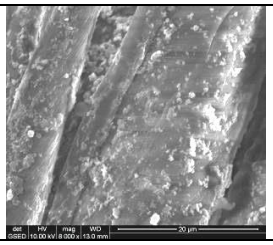
The photocatalytic efficiency under visible (Xenotest, Heraeus, Original Hanau) and solar light was evaluated by measuring the trichromatic coordinates (da*, db*, dL*, dE*) of the treated and un-treated fabrics stained with 0.0064 g/L methylene blue on a Hunter lab spectrophotometer, at 10° observer angle and D65 light.

3. RESULTS

3.1 Surface morphology

The aspect and the SEM images of fabrics treated with 0.16g/L GO are shown in the Table 1.

Table 1: *SEM images of the treated fabrics*

			
			
a.	b.	c.	d.

The treatment with TiO2 –Fe (1%)-N +2% GO completely changes the color of the material which becomes grey. The shade is intensified as the number of treatments increases. After the 1st treatment, the particles are randomly disposed on the material surface, most of them being agglomerated. After the 2nd treatment, the cotton fibers are covered with a large number of particles with different dimensions (329.8nm, 412.1nm, 450.6nm, 517.7nm. 778.7nm) less agglomerated than in the 1st treatment. The 3rd treatment leads to a more uniform coverage of the material surface with large particles which size vary from 257.6nm to 1.08μm.

The initial uneven distribution of particles is due to the non-uniformity of the fabrics and to the low adherence of the particles on the material surface. As ultrasonication time increases the nanoparticles size decreases and their dispersability in the treatment bath increases. Consequently, the number of particles deposited on the material increases. By lengthening the sonication time over 60 minutes, the slurry temperature increases which increases the number of collisions between the nanoparticles. As a result, the effect of dispersion decreases, nanoparticles form large aggregates, most of them remaining in suspension.

3.2 EDX elemental analysis of the fabrics treated with TiO2 –Fe (1%)-N +2%

The energy dispersive spectroscopic (EDX) microanalysis results are shown in the Table 2.

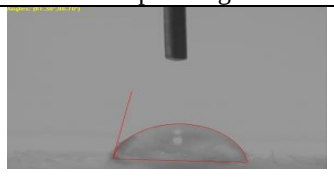
Table 2: *EDX elemental microanalysis of TiO2 –Fe (1%)-N +2% GO deposited on knit*

Element	1st treatment	2nd treatment	3rd treatment
	Wt %	Wt %	Wt %
C K	39.70	31.42	30.72
N K	-	10.11	10.76
O K	53.70	41.85	41.58
TiK	**6.60**	**14.79**	**13.91**
FeK	-	1.83	3.03
Total	100	100	100

3.3 Evaluation of the cotton fabrics wettability

Table 3 shows results of the water contact angle measurements.

Table 3: *Contact angles of cotton knit treated with TiO_2 –Fe (1%)-N +2% GO*

Nr. crt	Sample	Sample image	Left angle	Right angle
1	after 2nd treatment		76.4º	80.70º
2	1st and 3rd treatment	-	Hydrofil material (10 measurements)	

The first and third treatment does not modify the hydrophilic properties of the initial cotton knit, the drop of water being absorbed instantly by the fabric. The contact angle after the 2nd

treatment is about 80 degrees, which would indicate a slight hydrophobicity due to increasing amount of graphene deposited on material. However, taking into account the very small time of water absorption, of around 1 to 2 sec, it can be considered that the material is substantially hydrophilic.

3.4 Evaluation of electrical resistivity

The treatment with TiO_2 –Fe(1%)-N +2% GO doesn't improve the electrical properties of the knit.

Table 4: *Electrical resistivity of the treated cotton knit*

Sample	Surface resistivity, Ωsq	Volume resistivity, Ωcm	Thickness, mm
3rd treatment	$2.43x10^{13}$	$6.99\ x10^{14}$	0.90

3.5 Evaluation of the photocatalytic activity of the treated fabrics

The aspect and the color parameters of the exposed treated fabrics in comparison with the untreated fabrics are shown in the tables nr. 5 -7.

Table 5: *Aspect of the treated knit exposed to visible and solar light*

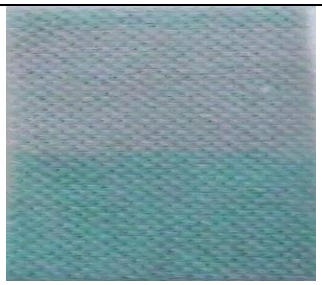
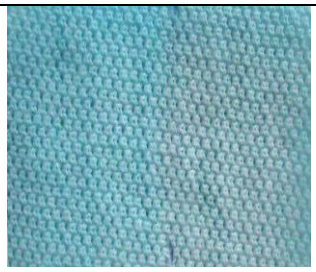
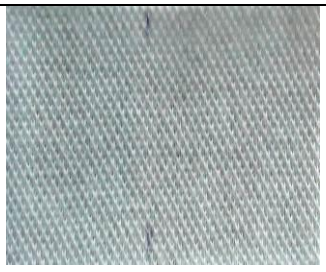
Fabrics exposed 4 hours to visible light	
Blank	3rd treatment
	
Fabrics exposed 4 hours to solar light	
Blank	3rd treatment
	

Table 6: *Trichromatic coordinates of the knit exposed 4 hours to visible light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	Note
Blank	77.38	-8.33	-17.65					
Knit-3rd treatment	74.72	-2.63	-2.68	-2.66	-5.7	14.97	16.24	1.00

Table 7: *Trichromatic coordinates of the knit exposed 20 hours to solar light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	Note
Blank	81.17	-5.54	-12.85					
Knit-3rd treatment	76.78	-1.85	-0.43	-4.39	3.69	12.42	13.68	1.00

The negative value of the difference of lightness coordinates (dL*) demonstrates that the treated fabrics exposed to visible and solar light are darker than the control sample, due to the black color of graphene and to the absorption of a higher amount of methylene blue by doped TiO_2 / graphene present on the material. At the same time, the color of the treated material is different from the treated blank as both da* and db * are positive, indicating the shift to red and yellow of the treated samples, respectively. Color differences indicated by high values of dE * and notes greyscale (differences are four tones to the blank) show a sharp degradation of the dye.

4. CONCLUSIONS

Ultrasound is an effective method to generate and apply the nano-particles on textile materials.

By selecting the suitable processing parameters, relatively uniform deposited layers with a high content of TiO_2-graphene could be deposited on materials.

The fabrics treated with TiO_2-graphene have photocatalytic activity demonstrated by intense discoloration of methylene blue both under visible and solar light.

ACKNOWLEDGEMENTS

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

REORGANIZATION OF THE TECHNOLOGICAL FLOW AT CLOTHING COMPANY THROUGH THE PRODUCTION SCHEDULE

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Abstract: *One of the main difficulties that light industry, namely clothing manufacturing sector faces today is inadequate organization of production processes. This is one of the most common and most serious obstacles in companies in the country, leading to low productivity. In order to reveal the causes of the problem and to develop solutions for change, it is proposed to conduct a study of a company facing difficulties in organizing the production process. It is important that the method/tool applied for the study is able to solve the problems occurring in the production process with minimum effort and maximum efficiency. The study was conducted within the process of manufacturing of a model of special clothing, namely clothing for doctors. The study was conducted within February-March 2016 at a clothing company of the Republic of Moldova. The study conducted shows that the transport issue in the technological flow can be solved by applying the production schedule, which eventually increases labor productivity by eliminating the time necessary to transport the labor object from one place of work to another, leading to economic growth considerable for the company. Following the assessments referring to the proposed improvements to organize the technological flow, there should be a 20% reduction in manufacturing time of a product, which will directly increase the revenue of the company by at least 10%.*

Key words: *movement, route, change, way, job, revenue.*

1. INTRODUCTION

One of the main difficulties that light industry, namely clothing manufacturing sector faces today is inadequate organization of production processes. This is one of the most common and most serious obstacles in companies in the country, leading to low productivity. In order to reveal the causes of the problem and to develop solutions for change, it is proposed to conduct a study of a company facing difficulties in organizing the production process.

Currently, there are several methods used for the study of the organization of production processes [1-7]. Variety of methods is explained by many problems arising within production process, as well as by various ways of solving them. The appropriate solution method is being chosen in terms of the problems that need to be addressed. It is important that the method/tool applied for the study is able to solve the problems occurring in the production process with minimum effort and maximum efficiency. The choice of the tools that will be applied in processes is a very important step in the study of labor, because the whole study conducted will depend on the method/tool [1].

The tools, commonly used in the labor study, are presented in the table 1 [2-5].

Table 1: *Methods of study of the production process and means for recording and analyzing methods*

No.	Name of the method	Means for recording and analyzing methods
1	General analysis of the process implementation	The general scheme of the process implementation.
2	Detailed analysis of the process implementation	Detailed chart of the process implementation.
3	Analysis of movements	The general scheme of the process implementation. Detailed chart of the process implementation. Production schedule. Wire diagram.
4	Analysis of arrangements	Arrangement plan. Reduced methods (models). Link method. Method of fictitious ranges.

The main purpose of the labor study is to increase labor productivity by reducing arduousness and efforts made to achieve the expected results [6]. Accordingly, a logical scheme has been established to render the close link between the labor study and the overall objective of each organization: increased revenues.

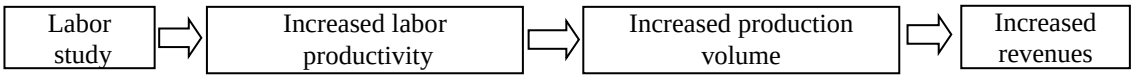


Fig. 1: *Influence of the labor study on economic efficiency of processes*

The labor study influences productivity by reducing the length of the production cycle and the time of processing or transportation, having an essential effect on the results, obtained within the production process [7].

2. REORGANIZATION OF THE TECHNOLOGICAL FLOW AT CLOTHING COMPANY THROUGH THE PRODUCTION SCHEDULE

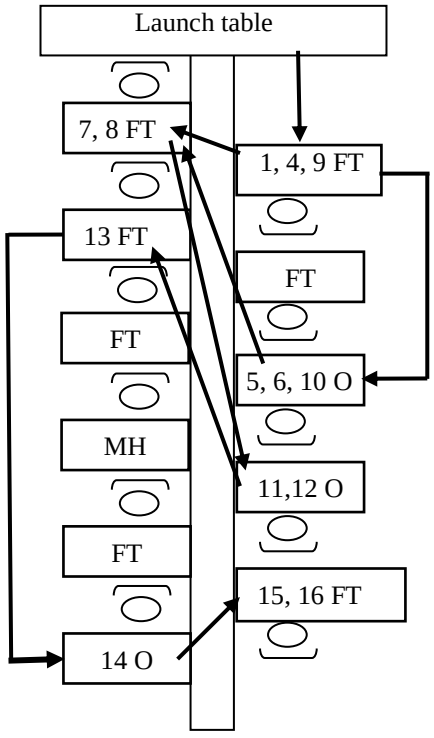
Of all the existing methods the best appropriate one to organize the technological flow in terms of the way the labor object goes through is the production schedule.

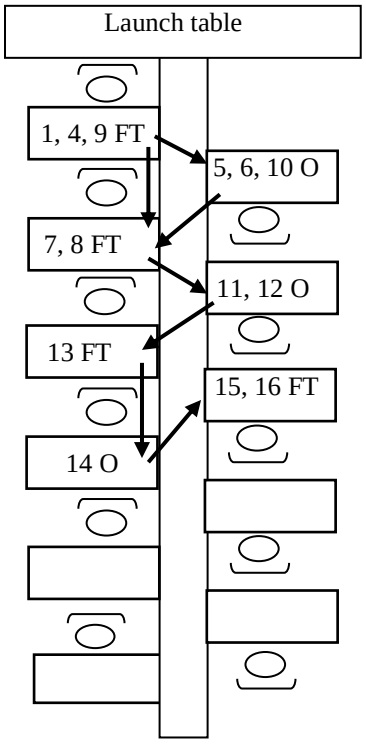
The need to study the movement of labor objects within the production process results from the fact that it tends to obtain beneficial options for movement or displacement by: avoiding unnecessary transport; avoiding returns in the flow; avoiding agglomerations; reducing distances. In order to achieve higher labor productivity at closing companies it is necessary for the production process of the technological flow to be organized as efficiently as possible. Therefore, it is proposed to efficiently organize the production process by determining the optimal route of transportation of materials and semi-finished materials within technological flows.

The study was conducted within the process of manufacturing of a model of special clothing, namely clothing for doctors (fig. 2). The study was conducted within February-March 2016 at a clothing company of the Republic of Moldova. Direct observations within the company subject to study revealed the following problems: lack of staff to manage and coordinate the production process; time standards inconsistent with reality; uneven division of labor; failure to comply with the consecutive order of technological operations; incorrect arrangement of operations for the technological flow.

Fig. 2: *Clothing for doctors*

To address the aforementioned situations it is proposed to establish a production schedule of the technological flow (fig. 3). The analysis of the existing production schedule shows that the routes the labor object goes through within the technological flow are too long and unjustified, to walk certain jobs, with the presence of a number of returns and inappropriate distribution of work tasks in the process, contradicting the rules to design the flows of materials and conditions for efficient organization of processes.





Where: **FT** – sewing machine with flat table; **MH** – sewing machine with handle; **SM** – special machine; **I** - in-between table; **O** – overlock sewing machine; 1, 2…n – number of the operation of technological order

Fig. 3: *Production schedule, existing method*

Fig. 4: *Production schedule, improved method*

A method for relocation of equipment and distribution of tasks within the flow, for the model analyzed, is shown in the figure 4. The improvement of the production schedule involved the relocation of equipment and redistribution of work tasks within the technological flow, taking into

account the existing work method, making no changes in the workload of employees. In such a manner only overlock sewing machines that represent key points that need to be changed to launch this model were relocated. Within the technological flow they are related to the distribution of tasks at places of work and allow transmitting the milestone package on the table located between the two rows of equipment. Making these changes enabled to organize the flow in such a way that any movement within the technological flow is logical, with rational consumption of time on the part of workers, providing a significant increase in labor productivity.

3. CONCLUSIONS

Organization of the production process is a very important step within each industrial company; therefore it is necessary that the company's management periodically, depending on the situation, reorganizes the production process for its proper functioning.

The use of labor study methods enables to organize the production process in an efficient manner, allowing to increase the use of the company's available resources.

The study carried out and the improvements in the technological flow for the model analyzed shows that the route the labor object goes through has significantly reduced from 23 m initially to 11 m in the improved version. This results in saving working time of executors or master transporting the labor object from one place of work to another. The benefits of reducing the distance, traversed by the labor object, implies not only saving time, but also creating a psychological environment favorable to workers, as they are no longer encumbered by transmission of milestones package for long distances, that needs to be taken from the place of work, as it is possible to pass it from hand to hand without considerable effort.

The study conducted shows that the transport issue in the technological flow can be solved by applying the production schedule, which eventually increases labor productivity by eliminating the time necessary to transport the labor object from one place of work to another, leading to economic growth considerable for the company.

Following the assessments referring to the proposed improvements to organize the technological flow, there should be a 20% reduction in manufacturing time of a product, which will directly increase the revenue of the company by at least 10%.

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ANNALS OF THE UNIVERSITY OF ORADEA
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ASSEMBLY LINE BALANCING in a CLOTHING COMPANY

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Abstract: *Assembly lines take the attention of researchers and companies because of its great effect on efficiency. Efficiency in assembly lines has an important role on cost and quality which are the basic fundamentals of competition. Assembly lines contain a number of workstations and tasks (jobs) are processed in these stations and are moved from station to station. The tasks are assigned to each station regarding a cycle time. The cycle time is the maximum available time for the production of a job at any workstation. The assingning of jobs to workstations is based on the objective of minimizing the workflow among the workstations, reducing the throughput time as well as the work in progress and thus increasing productivity. If the jobs are not allocated in balance, this will cause idle workstations and waste of workforce besides the loss of overall efficiency. In this study, an assebly line balancing problem was examined for a five pocket denim trousers in a clothing company. Firstly, priority associations and standard durations of operations of denim trousers were determined. Then, assembly line balancing study was carried out by using ranked positional weights assembly line balancing method developed by Helgeson and Birnie to increase the production in a clothing company manufacturing five pocket denim trousers.*

Key words: *Assembly line, Denim, Ranked Positional Weights Method, Clothing, Efficiency*

1. INTRODUCTION

In some of the manufacturing enterprises, the manufacturing process is performed on one or more lines. By the addition of various raw materials and semi-products from the beginning of the production lines, the product is obtained at the end of the production line. As the sequences and the balance of operations in the line will affect the efficiency, the designing of the production lines is very important for the companies.

Since there is a large number of operations in the production line and large quantities of production are made, even small improvements that can be made on the production line, will provide high productivity increase. In this study, a line balancing study was carried out for a denim trousers production line in a garment factory. With this study, it was aimed to resolve not only the wrong settlement patterns and lost times in the production line but also were tried to increase labor productivity.

2. ASSEMBLY LINE BALANCING

The assembly line is a production model defined as the transfer of materials along a line through labor or automatically. Operations on the part of the assembly line are carried out at work stations arranged along the line [1]. Workers at work stations do their own one or more operations to ensure that semi-finished products entering the production line exit as products at the end of the line. One of the most important problems in assembly line management is to group the tasks of consecutive workstations. The allocation of jobs to workstations is based on the objective of minimizing the workflow among the workstations, reducing the throughput time as well as the work in progress and thus increasing productivity [2]

2.1 Basic Concepts Used in Assembly Line Balancing

Station: A unit where one or more operations on the assembly line are made by the employee. One or more people can work in a workstation depending on the need for operation [4, 5].

Cycle time (C): The cycle time is the maximum available time for the production of a job at any workstation [3]

Cycle time= (Production time per day)/(Output per day)

Total operation time: Sum of task times of all work items on the line.

Station time: It is the total time required for completing the tasks in the station. In order to avoid delay between stations, station time cannot be smaller than the longest transaction time in the station and greater than the cycle time.

Minimum Number of Stations Required: The minimum number of workstations required for a product to run on a specified cycle time.

Number of station = (Total operation times)/ (Cycle time)

Precedence Matrix: This matrix provides the expression of the relationships between tasks. For transactions that have a direct or indirect priority relationship between each other, "1" is placed in the intersection cell of the line of prior task and the column of the following tasks "0" is placed in the other cells.

Line efficiency (E): It is the ratio of total operation time to cycle time and the actual number of stations.

LE %= (Total operation time)/(Actual no of stations X Cycle time)*100

Balance Delay: A measure used to indicate the imbalance of work or the distribution of employees to workstations. In other words, it shows the idle time ratio on the line.

BD=((Actual no of stations X Cycle time- Total operation time))/(Actual no of stations X Cycle time)*100

Theoretical efficiency (TE): Efficiency when the line is established with minimum number of stations without exceeding the specified cycle time.

3. MATERIAL METHOD

Assembly line of five pocket denim trousers (Fig 1) was examined in this study. Operation list, precedence relatons were determined for the model. After that, the base operation times of processes were measured in seconds by the help of a chronometer. A 10% allowance was added to these base operation times in order to get standard times. Ranked Positional Weighted Method provides fairly quick and acceptable solutions compared to other methods, and the solutions obtained together give approximate values. Therefore, this method was selected to be used in this problem. The steps of Ranked Positional Weight Method are as below [6];

Step1. Find the positional weights of each task. The positional weight of an operation is calculated by summing the operation times of other operations which follows that operation in series

Step 2. Rank the tasks based on their positional weights. The task with the highest positional weight is ranked first

Step 3. Proceed to assign tasks to the workstations, where tasks with the highest positional weight and rank are assigned first

Step 4. If additional time remains at any workstation after assignment of an operation, assign the next succeeding ranked operation to the workstation, as long as the operation does not violate the precedence relationships and the station times do not exceed the cycle time

Step 5. Repeat steps 3 and 4 until all elements are assigned to the workstations

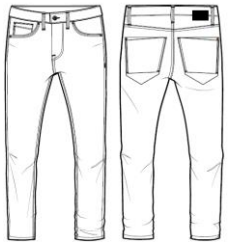

Fig 1: *Five pocket denim trousers*

4. RESULTS

The determined precedence matrix (Fig 2) and the flow chart (Fig 3) is given below.

	Task	Operasyon Name	Standard Time	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	Position Weight
P	1	Stitch zipper to fly	15		1																				+										+	+	+	+	+	+	+	+	+	+	+	246
P	2	Right fly overlock	3																						2										+	+	+	+	+	+	+	+	+	+	+	234
P	3	Left fly overlock	3																		3	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	363
P	4	Coin pocket seam	6					4	+	+	+	+	+	+	+						+	+	+	+	+										+	+	+	+	+	+	+	+	+	+	+	418,8
P	5	Insert coin pocket	18						5	+	+				+						+	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	418,2
P	6	Coin pocket bartack seam	4,8							6	+	+			+						+	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	415,2
P	7	Front pocket facing coverstitch	19,2								7	+			+						+	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	410,4
P	8	Front pocket bag overlock	15									8			+						+	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	391,2
P	9	Front pocket bag blind stitch	18												9						+	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	394,5
P	10	Back pocket seam	11,4											10							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	448,2
P	11	Join back pocket	25,8												11						+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	462,6
P	12	Trimming preparation and attaching seam	13,2																		12	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	376,2
P	13	Stitch waistband in series	9															13	+																				+	+	+	+	+	+	+	155,4
P	14	Waistband interlining	8,4															14																					+	+	+	+	+	+	+	146,4
P	15	Waistband wrapping	2,4																																				15	+	+	+	+	+	+	140,4
P	16	Sewing loops in series	4,2																	16																								+	+	+	68,4
P	17	Belt loop forming	4,2																																							17	+	+	+	64,2
F	18	Stitching left fly to front and edge seam	16,8																			18	+	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	363
F	19	Front fly edge stitch	9,6																				19	+	+	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	346,2
F	20	Fly topstitch	12																					20	+	+	+	+							+	+	+	+	+	+	+	+	+	+	+	336,6
F	21	Attach binding to front pocket	18																						21	+	+	+							+	+	+	+	+	+	+	+	+	+	+	324,6
F	22	Join front pieces	22,8																							22	+	+							+	+	+	+	+	+	+	+	+	+	+	306,6
F	23	Seam front pieces with two needle	22,2																								23	+							+	+	+	+	+	+	+	+	+	+	+	283,8
F	24	Pocket bag fastening	27																									24							+	+	+	+	+	+	+	+	+	+	+	253,2
F	25	Front piece overlock	18																										25						+	+	+	+	+	+	+	+	+	+	+	234,6
F	26	Bartack	8,4																																26	+	+	+	+	+	+	+	+	+	+	216,6
B	27	Back and yock joint	15																											27	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	282
B	28	Center back seaming	16,8																												28	+	+	+	+	+	+	+	+	+	+	+	+	+	+	267
B	29	Back piece side overlock	15,6																													29	+	+	+	+	+	+	+	+	+	+	+	+	+	250,2
B	30	Join back pocket	14,4																														30	+	+	+	+	+	+	+	+	+	+	+	+	234,6
B	31	Back pocket manuel bartack stitch	12																															31	+	+	+	+	+	+	+	+	+	+	+	220,2
A	32	Close inside leg 5 thread overlock	16,8																																32	+	+	+	+	+	+	+	+	+	+	208,2
A	33	Inside legs seaming	12																																	33	+	+	+	+	+	+	+	+	+	191,4
A	34	Close outside legs	24																																		34	+	+	+	+	+	+	+	+	179,4
A	35	Side edge stitch	17,4																																			35	+	+	+	+	+	+	+	155,4
A	36	Join waistband	18																																				36	+	+	+	+	+	+	138
A	37	Close waistband	18																																					37	+	+	+	+	+	120
A	38	Side seam ironing	18																																						38	+	+	+	+	102
A	39	Hemming	24																																							39	+	+	+	84
A	40	Automatic loop stitching	18																																								40	+	+	60
A	41	Side bartack	13,2																																									41	+	42
A	42	Final check	24																																										42	28,8
A	43	Open buttonhole	4,8																																											4,8
			617,4																																											

Fig 2: *Precedence matrix of five pocket denim trousers*

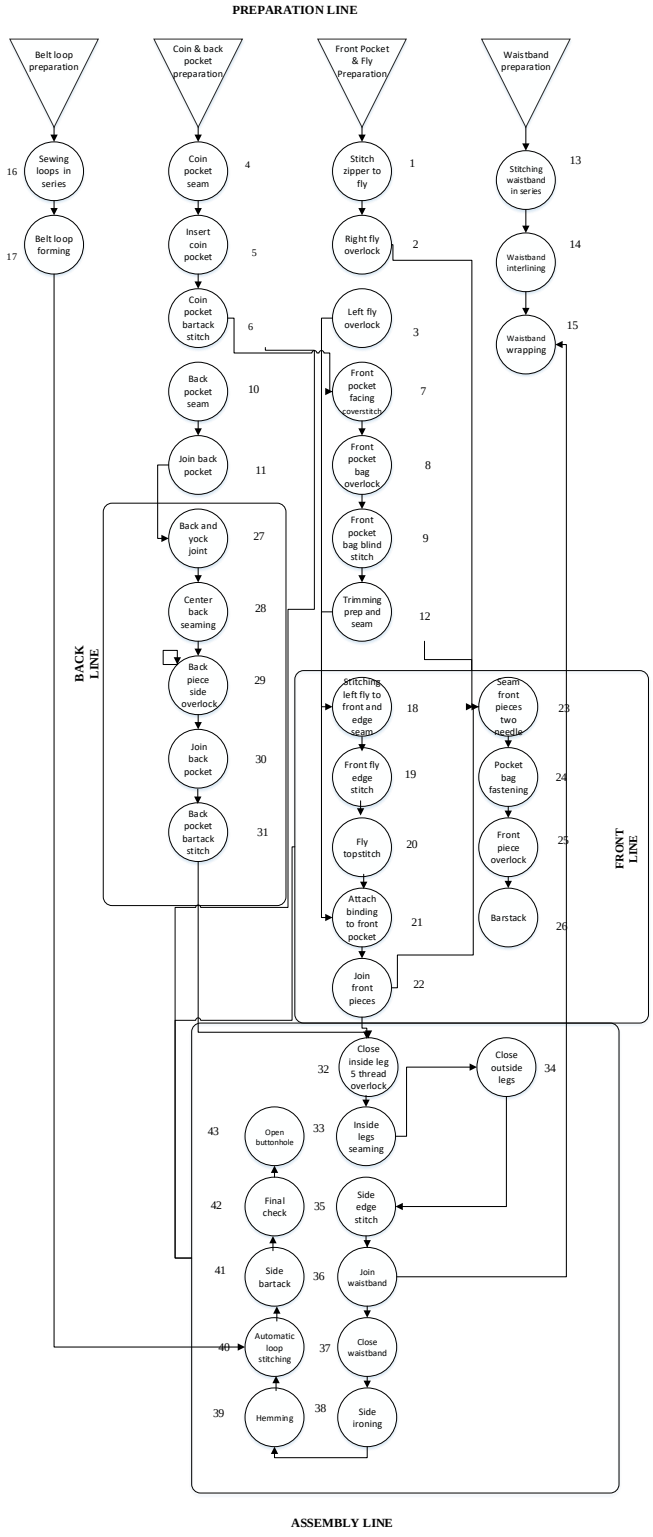

Fig 3: *Flow chart of five pocket denim trousers*

In figure 2, the precedence relations and positional weights of the operations are seen. Before assigning the operetaions to workstations cycle time should be calculated.

C = T / N = (545 minute* 60 seconds.) / 1500 (pieces/day) = 21,8 seconds

C = 22 seconds.

Minimum number of required workstations is as below;

n_{min} = Max (n_{min}; $n_{probable}$)

n_{min}= [Σ t_i / C]$^+$ = [617 /22]$^+$ = 28,04

$n_{probable}$ = t_i> (C/2 = 22/2 = 11) Probable tasks = 31 (1, 5, 7, 8, 9, 10, 11, 12, 18, 20, 21,22 23, 24, 25, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42)

n_{min} = Max (28; 31) = 31 minimum number of workstations

STATION NUMBER	TASK NUMBER	TASK NAME	POSITIONAL WEIGHT	TASK TIME	CUMULATIVE TASK TIME	LEISURE TIME
PREPARATION						
1	10	Back pocket seam	448,2	11,4	11,4,	10,6
2	11	Join back pocket	462,6	25,8	25,8	-3,8
3	4	Coin pocket seam	418,8	6	6	16
	5	Insert coin pocket	418,2	18	24	-2
4	6	Coin pocket bartack seam	415,2	4,8	4,8	17,2
	7	Front pocket facing coverstitch	410,4	19,2	24	4,8
5-6	8	Front pocket bag overlock	391,2	15	15	29
	9	Front pocket bag blind stitch	394,5	18	33	-4
7-8	12	Trimming preparation and attaching seam	376,2	13,2	13,2	30,8
	1	Stitch zipper to fly	246	15	28,2	15,8
	2	Right fly overlock	234	3	31,2	12,8
	3	Left fly overlock	363	3	34,2	9,8
	13	Stitch waistband in series	155,4	9	43,2	0,8
9	14	Waistband interlining	146,4	8,4	8,4	13,6
	15	Waistband wrapping	140,4	2,4	10,8	11,2
	16	Sewing loops in series	68,4	4,2	15	7
	17	Belt loop forming	64,2	4,2	19,2	2,8
FRONT PREPARATION						
10	18	Stitching left fly to front and edge seam	363	16,8	16,8	5,2
11	19	Front fly edge stitch	346,2	9,6	9,6	12,4
	20	Fly topstitch	336,6	12	21,6	0,4
12	21	Attach binding to front pocket	324,6	18	18	4
13	22	Join front pieces	306,6	22,8	22,8	-0,8
14	23	Seam front pieces with two needle	283,8	22,2	22,2	-0,2
15-16	24	Pocket bag fastening	253,2	27	27	17
	25	Front piece overlock	234,6	18	45	-1
17	26	Bartack	216,6	8,4	8,4	13,6
BACK PREPARATION						
18-19-20-21	27	Back and yock joint	282	15	15	73
	28	Center back seaming	267	16,8	31,8	56,2
	29	Back piece side overlock	250,2	15,6	47,4	40,6
	30	Join back pocket	234,6	14,4	61,8	26,2
	31	Back pocket bartack stitch	220,2	12	73,8	14,2
ASSEMBLY LINE						
22	32	Close inside leg 5 thread overlock	208,2	16,8	16,8	5,2
23	33	Inside legs seaming	191,4	12	12	10
24	34	Close outside legs	179,4	24	24	-2
25	35	Side edge stitch	155,4	17,4	17,4	4,6
26	36	Join waistband	138	18	18	4
27	37	Close waistband	120	18	18	4
28	38	Side seam ironing	102	18	18	4
29	39	Hemming	84	24	24	-2
30	40	Automatic loop stitching	60	18	18	4
31	41	Side bartack	42	13,2	13,2	8,8
32	42	Final check	28,8	24	24	-2
33	43	Open buttonhole	4,8	4,8	4,8	17,2

Fig 4: *Balancing of five pocket denim trousers assembly line*

The assignments of operations to workstations were done according to positional weights by following the steps of used method. The results are seen in figure 4. After assignment of operarations to the workstations, balance delay, theoretical efficiency and line efficiency were calculated as below and the efficiency results are in given in Table 1.

BD(%) = (33*22 – 617,4) / (33*22) = %14
TE (%) = [617,4/ (28,06*22)] *100 = %100
LE (%) = [617,4/ (33*22)] *100 = %85

Table 1: *Efficiency results of five pocket denim trousers assembly line*

	Number of tasks	**Cycle time C (seconds)**	**Minimum Number of workstations**	**Assigned number of workstations**	**Theoretical Line Efficiency TE (%)**	**Line Efficiency LE (%)**	**Balance Delay BD (%)**
Assembly line	43	22	31	33	%100	%85	%14

5. CONCLUSION

Assembly line balancing is an extremely important issue for using resources efficiently and reducing the costs in the garment industry. In this study, the production flow of a five pocket denim trousers was examined. According to the defined production flow, operation times of each operation were obtained by holding time with a chronometer. Then the positional weights of the operations were calculated and the tasks were assigned to the workstations regarding these positional weights. Thus, an efficient production line system was tried to be established. Theoretical efficiency is calculated according to the theoretical minimum number of workstations and it is preferable to obtain the closest results to this value. The obtained line efficiency is 85% and the balance loss is about 14%. Due to the small number of work items, the high priority relationships, and the large variety of machines, assigment of tasks to the workstations has less flexibility. Therefore, high balance loss can sometimes be normal. In general, it is not desired to get the line efficiency is to be under 80% [7]. The results of our model is over the general expectation.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE STUDY OF THE CHARACTERIZATION INDICES OF FABRICS BY PRINCIPAL COMPONENT ANALYSIS METHOD

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Abstract: *The paper was pursued to prioritize the worsted fabrics type, for the manufacture of outerwear products by characterization indeces of fabrics, using the mathematical model of Principal Component Analysis (PCA). There are a number of variables with a certain influence on the quality of fabrics, but some of these variables are more important than others, so it is useful to identify those variables to a better understanding the factors which can lead the improving of the fabrics quality.*
A solution to this problem can be the application of a method of factorial analysis, the so-called Principal Component Analysis, with the final goal of establishing and analyzing those variables which influence in a significant manner the internal structure of combed wool fabrics according to armire type. By applying PCA it is obtained a small number of the linear combinations (principal components) from a set of variables, describing the internal structure of the fabrics, which can hold as much information as possible from the original variables. Data analysis is an important initial step in decision making, allowing identification of the causes that lead to a decision- making situations. Thus it is the action of transforming the initial data in order to extract useful information and to facilitate reaching the conclusions. The process of data analysis can be defined as a sequence of steps aimed at formulating hypotheses, collecting primary information and validation, the construction of the mathematical model describing this phenomenon and reaching these conclusions about the behavior of this model.

Key words: *Principal Component Analysis, degree of compactness, fabric, porosity, factorial axis.*

1. INTRODUCTION

Principal components analysis (PCA) is a descriptive method for multivariate analysis/ multi-dimensional of data, which aims at decreasing the size of the matrix in which are shown the data to be analyzed. This technique aims to reduce the number of controlled variables (columns) of the matrix data, as far as possible two or three. Thus based on information about each group/types of fabrics, it is desirable that instead of interrelated variables to have only two or three new variables, called components. The PCA goal is to extract the smallest number of components to recover as much of the total information contained in the initial data [1]. The objectives of PCA are: synthesizing initial information contained in a large table; highlighting similarities or differences between data (individuals); highlighting the correlations between variables; explaining the similarities or differences between data (individuals); in terms of the considered variables [2;3]. At the beginning ,the methods of multivariate analysis of data were applied in fields of humanities:

biology, psychology, sociology [4-6]. Later, they were applied in numerous areas such as psychometry, genetics, medicine, economic industry [7;8]. Outstanding contributions to theoretical and practical development of these methods had,in particular, Galton and K. F. Pearson, by the studies in the field of regression and correlation analysis, Spearman and H. C. Hotteling by factor analysis and research of the principal components analysis. Nowadays, more specialized softwares allow the use of a variety of the methods for multivariate analysis of data for statistical processing of the research results: SPSS, STATISTICA, SAS, ADDAD [8-10].

2. EXPERIMENTAL PART

2.1. Materials and methods

In this study, there were analyzed four articles from five groups of worsted type fabric, made of different compositions, representing the number of individuals so:

Group A (100% Wool) - encoded items: A1; A2; A3; A4;
Group B (45% Wool + 55% Pes) - encoded items : B1; B2; B3; B4;
Group C (45% Pes + 55%Wool) - encoded items: C1; C2; C3; C4;
Group D (44%Pes + 52% Wool +4%Dorlastan) - encoded items: D1; D2; D3; D4;
Group E (60% Pes + 40% Celo) - encoded items: E1; E2; E3; E4

In making the fabrics from groups **A, B, C** and **E** , they were used Sirospun yarns which are twisted appearance yarns, called Jasper or yarn from double roving fibers. At group **D** fabrics, the weft threads are elastomeric yarns with core made of filament and their sheaths are made of fibers obtained also by the Siorospun process, through simultaneous supplying of the drawing frame with the roving and the filament core.

The joining of the two components takes place in front of the delivery rollers so that by simultaneous twisting of them it is made the yarn structure with the filament core covered by the fibers. Using two rovings which will be rolled separately and a filament core at one of the sides, it is obtained a twisted yarn from a spun yarn and a core yarn. Most polymers and elastomers used for industrial or commercial applications are composites, which contain solid fillers.

Analysis of fabrics structure and the manner of calculation of these indicators reflect the real state of the internal structure of the fabric in accordance with the armure. The values of the characterization indices of the combed wool-type fabrics were processed in SPSS using PCA. The variables used in the analysis are: volumetric filling coefficient, **Cvu**; the degree of compactness, **Kt** (%); the texture coefficient, **Ct**; the coverage percentage, **Et** and porosity, **Pz** (%).

2.2. Results and discussions

After processing the data in SPSS programme, applying PCA, the following results were obtained on statistical variables: descriptive statistics indicators (Descriptive Statistics); the correlation matrix; calculated values for both $\chi 2$ test statistics and **KMO** statistics; the variance of the variables; eigenvalues and variance explained by each factorial axis; variable coordinates on factorial axes; contributions of the variables at the inertia of factorial axes and graphics.

1. Descriptive Statistics Indices

The statistical parameters calculated for each variable are presented in Table 1 (output Descriptive Statistics).

Analyzing the data from Table 1, which contains information about each independent analyzed variable it can be seen that:

- the variable "Cvu, volumetric filling coefficient" is characterized by (39.33) average and (160,36) variance; the maximum volumetric filling coefficient was obtained to Article **D4**, made of

44% Pes + 52% Wool +4% Dorlastan, **Cvu=65,32**, and the minimum value was obtained to Article **A1** made of 100% wool , **Cvu=21,34;**

- the variable "**Kt** (%), degree of compaction" is characterized by the average (87.53) and the variance (41.895); the maximum value of the degree of compaction was obtained for Article **B4** made of **45% Wool + 55% Pes, Kt = 98,29%** and the minimum value for Article **A1** made of **100% Wool, Kt = 75,23%;**

Table 1: *Descriptive Statistics*

Variables	N	Minimum	Maximum	Mean	Std. Deviation	Variance
Cvu	20	21,34	65,32	39,3340	12,66344	160,363
Kt(%)	20	75,23	98,29	87,5275	6,47263	41,895
Pz(%)	20	58,50	79,21	67,4185	5,17203	26,750
Ct	20	92,10	114,20	97,5000	4,85191	23,541
Et	20	85,40	106,30	94,0150	6,56973	43,161
Valid N (listwise)	20					

Analogous to this, the other variables are analyzed. Following this independent analysis of every variable it is observed that the homogeneous variable is that related to the coefficient of density. The same trend is observed for the variable "coverage percentage".

2. Correlation Matrix (output of Correlation Matrix)

The correlation matrix shows the correlation coefficient values of the variables considered in pairs. It is a square matrix symmetrical about the main diagonal (equal to one, because a variable is perfectly correlated with itself). The shape of the correlation matrix is shown in Table 2, after the data have been standardized

Table 2: *Correlation Matrix*

		Cvu	Kt(%)	Pz(%)	Ct	Et
Correlation	Cvu	1,000	0,508	0,222	-0,371	0,063
	Kt(%)	0,508	1,000	0,252	-0,360	-0,423
	Pz(%)	0,222	0,252	1,000	-0,307	-0,420
	Ct	-0,371	-0,360	-0,307	1,000	-0,093
	Et	0,063	-0,423	-0,420	-0,093	1,000
Sig. (1-tailed)	Cvu		0,037	0,174	0,054	0,396
	Kt(%)	0,037		0,142	0,060	0,032
	Pz(%)	0,174	0,142		0,094	0,033
	Ct	0,054	0,060	0,094		0,348
	Et	0,396	0,032	0,033	0,348	

a. Determinant = 0,321

The analysis of the correlation coefficients of the matrix allows the assessment of the application of the PCA. High values of coefficients (greater than +0.5 and less than -0.5) shows that there are significant statistically links between the considered variables (direct connection if the coefficient values are positive, the reverse link if the coefficient values are negative). For example, from Table 2 it is observed that there are:

- significant statistical connections (direct link) between: Cvu and Kt (%); Kt(%) and Cvu;
- significant statistical connections (indirect link) between: Cvu and Ct; Kt (%) and Ct, Et; Pz (%) and Ct, Et; Ct and Cvu, Kt (%), Pz (%), Et; Et and Kt (%), Pz (%), Ct.

In this case, PCA can be applied. A feature of the correlation matrix is that the number of correlation coefficients increases greatly when the number of variables (k) included in the analysis

increases, regardless of the volume of statistics community. The number of the correlation coefficients is: k (k-1)/2. For the experimental data which are showing values for five variables, the number of the correlation coefficients is 10 (Table 2).

3. The Eigenvalues λ_k associated with each factorial axis and the total variance explained by each factorial axle (output of Total Variance Explained)

The eigenvalues of the correlation matrix are shown in the Total Variance Explained output, initial Eigenvalues column (Table 3).

Table 3: *Total Variance Explained*

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	2,082	41,640	41,640	2,082	41,640	41,640
2	1,289	25,786	67,426	1,289	25,786	67,426
3	0,774	15,470	82,897			
4	0,596	11,910	94,807			
5	0,260	5,193	100,000			

Extraction Method: Principal Component Analysis.

Table 4 shows that the eigenvalues of the correlation matrix are: $\lambda_1 = 2{,}082;\ \lambda_2 = 1{,}289;$ $\lambda_3 = 0{,}774;\ \lambda_4 = 0.596;\ \lambda_5 = 0{,}260$

The eigenvalues correspond to inertia explained by the factorial axes. Their sum is the total inertia of the cloud of points equal to the number of statistical variables of the original data table or the amount of elements from the main diagonal of the correlation matrix. Based on the values from Table 6 it may result:

$$\sum_{k=1}^{k} \lambda_k = 2{,}082 + 1{,}289 + 0{,}774 + 0{,}596 + 0{,}260 = 5 \quad \textbf{(1)}$$

The first factorial axis explains 2,082/5 = 41,64% of the total variance of the cloud points.

The first two factorial axes together explain 42.929% of total variance.

The number of factorial axes which are to be interpreted in the PCA was chosen according to the Kaiser criterion (1960) which implies the choice of that number of factorial axes for which the corresponding own values are higher than one. According to this criterion, two factorial axes are chosen, corresponding to their own values ($\lambda_1 = 2{,}082;\ \lambda_2 = 1{,}289$) >1.

These axes explain the biggest differences between statistical units in terms of the considered variables.

4.The coordinate of X_j variable on k factorial axis (output of the Component Matrix)

The values of the coordinate variables on the two-factorial axis are shown in Table 5.

The values in Table 4 shows the position of the variables on the factorial axes. For example, the variable "Cvu" has a coordinated position on the first factorial axis (0.622) and a positive coordinated on the second factorial axis (0.516); the variable will be plotted in the positive values quadrant of the first factorial axis and in the positive values quadrant of the second factorial axis.

The high values of the coordinate of variables on the factorial axes listed that are strongly correlated with that factorial axis.

For example, the variables "Kt (%)" and "Pz (%)" are correlated with the first factorial axis indicating that these variables explain significantly the differences between the statistical units (it means,there are significant differences between statistical units in terms of the recorded values for these variables). The coordinates of the variables on the factorial axes represent the coefficients of the linear equation of the relationship/links between variables.

Table 4: *Component Matrix*

Variables	Component	
	1	2
Cvu	0,622	0,516
Kt(%)	0,787	-0,072
Pz(%)	0,675	-0,295
Ct	-0,625	-0,520
Et	-0,480	0,813

Extraction Method: P.C.A

For example, for the data from Table 5, the first axis is a new variable defined by the linear combination of the initial variables, having the form:

$$F_1 = 0{,}622\ Cvu + 0{,}787\ Kt + 0{,}67Pz - 0{,}625\ Ct - 0{,}480\ Et \quad \textbf{(2)}$$

In order to identify the variables that explain the second factorial axis, those variables are selected from Table 4 (Component 2 column) that have higher coordinate values. It is noted that the realization of the second factorial axis is explained, only by the variables "Cvu" and "Et".

5. Graphical representation

The representation of the variable points in the first two factorial axes is shown in Figure 1. The first factorial axis represented on the horizontal indicates that between the "Kt (%)", "Pz (%)" and "Cvu" variables there is a strong direct connection and between the variable "Kt (%)"and the variable"Et "there is a reverse link.

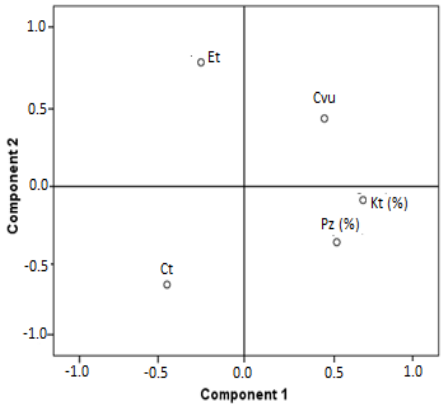

Fig.1:*Position of variables on the first two factorial axes*

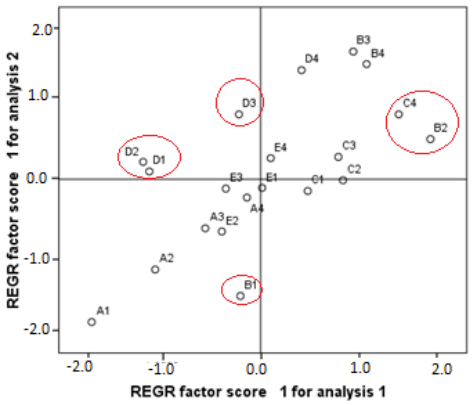

Fig.2:*Position of varieties of fabrics on the first two factorial axes*

The variables representative for the second factorial axis, represented on the vertical, are "Et" and "Pz (%)" between which there is a reverse link. The graphical representation of the variety of fabrics, from the five groups, on the first two factorial axes is shown in Figure 2.

3. CONCLUSIONS

The first axis factorial highlights two groups of types of fabrics: the first group is made up of articles **B2** and **C4** (with an extreme position to the right of the graph in Figure 2), and the second group of items **D1** and **D2** (with an extreme position to the left of the same graph).

The articles from the first group is characterized by higher values than average, of the following characteristics: volumetric filling coefficient, degree of compactness and porosity of woven fabrics, because the percentage of polyester fibers in the composition of the threads, as opposed to items in the second group, items **D1** and **D2**, in which the yarns have in their composition 4% Dorlastan.

The second factorial axis highlights the **B1** item, which is characterized by high values of compactness, volumetric filling factor and porosity of the fabric, unlike the **D3** item where the degree of compaction and porosity of fabrics are below the average.

By using **PCA** on indices for characterizing the worsted type fabrics it may be noted that the number of data matrix variables was reduced to two components, namely the degree of compactness, Kt (%) and the porosity, Pz (%), whose values reflect the real state of the internal structure of the fabric, in accordance with its armure.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

BENDING BEHAVIOUR OF MAGNETIC COTTON YARNS

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***Abstract*:** *Magnetic yarns are composite yarns, i.e. they combine elements of various natures and properties, with proven potential for electromagnetic interference (EMI) shielding. In this paper, different mixtures of hard and soft magnetic powder were chosen to cover materials made of cotton yarn. The physical properties and bending behaviour of the produced composite yarns were investigated in order to evaluate the yarns for further textile processing.The cotton yarn used as base material was covered with hard (barium hexaferrite $BaFe_{12}O_{19}$) and soft (Black Toner) magnetic particles. An in-house developed laboratory equipment has been used to cover the twist cotton yarns with seven mixtures having different amounts of magnetic powder (30% – 50%). The bending behavior of the coated yarns was evaluated based on the average width of cracks which appeared on the yarn surface after repeated flexural tests. The obtained results revealed that usage of a polyurethane adhesive in the coating solution prevents crack formation on the surface of hard magnetic yarns after flexural tests. At the same time, the higher the mass percentage of hard magnetic powder in the mixture, the higher was the cracks' width. The soft magnetic yarns are more flexible and a smaller crack width is observed on their surface. Both the coating solution composition and the powder diameter are expected to influence the bending behaviour of coated yarns.*

Key words: *coated cotton yarn, hard and soft magnetic powder, bending behaviour*

1. INTRODUCTION

Nowadays textile materials go well beyond common domestic use finding applications in various fields such as agriculture, construction and medicine. During the last decade, there is a growing interest in the field of intelligent textiles, which are textiles that are sensitive to changes in the environment through a series of features such as: electrical conductivity [1]; photo-luminescence; UV protection; catalytic and antistatic characteristics; antimicrobial and self-cleaning characteristics, that prevent or limit the spread of fire; magnetic and electromagnetic shielding properties [2]. Among these, magnetic textiles are becoming increasingly popular and demanded due

to their well-known special properties confered by the functionalization with magnetic elements in powder form.

Magnetic micro/nano powders are known for their application in electromagnetic interference (EMI) shielding which gives rise to many problems as electronic equipment operates in close proximity [3]. Consequently, potential applications can be foreseen in communications, computations, automations, space, medicine, etc.

In the literature, the term "magnetic textile yarns" defines yarns containing electro-conductive metal fibers. The main characteristics of such yarns is ferromagnetism, i.e. they exhibit magnetic properties in the presence of an external magnetic field. Magnetic wires lead to different magnetic anisotropies according to the textile structure type in which they are inserted and their position in the structure. Thus, the magnetic properties of yarns inserted in different textile structures can be diverse and can be tuned to create suitable structures, customized according to the requirements of the targeted application [4], [5].

From structural point of view, magnetic yarns are composite yarns, i.e. they combine elements of various natures and properties. Their composition can contain spun twisted yarns, with or without core, with various structures and components. According to recent research, the inclusion of magnetic particles in the yarns transforms them into magnetic yarns [6], [7]. The yarns may contain both diamagnetic fibers (natural, artificial or synthetic) and fibers with permanent magnetic field and may be used in woven or knitted structures, with various geometries, depending on the polarity of the inserted yarn.

The magnetic characteristics can be obtained by using electro-conductive fibers in the yarn structure, introduction of magnetic powder into the fiber matter during fiber production or by coating with solutions having magnetic properties [3], [4].

In this paper, different mixtures of hard and soft magnetic powder were chosen to cover materials made of cotton yarn. The physical properties and bending behaviour of the produced composite yarns were investigated in order to evaluate the yarns for further textile processing.

2. MATERIALS AND METHOD

2.1 Materials

In this article, the reference yarn (consisting of three simple yarns) used as reinforcing element was a 100% cotton yarn with Z twist direction and 930 twists/m. Each single combed ring-spun yarn had S twist direction with 1058 twists/m, while the fineness was 10 tex.

Barium hexaferrite (BaFe), a hexagonal hard magnetic ferrite with a magnetoplumbite structure, which is a widely used ceramic permanent magnet, was supplied by Rofep, Romania. Black Toner 6745 CP-313, a composite, soft magnetic mixture powder (denoted as CP-313) widely used as ink carrier during the printing process, was purchased from Lanier Worldwide Inc. U.S.A. The basic characteristics of these magnetic materials are presented in Table 1.

Table 1: *Basic characteristics of magnetic materials*

Characteristic	**Value**	
Name	isotropic barium ferrite 1,	black toner
Class	hard ferromagnetic materials	soft ferromagnetic material
Chemical formula	$BaFe_{12}O_{19}$	mixture
Components	Fe_2O_3 and $BaCO_3$	Styrene acrylate resin (60-90%), Carbon black (5-10 %), Polypropylene wax (1-5 %), Organic pigment (0,5-1%), Silica (<1 %)

Average diameter	4-6 μm	1-2μm
Measured density	4458 kg/m^3	658 kg/m^3

Two SEM images of the BaFe and CP-313 sample are given in Fig. 1.

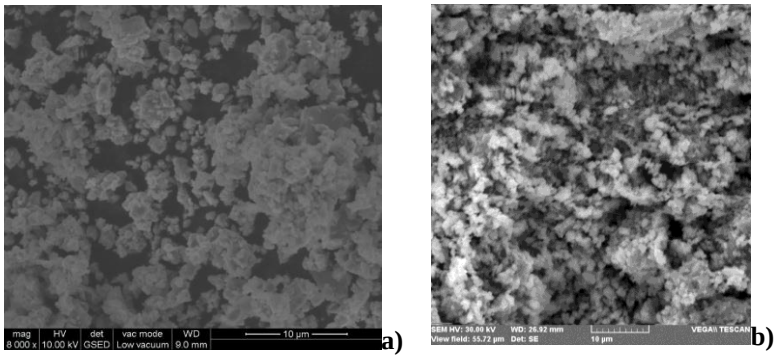


Fig. 1. *SEM images of (a) BaFe and (b) CP-313.*

Seven mixtures of hard and soft magnetic powder having different mass percentage of two polymers in viscous state (polyvinyl acetate PVAc and polyurethane resin PUR) and glycerol based plasticizer were used to cover the cotton yarns (see Table 2). Polyvinyl acetate is a widely used thermoplastic adhesive with good adherence to cellulosic materials. Polyurethane is used as adhesive due to its remarkable adherence.

Table 2: *Composition of coating solutions*

Yarns code	Type of core	Componets (wt%)
A1	100% cotton yarn	30% BaFe, 69% PVAc, 1% Gly
A2		40% BaFe, 50% PVAc,10% PUR
A3		45% BaFe, 52% PVAc, 3% Gly
A4		50% BaFe, 50% PUR
A5		30% CP-313, 45% PVAc, 10% PUR, 5% Gly
A6		40% CP-313, 57% PVAc, 3% Gly
A7		42,5 % CP-313, 54,5% PVAc, 3% Gly

2.2 Methodology

An in-house developed laboratory equipment, schematically depicted in Fig. 3, was used for coating. This laboratory device allows a primary orientation of the magnetic particles along an external electromagnetic field lines having a 0.14 T induction. Subsequently, the coated yarn was subjected to a more powerful magnetization until saturation.

The deposition process occurs in the magnetic mixture feed chamber which is equipped with a special calibration device spinneret type with a circular hole (500 μm in diameter). This ensures a uniform deposition of the polymer mixture. It also allows covering yarns having an average apparent diameter of less than 400 μm. After calibration, the coated yarn passes through a multi-polar magnetizing device having an induction of 0.7 T. The final stages of the process include heating, fixing of the coated layer and winding. The trajectory of the yarn during the deposition process causes the magnetic solution to adhere on its surface between the fibers of the surface layer.

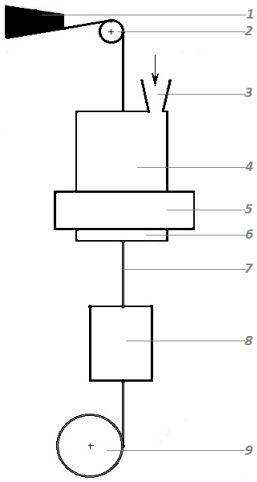


Fig. 3. *Coating in-house equipment: 1- bobbin yarn, 2 - guiding yarn device, 3- polymeric solution feeder, 4 - coating chamber, 5- air gap induction electromagnet, 6 - spinneret, 7 - coated yarn, 8 - dryer, 9 - winding drive*

The coated yarn samples were conditioned in a standard atmosphere of 65%±2% R.H. and a temperature of 20±2^{0}C in order to investigate their structural modifications and bending behavior.

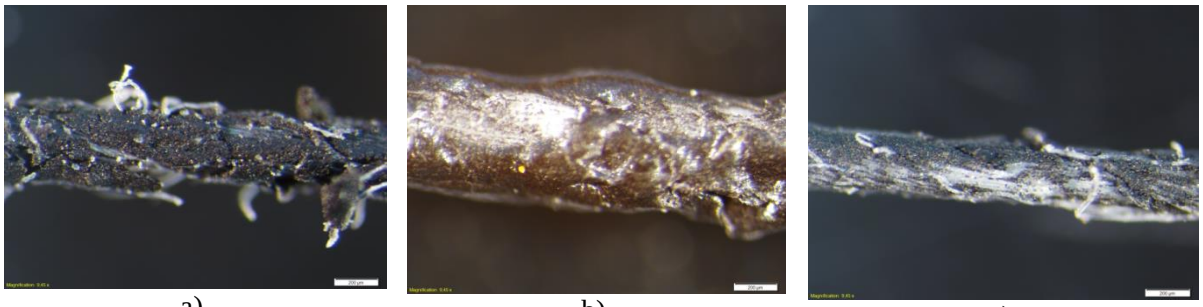
In order to estimate the bending behavior of coated yarns, a Tilmet 88 device was used [8]. Testing involved repeated flexural cycles (45 cycles/min) at an angle of 60^0 over a period of 11 minutes. All tests were repeated five times.

The samples had a length of 6 mm, which ensures enough space to identify the number of cracks formed on the coated yarn surface after repeated tests. The surface of the coated yarns was studied using a microscope type Olympus SZX 10 at a 9.45X magnification degree.

3. RESULTS AND DISCUSSION

The bending behavior of the coated yarns was evaluated based on the average width of cracks which appeared on the yarn surface after repeated flexural tests. Microscopic images taken at a magnification of x 9.45 were used to determine the values of the width.

Three optical images of coated yarns (sample A1 and A2 covered with hard magnetic powder; sample A6 covered with soft magnetic powder) after the third test are given in Fig. 4.



a) b) c)

Fig.4: *Microscope images: a) yarn A1 after 3rd flexural test, b) yarn A2 after 3rd flexural test and c) yarn A6 after 3rd flexural test*

The values of the average cracks' width, expressed in μm, are given in Table 4 and the graphic representations are presented in Fig. 5 and Fig. 6.

Table 4: *Tests results of measured yarns*

		Coated yarn						
		A1	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**
Average width (μm)	Before I-st test	7	0	8	0	5	10	3
	After I-st test	9	0	16	0	8	10	13
	After II-nd test	14	0	22	0	8	17	14
	After III-rd test	14	0	23	0	8	23	16
	After IV-th test	24	0	25	0	9	27	20
	After V-th test	25	0	27	0	12	35	20

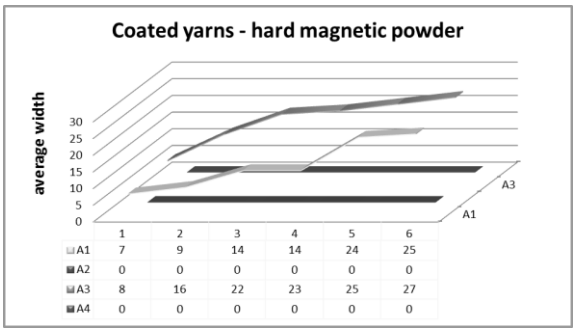


Fig. 5. *Average width of coated yarns A1-A4*

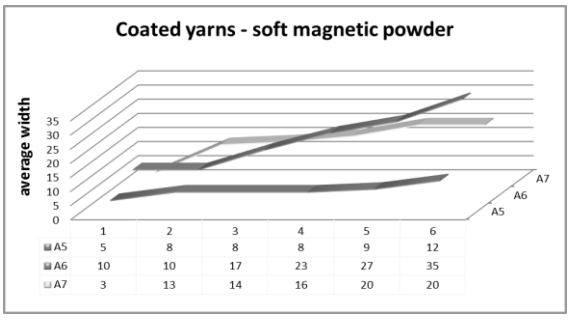


Fig. 6. *Average width of coated yarns A5-A7*

It is observed from Table 4 that, after repeated flexural tests the surface of samples A1 and A3 exhibits cracks. For example, a 15% increase of hard magnetic powder mass percentage when comparing A1 and A3 is leading to a 56% increasing of crack width after the 1st test. On the contrary, samples A2 and A4 are crack free which we believe is due to the presence of the PUR in the coating solution (see Table 2). PUR has a good elasticity due to a high weight percent of solid content (>99%) and low content of volatile products (<1%).

In the case of soft magnetic yarns, A5 to A7, these yarns are more flexible than hard magnetic yarns due to the average diameter of black toner that is smaller than isotropic barium ferrite. Thus, a lower cracks' width is observed on the surface of the soft magnetic yarns as compared to the hard magnetic yarns, having almost the same composition of the coating solution (e.g. A3 versus A7).

4. CONCLUSIONS

In this work, we have successfully prepared and characterized both hard and soft magnetic powder coatings on cotton yarns with respect to their bending behaviour. Seven coating solutions with various mass percentages of hard and soft magnetic powders, two polymers in liquid state and a glycerol were used in order to obtain coated yarns. An in-house developed laboratory equipment was employed for the coating process.

Bending tests involved repeated flexural cycles (45 cycles/min) at an angle of 60^0 over a period of 11 minutes. The evaluation of the bending behaviour indicated that the appearance of cracks on hard magnetic cotton yarns depends on the usage of the polyurethane adhesive in the coating solution. The higher mass percentage of hard magnetic powder from coating solution the higher is the crack width because yarns become more stiff.

For soft magnetic yarns, the average diameter of the black toner particles is smaller than in the case of isotropic barium ferrite. Consequently, these coated yarns are more flexible and a smaller crack width is observed on their surface. In conclusion, both the coating solution composition and the powder diameter are expected to influence the bending behaviour of coated yarns. Both these parameters can be tuned according to the desired application.

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ANNALS OF THE UNIVERSITY OF ORADEA
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NATURAL COTTON PRINTING WITH RED MACROALGAE BIOMASS OF *GRACILARIA GRACILIS AND GRACILARIA CORNEA*

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Abstract: *Environmental protection is gaining popularity in our society due to the accentuated and irresponsible use of natural resources. Consequently, measures need to be taken in all of the demanding industries, including the textile one, as more sustainable alternatives to the actually employed synthetic dyes. One of the solutions can be represented by the utilization of algal biomass as colorant matter. Therefore, this research work aimed the validation of the employment of lyophilized algal biomass in a conventional pigment-printing process. Two different Gracilaria genus species were employed for the comparison of color efficiency and printing suitability, Gracilaria cornea and Gracilaria gracilis. The printing process results revealed brown-red and pink uniformly printed cotton substrates, with good color strength (K/S=11,66 and 23,7 respectively) and good to excellent behavior (analyzed according to greyscale) to rubbing and laundering fastness. Both printed cotton fabrics proffer a special pattern generated by the algal biomass. In conclusion, lyophilized red algal biomass can be employed in the conventional printing process on cotton substrates with no need for previous pigment extraction treatments. This study can serve as a research line opener for further investigation in the application of algae in the textile finishing process.*

Key words: *algae, lyophilized biomass, textile, natural pigments, sustainability*

1. INTRODUCTION

Consumption and the consequently availability of natural resources have become a concerning issue in the societal and industrial development, due to the dramatic expansion of their usage in the last 40 years and the correlation with general environmental degradation [1]. When referring to one of the most demanding and polluting industry, the textile industry, the consumers tend to focus their demands on eco-fashion [2] and sustainability [3].

Taken into consideration that approximately 30 million of tons of textiles are consumed globally per annum and need 700000 tons of synthetic dyes for coloration. Enormous quantities, from which a high amount remains in the environment, accelerating its degradation [4]. This is forcing a continuous search for more sustainable alternatives, which could mitigate the harmful consequences generated by the synthetic dyes. Recent studies have centered the attention on the employment of algae, based on their relevant chemical constituents content, in industries as food [5], cosmetic and pharma [6], agriculture and animal feed [7].

The term algae refer to the photosynthetic organisms which are characterized as being prokaryotic and may be unicellular (microalgae) or pluricellular (macroalgae). By means of pigment content, they are divided into three kingdoms: Rhodophyta (red algae), Phaeophyta (brown algae) and Chlorophyta (green algae) [7]. Red algae is one of the algal phyla with high potential in coloration industries due to the visible tint of the biomass [8]. *Gracilaria genus* is a representative grouping of red seaweeds, with an important content of phycoerythrin (red pigment), generated as secondary metabolite and actually highly prized for its agar content for food and cosmetics industry [9].

Algal application in the textile industry has not been yet documented, neither in dyeing nor printing processes. Even though, research on pigment content and extraction methods have gathered important interest nowadays [10],[11],[12]. In function of the algae type, several added value products can be extracted, such as fatty acids, fats, oil, natural dyes, sugars pigments, antioxidants, etc.[13].

This research was focused on the demonstration and validation of the cotton printing process at laboratory level, involving lyophilized red macroalgal biomass. The aim of the research was to compare the printing processes involving two different algae species pertaining to the same genus, *Gracilaria.* The printing results showed uniformly printed fabrics, which were color characterized, observing the color strength values (K/S) of 11 and 24 respectively. The laundering and rubbing fastness measurements defined the color behavior to external physical agents, analyzed with the greyscale method, as *good* to *excellent*.

2. MATERIALS AND METHODS

2.1. Algal biomass cultivation and colorant matter preparation

Gracilaria gracilis is a cartilaginous, cylindrical red macroalgae, marine species, generally distributed on rocks and stones. It is considered a traditional source of agar. *Gracilaria cornea* also known as *Hydropuntia cornea*, is characterized by being a marine agarophyte, currently used in commerce as source of hydrocolloids [9].

Red algal biomass was employed as colorant matter and was supplied by Algaplus, Portugal. The two Gracilaria genus species, *Gracilaria cornea,* and *Gracilaria gracilis* were cultivated in an open-system culture, in industrial-scale cultivation tanks. The colorant matter applied in the printing process was obtained through a lyophilization process of the fresh biomass, resulting in the algal biomass powder, which was added to the mother printing paste, as described in table 1.

2.2. Textile printing process

In this research work, 200g/m^2 cotton fabrics (supplied by Intexter UPC, Spain) were used as textile substrates for the pigment-printing process, where the natural lyophilized products, were used as coloring matter. The conventional printing paste elaborated is presented in table 1.

Table 1: *Printing paste recipe*

Paste element	Mother paste	
Binder	Resin STK-100*	250 gr
Fixer	Color Center MC-LF*	25 gr
Thickener	Clear HC-35*	20 gr
Pigment	Lyophilized algal biomass	30% (reported to the total weight of the paste)
Water		703 gr
Total		1000 gr

*supplied by Color-Center, Spain

The printing process, carried out at laboratory scale, simulated a conventional industrial printing process, with a printing screen and scraper, and a uniformly applied pressure. According to the binder curing requirements, the printed fabrics were dried in a laboratory drying oven (supplied by Memmert, Germany) at 80ºC for 10 minutes and then further subjected to a curing stage at 110ºC for 2 minutes.

2.3. Printed fabrics characterization

2.3.1. Chromatic coordinates measurement and color characterization

In order to validate the color characteristics of the printed fabrics, the chromatic coordinates, CIELab values were measured with a Datacolor DC 650 (supplied by Datacolor, Spain), employing the requirements of the European accepted standard for textiles characterization (UNE-EN ISO 105-J01:2000). The main characteristics of the apparatus are illuminant D65, observant angle 10º, and a diffuse measuring geometry.

2.3.2. Color strength calculation

Dye uptake or *K/S* value represents a method for the fabric color strength calculation based on the measurement of the reflectance of the fabric at the maximum absorbance lengthwave. This measurement was done using a UV-VIS spectrophotometer Lambda 950 (supplied by Perkin Elmer, Spain) and the color strength was calculated by applying the formula developed by Kubelka and Munk [14]:

$$K/S = \frac{(1-R^2)}{2R} \quad \textbf{(1)}$$

Where,
K is the coefficient of adsorption,
S is the coefficient of scattering,
R is the reflectance value of the fabric at λ_{max}

The resulting value is directly proportional to the amount of dye present in the material.

2.3.3. Laundering and rubbing fastness

The color fastness to domestic and commercial laundering (UNE-EN ISO 105-C06:2010) was established by submitting samples of cotton of 10×4 cm to the Gyrowash apparatus (Supplied by James Heal, United Kingdom), in a canister together with 150 ml of water, 0.6g of detergent and 10 steel balls for 45 minutes at 25ºC.

The rubbing fastness followed the requirement of the standard UNE-EN ISO 105-X12:2003, which implies the employment of the Crockmeter apparatus (supplied by Atlas, Spain), where printed cotton samples of 14×5 cm are tested for dry and wet rubbing fastness. The rubbing is exercised on the fabric at 1 cycle per second meanwhile applying a force of 9 N, at a temperature of 20ºC. The wet rubbing involves an additional pretreatment of the fabric samples by impregnation until 95-100%.

3. RESULTS AND DISSCUSION

3.1. Color characterization

For the realization of the printing process *Gracilaria cornea* powder biomass was used to provide pink colors; meanwhile, *Gracilaria gracilis* was used to provide brown colors.

Table 2. confirms the colors obtained through the measurement of the chromatic

coordinates, which objectively place the color shades in the pink and respectively brown color sphere.

Table 2: *Chromatic coordinates values of printed cotton*

	Gracilaria gracilis	*Gracilaria cornea*
L*	76,55	72,08
a*	10,62	5,45
b*	9,27	21,37
(C*)	14,1	22,05
(h°)	41,11	75,7

*C=Chroma, h°=Hue angle

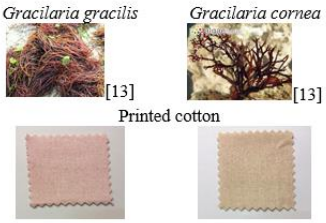

Fig. 1: *Fresh biomass and printed cotton with Gracilaria gracilis (left) and Gracilaria cornea (right)*

The color difference between the two Gracilaria species was calculated based on the chromatic coordinates measurements, in terms of ΔL* (19,9), as color lightness and ΔE* (13,89), as a parameter for color difference. The results show that the cotton fabric printed with *Gracilaria gracilis* presents lighter shades, and the Δ**E*** presents a significant nuance difference between the two strains employed in the experiments, even though they belong to the same algal genus.

Color efficiency was determined based on the reflectance strength of the printed fabrics, as shown in fig 2. through the fabrics spectrum.

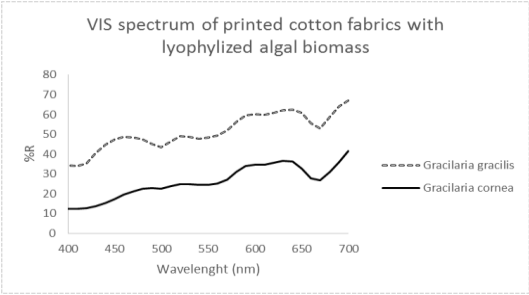

Fig. 2: *VIS spectrum of printed cotton fabrics with lyophilized algal biomass, no pigment extraction realized*

According to the principle of reflection, 100% of reflection corresponds to a white fabric (total light reflection), meanwhile, 0% of reflection corresponds to the black color, which absorbs all the emitted light fascile. In consequence, it can be observed that, according to the reflectance values, the biomass *Gracilaria gracilis* generates lighter colors, when compared with the cotton fabrics printed with the lyophilized biomass corresponding to *Gracilaria cornea*. It can also be confirmed that the two strains of algae employed in the experiments are pertaining to the same algae genus, based on the similar peaks of the color spectrums obtained.

The color efficiency of red macroalgae *Gracilaria gracilis* is characterized by a value of 23,70 which shows to be approximately double, than the one provided by *Gracilaria cornea* 11,66. Both values, when compared with scientific literature centered on dyeing or printing with red/pink natural colorants, show a good level of dye uptake [15].

3.2. Rubbing and laundering fastness

The results of the fastness of the printed cotton fabrics with lyophilized red macroalgae biomass belonging to the *Gracilaria genus* are presented in table 4.

Table 3: *Printed cotton substrates with lyophilized algal biomass rubbing and laundering fastness values*

Laundering fastness at 25ºC		*Gracilaria gracilis*	*Gracilaria cornea*
Change in color		3-4	3-4
Staining	Wool	4-5	4-5
	Acrylic	4-5	4-5
	Polyester	4-5	4-5
	Polyamide	4-5	4-5
	Cotton	4-5	4-5
	Acetate	4-5	4-5
Rubbing fastness	Wet staining	4	4
	Dry staining	4-5	4-5

1-Very poor 2-Poor·3-Moderate 4- Good 5- Excellent

In terms of color fastness to rubbing and laundering, both species show similar results when reported to the grayscale, characterized as *good* to *excellent*. When compared with natural colorants, which come from other sources, it can be affirmed that the printing process with lyophilized algal biomass, originating from red macroalgae is viable and applicable on cotton substrates [15],[16].

4. CONCLUSION

The application of lyophilized algal biomass, as colorant matter, obtained from two red macroalgae belonging to the *Gracilaria genus*, in a conventional textile pigment-printing process, at laboratory scale, was demonstrated and validated successfully through this research work.

Taking into account that the application of a mordanting process is required in the majority of the dyeing processes which involve natural colorants [15] the actual study does not employ this process auxiliary. So, it can be affirmed that the color depends exclusively on the colorant matter, binder and fiber.

Textile characterization results show uniformly printed fabrics with variations of red color. Even though the two types of algal biomass appertain to the same genus, differences between the color shade and brightness were observed. The color efficiency and the textile spectrum show more intense and darker color generated by *Gracilaria cornea.*

The textile application validation is sustained by the rubbing and laundering fastness measured according to European standards, mandatory to be applied to the textile industry products. These results characterize the color behavior as *good* to *excellent* in terms of color fading when the fabrics were subjected to a laundering process, and when tested the rubbing staining on a white reference fabric.

In order to obtain a fully sustainable printing process, further experiments must be realized, to find natural alternatives, not only to the colorant matter but also to the auxiliary products employed in the process as resins, binders, and thickeners.

In conclusion, when placed in the environmental protection context, generated by resource scarcity and pollution emission by the industrial activities, finding more sustainable raw materials represents a great accomplishment and a first step in the mitigation process of the environmental degradation. As the textile industry is one of the most demanded and pollution generating industry, sustainable sources of colorant matter represent a way to make a positive change to a more aware society.

Acknowledgments: *This work was supported by the European research project ¨SEACOLORS¨ (Demonstration of new natural dyes from algae as substitution of synthetic dyes actually used by textile industries) within the LIFE 2013 ¨Environment Policy and Governance project application¨*

program. The continuation of this research line, involving algae used in applications for the textile industry will be realized through the research project ¨GREENCOLOR¨ (Study of the application of natural colorants in textile dyeing and printing processes) within the national local call IVACE 2017.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

DEVELOPING THE ORGANIZATIONAL CONTROL STRUCTURE BY MONITORING THE TECHNOLOGICAL PROCESSES IN THE TEXTILE GARMENT INDUSTRY

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Abstract: *In order to improve quality, any activity performed in garment production enterprises, must adhere to the following principles: the technical documentation must be observed first, and also all resources necessary for the proper functioning of the production process; conformity check must be carried out to fulfill production goals in advance; the technical specifications and documentation must be implemented and for proper execution there must exist a control method, consisting in discovering defects and correct them.*
In the garment industry, the situation is more difficult because of the large number of features present in its complex products, and the problems that may arise must be estimated. Thus, for different activities in quality assurance, experiments have been carried out which show that even the measurement results can be affected by human error. The training of inspectors is important inspection requires a high level of judgment in specific cases, which can be acquired only by experience. In many inspection situations, judgment is essential. Therefore, garment manufacturers must boost inspections, in order to keep the technological process under control.
This paper focuses on meeting certain objectives in establishing certain control structures for compliance of processes, by presenting a few criteria. After analyzing quality problems along the process flow, both in terms of the manufacturing process and product quality, we propose customized solutions by product type, to prevent and solve quality issues. This analysis of the control plan for the conformity of the technological processes will improve the production of garment manufacturers, from a technical as well as economical standpoint.

Key words: *process, conformity, quality, stages, operation, critical areas*

1. INTRODUCTION

Any activity carried out by garment manufacturers, in order to improve quality, must adhere to the following principles [1]:

- in order to conduct normal production activities, the technical documentation must be observed first, and also the technical, material and human resources necessary for the proper functioning of the production process;
- conformity check must be carried out at the start or during the execution of an activity, to fulfill production goals in advance;
- in order to manufacture correctly, the technical specifications and documentation must be implemented;

- for proper execution, which flows the same way each time, there must exist a control method, consisting in discovering defects in order to correct them.

In the garment industry, the situation is more difficult because of the large number of features present in its complex products, and the problems that may arise must be estimated. Thus, for different activities in quality assurance, experiments have been carried out which show that even the measurement results can be affected by human error.

The training of inspectors is very important, but in practice inspection requires an 'extreme' level of judgment in some specific cases, also called a sense of the craft, which can only be aquired with a lot of experience. In very many inspection situations, judgment is essential, the outcome being determined entirely by that judgment. For example: for a piece of fabric containing a lot of elastane and presenting many defects in the weave, the arrangement of the templates must be adjusted, so that the minor problems occur in less visible areas. The inspectors should be able to judge such matters in order to make the decision to reject or accept those products. Therefore, garment manufacturers must boost inspections, both during manufacture and upon completion, in order to keep the technological process under control.[2]

This paper focuses on meeting certain objectives in establishing certain control structures for compliance of processes, by presenting a few criteria.

2. CONTENT

Specifying the control structures for the conformity of the technological processes:

The purpose of inspecting the production flow is to achieve the desired quality through the following: preventive control, monitoring, and inspection in order to eliminate the nonconformities and defects as early as possible.

Any manufacturer that wants to set up a good control and supervision system for the manufacturing process has to choose its quality control structure for compliance by organizing in a certain way, both structurally and functionally, to enable the setting up of certain procedures [3]:

a) Establishing some control and inspection points, as well as nominating the employees along the technological lines in accordance with the complexity of the products being manufactured, so there is a quick reaction to situations which may occur during the manufacture process;

b) Control procedures which pertain to:

- type of inspection (full inspection of the batch, inspection by statistical survey of the operations, product and process audit);
- specifying the control means and tools employed;

c) Control procedures, so activities related to quality assurance do not negatively impact production, but help raise quality standards and productivity. These procedures provide data regarding:

- operations whose control is mandatory;
- establishing acceptance parameters for semi-finished and finished products, depending on whether the inspection happens on the production line or at the end;
- establishing the procedure for products with defects and nonconformities;
- choosing which data will be recorded.

The procedure for choosing the quality control points in the "critical" manufacture areas.[4]

The following stages for determining the "critical" manufacture areas are:

a) Choosing the product's "critical" areas, which affect the product's appeal to customers.

Preparing the product for production with centralization operations based on data already present in the garment manufacturer's database, starting with an analysis of product components,

which requires a distinct study of the areas which mainly define quality, based on different criteria, even if at consumer level these characteristics are rarely noted, or are ignored altogether. The quality level must be assured by the manufacturer by identifying the products "critical" areas in the design stage, by analyzing the product's quality based on the following criteria: aesthetic, reliability, maintainability, psychosensorial comfort, effect on tolerance intervals, technical documentation, technical parameters of the tools and equipment.

For a pair of pants, for example, the critical areas (from an aesthetic point of view) is observed in a different manner (figure1a and 1b) based of different stages of manufacturing [5]:

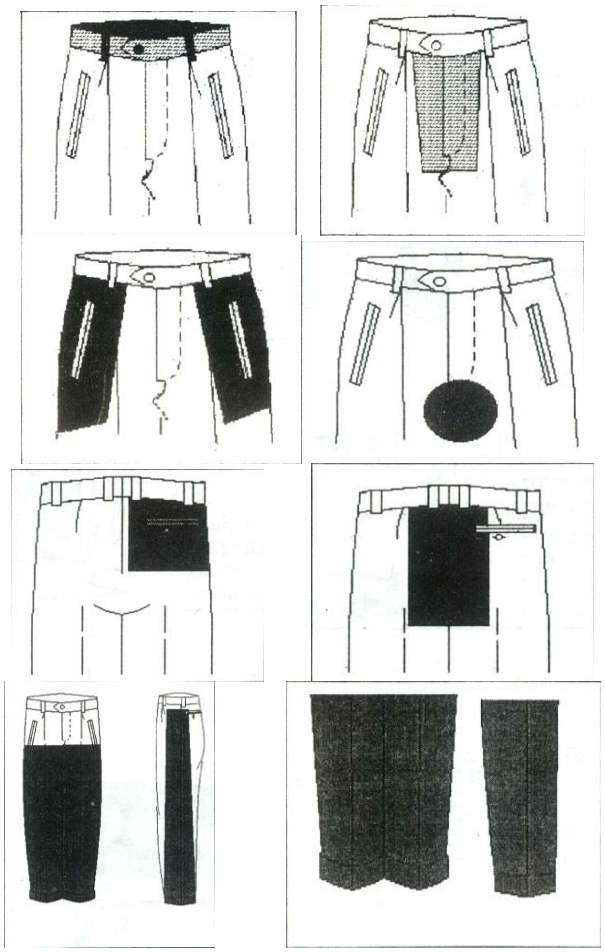

***Fig.1a**. Aesthetic implications appearing*
when working on the product details and assembling them on the pants.

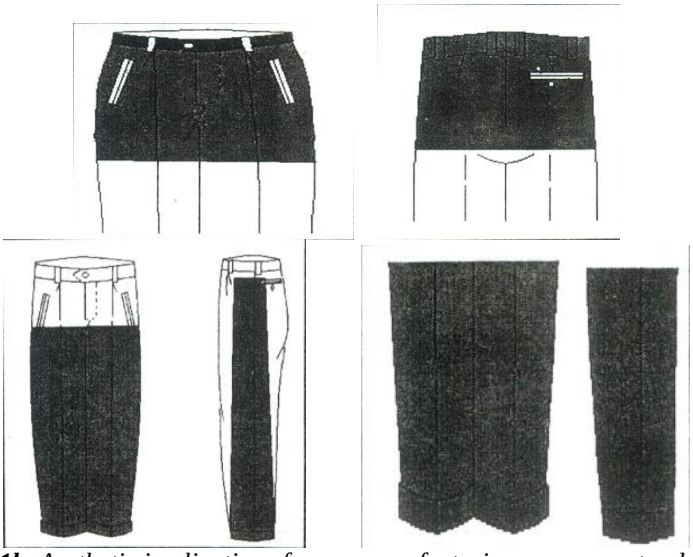

Fig.1b. *Aesthetic implications from a manufacturing accuracy standpoint*

b) Defining the "critical" areas of the technological process which must be kept under constant control.

Following the analysis of defects on the production line for the product, each quality indicator is given a weight based on the formula [6]:

$$F = \sum_{i=1}^{n} a_i / \sum_{i=1}^{n} n_i \cdot 100 \quad \textbf{(1)}$$

where:

F = defect occurrence frequency

a_i = number of products with the same defect

n_i = number of rejected products on that particular day "i"

i = 1- 5 the number of days during which the number of rejected products was observed.

Based on this study we have established priorities to reduce high percentages of rejected products, those specific operations or stages being the product's critical areas which must be prioritized to be kept under control.

Daily control points were established based on the above procedure and a relatively high quality was achieved, while also constantly eliminating as much nonconformity as possible during the manufacturing operations and stages.

The team members that will inspect the critical operations must observe each technological line, two operations with the highest rejection frequency, and a third operation with a lower rejection rate. Operations within the process are chosen as inspection points, where a few succesive components (3-4 pieces) are are verified, a few times each day.

Stock can be taken weekly, and an operation can be considered fixed when the nonconformity count (during this operation) is within accepted limits.

If there is no decrease in the number of nonconformities, the operation or critical stage will be analyzed again, in detail, and the necessary measures will be taken.

c) Creating the necessary conditions for execution and inspection, especially in the critical processing areas, which materialize by:

- control templates for certain benchmarks concerned with shape and size;

- information which can be represented in a chart, to highlight the correct path of execution and control for that particular operation. May be accompanied by possible wrong options to insure the partnership between operators and inspectors.

In the final stage, the documentation regarding remedies for the observed problems is prepared. [7]

For a pair of pants, a blueprint is presented, where we can identify the main critical areas – see figure 2.

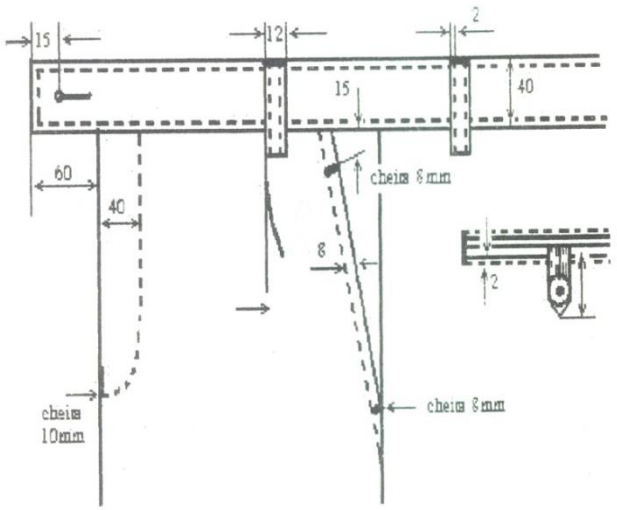

Fig.2: *Pants – critical operation – manufacturing the opening of the side pocket*

To remove subjectivity, data sheets are prepared, containing information referring to the quality of operations which form the critical areas of the product, to define the quality of said operations.

In the case of the pants, the critical operations would be the following: execution of the zipper opening, inserting the zipper, keeping belt loops symmetry, manufacture of the side and back pockets etc.

Establishing control procedures specific to garment manufacturers

Finding and fixing nonconformities requires great effort on the side of the human factor, and also high costs even when the activity is well coordinated.

To prevent and eliminate defects it is necessary to adequately size the manufacturer's quality control program and also to go through the following stages:

d) setting up an organization responsible with going into production and observing the technological process;

e) managing all control methods in accordance with standards and the tools available within the enterprise;

f) organizing activities, training the employees grouped by operations and establishing a program for entering into and observing production;

g) acquiring quality control tools and means.

5. CONCLUSIONS

Following an analysis of the quality problems occurring in the technological flow, from a manufacturing process standpoint as well as a product quality one, we suggest specific solutions for each type of product, in order to prevent and solve quality problems.

This analysis of the control plan for conformity of the technological processes will improve the results of a garment manufacturer, from a technical standpoint as well as an economical one.

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ANNALS OF THE UNIVERSITY OF ORADEA
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ENCAPSULATION OF *HYPERICUM PERFORATUM* L., JOJOBA OIL AND JASMINE OIL BY SPRAY DRYING AND THEIR APPLICATIONS IN TEXTILES

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Abstract: *Microencapsulation is a technique that allows liquid or solid agents, such as pharmaceutical agents, pesticides, insect repellent agents, dyes, cosmetics and fragrances, to be encapsulated by a suitable barrier wall. Liquid or solid agents that are encapsulated are called core material. The importance of functional finishes have been increasing rapidly in the World. Microencapsulation is an alternative way to achieve the functional finishes because of their unique properties, such as controlled release, protection against to hazardous and destructive media, and providing higher surface area. In this study, jojoba, jasmine and St. John's Wort oils, were encapsulated according to spray drying method. St. John's Wort and jojoba oils were used at 1:1 ratio as fixed oil. Jasmine essential oil was added to fixed oil mixture at two different ratios. After preparing the core mixture, encapsulation studies were performed three different core : wall ratios. Morphological analyses of microcapsules were carried out using SEM (Scanning Electron Microscope). FTIR spectroscopy spectrums of microcapsules were determined (Fourier Transform Infrared). Particle size distribution microcapsules were analyzed by laser scattering measurement method. DSC (Differential Scanning Calorimetry) thermographs of microcapsules were obtained. All microcapsules were applied to 100% cotton knitted fabrics. Strength to washing of fabrics were observed by SEM micrographs.*

Key words: *encapsulation, aromatherapy, Hypericum Perforatum L., jojoba oil, jasmine oil*

1. INTRODUCTION

Capsulation technology seems unbeatable in conferring functional properties to textile products, especially prompted controlled release. Active substances that have different properties can be encapsulated and applied to the fabric so that many functions are imparted to the fabric. “Cosmetic textiles”, has now opened up new opportunities and markets in the textile industry, especially in sport and leisure wears [1].

Essential oils assist in the protection of plants from disease, parasites and changes in climatic conditions, and are extracted from various parts of many different plants to be utilised in the food and perfumery industries and in aromatherapy [2]. Aromatherapy is a science and an art in which essential oils, derived from herbs, flowers, and other plants, are used for health, well-being, and medical treatment [3].

Hypericum perforatum L. (St. John's Wort) is a perennial herb that is commonly known as St. John’s Wort, which contains phloroglucinol derivatives (hyperforin, adhiperforin),

naftodiantrones (hypericin, pseudohypericin, protohypericin, protopseudohypericin), phenolic acids and a large number of flavonoids such as rutin and quercetin [4], [5].

Jojoba oil, which is obtained from seeds of jojoba plant, is a non-irritating and non-comedogenic product that is used as a moisturizer in many skin care products [6], [7].

Jasminum grandiflorum L. (=*Jasminum officinale* L. *var. grandiflorum* (L.) Kobuski) is widely consumed as infusion, due to its pleasant taste, and has therapeutic properties against psychiatric disorders and other illnesses [8].

In this study, we aimed to production of microcapsules with three different effects including skin care, pleasant fragrances and antibacterial effect for sports and leisure clothing and then application of that microcapsules to the textile product. For this purpose, jojoba oil was used for skin care, jasmine essential oil was used for pleasant fragrance peculiarities and St. John's Wort oil was used for antibacterial properties.

2. EXPERIMENTAL

2.1 Materials

St. John's Wort oil was kindly supplied by Mecitefendi (Turkey). Ethyl cellulose (100 cp), ethyl acetate, essential oils and other materials were purchased from Sigma-Aldrich. Scoured, bleached 100% cotton knitted fabric was kindly supplied by UNITEKS (unit weight 150 g/m^2, 21 courses/cm and 16 wales/cm). N-methylol dihydroxy ethylene urea was used as crosslinking agent (Rucon Fas, Rudolf-Duraner, Turkey)

2.2 Method

2.2.1 Preparation of Microcapsules

St. John's Wort oil and jojoba oil was used 1:1 ratio as fixed oil and core wall : essential oil ratios were given at Table 1. Microcapsules were produced by using spray drying method at the LabPlant spray-drying apparatus and the inlet temperature was 100 ^oC, exhaust temperature was 90 ^oC. Wall material : solvent ratio was selected 2%. Active ingredients were weighed at specified ratios and 250 ml solvent added. Ethyl cellulose was slowly added while the solution was mixed with a magnetic stirrer. After the ethyl cellulose had completely dissolved, the solution was fed to the spray dryer apparatus.

Table 1: *Microcapsule ratios*

Microcapsules	Oil:Wall Material Ratio			Jasmine Essential Oil:Fixed Oil Ratio	
	1:2	1:3	1:4	1:3	1:5
Y1			√		√
Y2			√	√	
Y3		√			√
Y4		√		√	
Y5	√				√
Y6	√			√	

2.2.2 Application To Textiles

Microcapsules (20 g/L) were applied to 100% cotton knitted fabrics using a 60 g/L suitable crosslinking agent (Rucon Fas-Rudolf Duraner) according to impregnating method (90% pickup). Drying and curing (3 min.) was carried out at 110 and 150 ^oC respectively.

2.2.3 Washing of Fabrics

Washing of microcapsule impregnated fabrics were performed by using Atlas Linitest apparatus according to TS EN ISO 105- C06 A1S test standart.

2.2.4 Analyses

SEM micrographs were done at FEI QUANTA 250 FEG. Before SEM analysis, the samples were covered with gold. FTIR analyses were performed at Elmer Spectrum BX device in the range of 650-4000 cm^{-1}. Resolutions were selected 4 cm^{-1}, while the number of scanning is 20. DSC results were obtained using Pyris Diamond device (Perkin Elmer). Particle size analysis studies were performed at Haribo Partica LA-950 V2 device with by laser scattering measurement method. 3% Tween 20 was used for dispersed particles uniformly in water.

3. RESULTS

3.1 Morphology of Microcapsules

SEM micrographs of morphology of microcapsules are shown in Figure 1. As can be seen in figure, some of the microcapsules have spherical shape with smooth surfaces, however some of them in the shrinked form. This result is compitable with the literature and can be attrubitued to rapid evaporation of ethyl acetate from core of the microcapsules [9].

3.2 SEM Analysis of Microcapsule Impregnated Fabrics

Figure 2 depicts microcapsules on cotton fabric. Microcapsules successfully applied to cotton fabrics. Figure 3 shows the cotton fabrics after 1 washing. Microcapsules were onto cotton fibers after 1 washing.

3.3 FTIR Analysis

Figure 4 depicts the FTIR results of jasmine oil, jojoba oil, St. John's Wort oil and microcapsules. When the FTIR analysis results are examined, the peaks were seen at 2853-2858 cm^{-1} due to asymmetrical and symmetrical stretching vibration of methylene (—CH2) group. Peaks of ester carbonyl functional group of the triglycerides were observed around 1740 cm^{-1}. A peak of bending vibrations of the CH_2 and CH_3 aliphatic groups around 1465 cm^{-1} was only observed in the case of pure oils. After encapsulation of them, that peak was disappeared. A board peak between 1000-1150 cm^{-1} was observed due to nature of cellulose (C-O-C asymmetrical stretching, C-C, C-OH, C-H ring vibrations) [10]. All characteristic peaks of oils were observed at spectrum of all microcapsules. This result indicates that all microcapsules contain active ingredients.

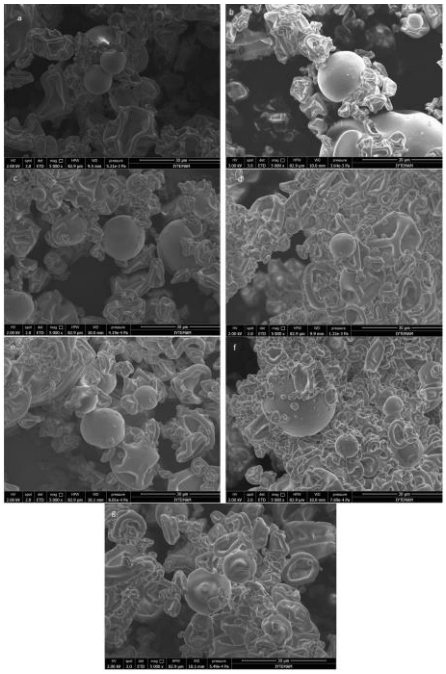

Fig. 1*: SEM Micrographs of Microcapsules* ***a.*** *Blank Microcapsules* ***b****. Y1* ***c.****Y2* ***d.*** *Y3* ***e.*** *Y4* ***f****. Y5* ***g****.Y6*

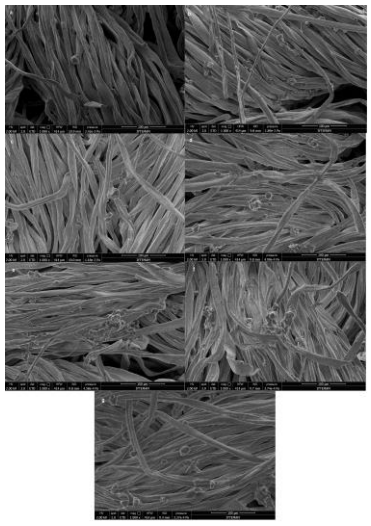

Fig. 2*: SEM Micrographs of Microcapsule Impregnated Fabrics Before Washing* ***a.*** *Blank Microcapsules* ***b****. Y1* ***c.*** *Y2* ***d.*** *Y3* ***e.*** *Y4* ***f****. Y5* ***g****. Y6*

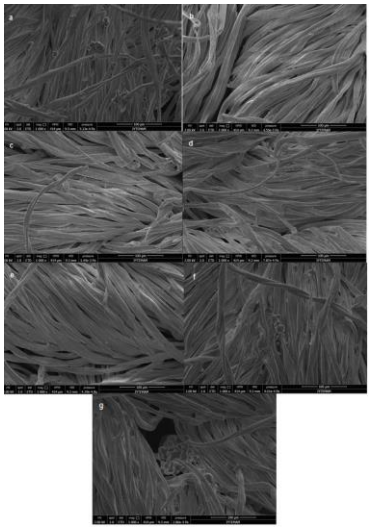

Fig. 3*: SEM Micrographs of Microcapsule Impregnated Fabrics After One Washing* ***a.*** *Blank Microcapsules* ***b****. Y1* ***c.*** *Y2* ***d.*** *Y3* ***e.*** *Y4* ***f****. Y5* ***g.*** *Y6*

3.4 DSC Analysis

Figure 5 shows DSC thermographs of microcapsules. When the DSC analysis results are examined, there is no peak of enthalpy change. It can be inferred that the capsules have completely confined the active ingredients, thus concealing the thermal behavior.

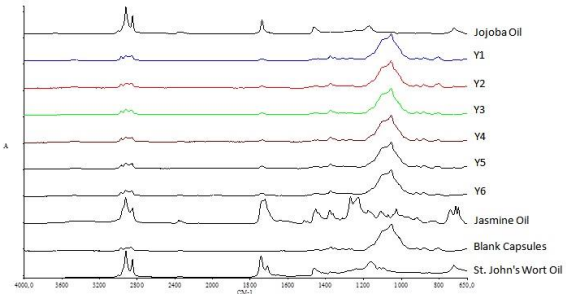

Fig. 4: *FTIR spectrums of jasmine oil, jojoba oil, St. John's Wort oil and microcapsules*

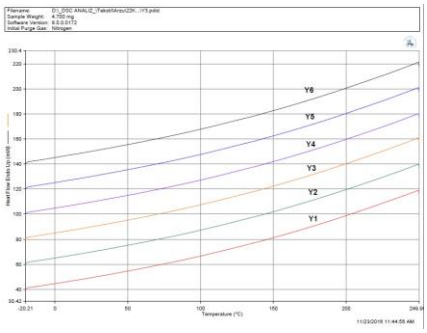

Fig. 5: *The graph results of the DSC analysis*

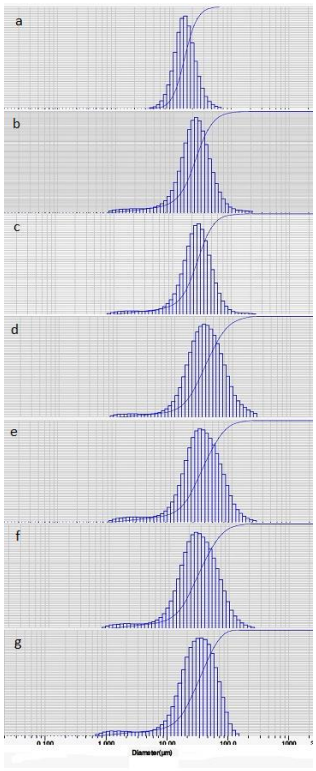

Fig. 6*: Particle Size Distribution Graphics of Microcapsules*
a. *Blank Microcapsules* ***b.*** *Y1* ***c.*** *Y2* ***d.*** *Y3* ***e.*** *Y4* ***f.*** *Y5* ***g.*** *Y6*

3.5 Particle Size Analysis

According to the particle size analysis, the mean size of blank capsules was approximatley 17 µm and the mean size of capsules containing oil mixture were between 27-43 µm (Figure 6). Thus, it can be concluded that the particle size distrubitions of microcapsules were enough for textile applications.

3. CONCLUSIONS

In this work, mixture of Jojoba oil, St. John's Wort oil and jasmine oil were microencapsulated by spray drying apparatus using ethyl cellulose. Three different core : wall ratios were applied. The results show that oil mixtures were encapsulated by ethyl cellulose and obtained microcapsules had appropirate particle sizes to apply the textiles. Obtained microcapsules were applied to the 100% cotton knitted fabrics. Further studies are antimicrobial testing, GC and HPLC analyses of applied fabrics. Washing resistance also will be investigated against to 5 and 10 washing cycles.

4. ACKNOWLEDGMENTS

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PHOTOCATALYTIC EFFECT OBTAINED ON TEXTILE BY FINISHING TECHNIQUES

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Abstract: *This study approached the experimentation of deposition by padding of commercial photocatalytic dispersion AERODISP® W 740 X with 40% solid content of TiO_2 on RIPSTOP fabric, made of 100% cotton yarns Nm 70/1 and a network of polyester filament yarns 330 dtex, both in warp and weft directions. The deposition of photocatalytic dispersions on the textile material have been realised by treatment in concomitent phase of textile support with photocatalytic dispersions and with chemical substances used in fixation of TiO_2 nanoparticles. As chemical substances used in fixation of TiO_2 nanoparticles different crosslinking agents have been used: Itobinder AG (acrylic copolymer), Itobinder U30 NEW (polycarbonate urethane polymer) and Itocoat LJ25 (urethane resin). Itocatalyst SCS and Itocatalyst A were used as catalysts. Photocatalytic activity of functionalized textile materials was evaluated by determining the photodegradation efficiency of methylene blue dye as pollutant, measuring the color difference of the irradiated samples compared with non-irradiated samples. Washing durability of the samples treated with photocatalytic dispersions was conducted qualitatively by determining the photocatalytic activity remaining on the textile fabrics after 1 washing cycle. Electron microscopy was used for viewing the distribution of TiO_2 particles on the surface of textile materials treated with the photocatalytic dispersions. Ti content existing on the surface of the textile materials was performed by energy dispersive X-ray spectroscopy.*

Key words: *photocatalytic textiles, TiO_2, photodegradation efficiency, washing durability*

1. INTRODUCTION

A very important segment of the application of TiO_2 in the textile industry is resolving the problem of binding nanoparticles to the fabric. The central problem is to assure tight binding of nanoparticles to the surface of textiles in order to increase the durability of the desired properties. The literature stated several methods used for this purpose, these are the following: methods that uses covalent linking agents, a layer by layer methods, and methods for the introduction of reactive functional groups onto textile surface [1-6]. In order to obtain textile supports with photocatalytic activity was experimented at the laboratory level the deposition on the textile materials in different variants experimental of a commercial photocatalytic dispersion.

2. EXPERIMENTAL

2.1 Materials

Deposition of photocatalytic dispersions was performed on RIPSTOP fabric, with fibre

composition of 83% cotton/17% filament polyester, made of 100% cotton yarns, Nm 70/1 and a network of polyester filament yarns 330 dtex, both in warp and weft directions. For functionalization treatment the commercial dispersion AERODISP® W 740 X with 40 wt% TiO_2 P25 nano titanium dioxide in water have beend used (Evonik Degussa Corporation). As chemical substances used in fixation process of TiO_2 nanoparticles were used different crosslinking agents, supplied from LJ Specialities (UK): Itobinder AG (acrylic copolymer), Itobinder U30 NEW (polycarbonate urethane polymer) and Itocoat LJ25 (urethane resin). Itocatalyst SCS and Itocatalyst A were used as catalysts (LJ Specialities, UK).

2.2. Preliminary preparation of textile materials

Prior to functionalization treatments the textile fabrics were subjected to preliminary preparation: enzymatic desizing, hot alkaline treatment and bleaching.

2.3. Treatment of textile materials with photocatalytic dispersions

The deposition of photocatalytic dispersions on the textile materials was realised through treatment in concomitant phase of textile support with photocatalytic dispersions and with chemical substances used in fixation process of TiO_2 nanoparticles. The treatment of textile materials with photocatalytic dispersions was performed by padding, on the laboratory padder, under the following conditions: 2 passes, 2 bar squeezing pressure. Drying and curing of textile materials was made on the drying/curing/heat-setting/vaporization**,** model TFO/S 500 mm (ROACHES, UK).

Table 1: *Codification of experimental variants*

Code	Content of treatment bath	Technological parameters
AV_1	**1.** 50 mL/L AERODISP W 740 X **2.** 20g/L Itobinder AG	**1.** Padding; **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 120 s
AV_2	**1.** 50 mL/L AERODISP W 740 X **2.** 30 g/L Itobinder U30 **3.** 1g/L Itocatalyst SCS	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
AV_3	**1.** 50 mL/L AERODISP W 740 X **2.** 20 g/L Itocoat LJ 25 **3.** 1g/L Itocatalyst A	**1.** Padding **2.** Drying: 120^{0}C, 120 s **3.** Curing: 160^{0}C, 120 s
AV4	**1.** 50 mL/L AERODISP W 740 X	**1.** Padding; **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 240 s
BV1	**1.** 12.5 mL/L AERODISP W 740 X **2.** 20g/L Itobinder AG	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
BV2	**1.** 12.5 mL/L AERODISP W 740 X **2.** 30 g/L Itobinder U30 **3.** 1g/L Itocatalyst SCS	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
BV3	**1.** 12.5 mL/L AERODISP W 740 X **2.** 20 g/L Itocoat LJ 25 **3.** 1g/L Itocatalyst A	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 160^{0}C, 120 s
BV4	**1.** 12.5 mL/L AERODISP W 740 X	**1.** Padding; **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 240 s
CV1	**1.** 5mL/L AERODISP W 740 X **2.** 20g/L Itobinder AG	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
CV2	**1.** 5mL/L AERODISP W 740 X **2.** 30 g/L Itobinder U30 **3.** 1g/L Itocatalyst SCS	**1.** Padding; **2.** Drying: 120^{0}C, 120 s **3.** Curing: 150^{0}C, 240 s
CV3	**1.** 5mL/L AERODISP W 740 X **2.** 20 g/L Itocoat LJ 25 **3.** 1g/L Itocatalyst A	**1.** Padding; **2.** Drying 120^{0}C, 120 s **3.** Curing: 160^{0}C, 120 s
CV4	**1.** 5mL/L AERODISP W 740 X	**1.** Padding: **2.** Drying: 120^{0}C, 120 s; **3.** Curing: 150^{0}C, 240 s

The samples codification, technological parameters and the composition of treatment baths are found in the Table 1.

2.4. Methods

2.4.1. Evaluation of photocatalytic activity of functionalizaed textile materials

Photocatalytic activity of textile fabrics treated with synthesized dispersions was evaluated by determining the photodegradation efficiency of methylene blue dye (MB) used as aqueous solution of 0.008 g/L. Textile materials treated with each type of photocatalytic dispersion were immersed for 5 minutes in MB solution. Subsequently, the samples have been subjected to UV irradiation for 6 hours using the "dark room" type CN 15 LC (Vilber Lourmat, France). Incorporated lamps (2 x 15 W) were the sources of ultraviolet radiations and emitted radiation of λ_{max} (emission) = 365 nm and respectively 254 nm. Evaluation of the photocatalytic activity was performed by measuring the color difference of the irradiated samples compared with non-irradiated samples (reference). Color measurements were performed according to ISO 105 J03:2001, using the Spectroflash 650 spectrophotometer (Datacolor, Switzerland) and the light source was the illuminant D65/10. Values obtained for chromatic parameters and color difference are the average of 5 individual measurements carried out on the treated samples with photocatalytic dispersions and on the standard samples considered, treated only with photocatalytic activity (AV_4, BV_4, CV_4).

2.4.2. Durability to washing

The washing durability of the samples treated with photocatalytic dispersions was determined only for the samples which show the significant photocatalytic effects. The samples treated with photocatalytic dispersions have undergone a washing cycle using REDKROME equipment (Ugolini-Italia) under the following conditions: 2g/L detergent containing no phosphate and bleaching agent, at a temperature of 40^0C for 30 minutes. Samples were subsequently rinsed and freely dried horizontally. The washed and unwashed samples were immersed for 5 minutes in a solution of methylene blue (0.008 g/L) and then exposed for 6 hours to UV irradiation (λ_{max}=365 nm). Evaluation of treatment durability to washing was conducted qualitatively by determining the photocatalytic activity remaining on the textile fabrics after washing, by spectrophotometric measurement of color difference between the washed-irradiated sample and the washed-non-irradiated sample.

2.4.3. Electron microscopy

Vizualization of distribution of TiO_2 particles on the surface of textile materials was conducted using Quanta 200 (FEI, Netherlands) electron microscope with X-EDS module integrated.

2.4.4. Energy-dispersive X-ray spectroscopy

Highlighting the Ti content existing on the surface of the textile materials treated with the photocatalytic dispersions was performed by energy dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSIONS

3.1. Evaluation of photocatalytic activity of the functionalized textile materials

Color difference parameters were determined considering as reference the non-irradiated samples treated with photocatalytic dispersions, their values being given in Table 2. Analyzing the values of the colour difference parameter measured for the treated samples with commericals

photocatalytic dispersions is found that photocatalytic activity diminushes gradually way with the decreasing of TiO_2 content from treatment bath, the smallest values for the difference of lightness (DL*) obtaining for the samples of C batch, with a content of 5 mL/L AERODISP W 740 X. The textile materials treated with photocatalytic dispersions, without addition of crosslinking agents (AV_4, BV_4 and respectivly CV_4 samples) presents photocatalytic efficiency, the values obtained for DL* having positive values higher with 8 absolute units (AV_4, λ = 365 nm), 5 absolute units (BV_4, λ = 365 nm) and respectivly 3 absolute units (CV_4, λ = 254 nm) in comparison with the sample of non-irradiated refference. The addition in the treatment bath of binders diminishes in lesser or bigger way the photocatalytic efficiency of treated samples with photocatalytic dispersion, the biggest reduction of the photocatalytic activity obtaining in the case of sample with high content of photocatalytic dispersion (50 g/L AERODISP W 740 X) and the binder based on acrylic copolymer (sample AV_1), the smallest reduction being observed in the case of sample which containing binder based on polycarbonate urethane (sample AV_2). In the case of samples treated with a low content of photocatalytic dispersion (5 g/L AERODISP W 740 X (Code C) the reduction effect of photocatalytic efficiency in the presence of the binders is not observed.

Table 2: *Color difference parameter values obtained for samples treated with photocatalytic dispersions*

Sample code	Irradiation	Colour difference parameters			
		DL*	DC*	DH*	DE*
AV_1	365 nm	4.66	-11.06	-1.56	12.11
	254 nm	4.28	-9.23	-1.71	10.32
AV_2	365 nm	6.17	-14.42	-1.52	15.76
	254 nm	5.20	-11.10	-1.70	12.38
AV_3	365 nm	5.66	-12.08	-1.40	13.41
	254 nm	5.23	-9.91	-1.42	11.29
AV_4	365 nm	8.51	-18.20	-2.78	20.29
	254 nm	3.71	-8.13	-0.51	8.95
BV_1	365 nm	4.00	-10.75	-0.74	11.49
	254 nm	3.20	-8.93	-1.04	9.54
BV_2	365 nm	3.49	-10.84	-0.01	11.39
	254 nm	5.41	-13.21	-1.36	14.34
BV_3	365 nm	3.60	-9.86	-0.30	10.50
	254 nm	2.87	-8.79	-0.75	9.27
BV_4	365 nm	5.41	-12.03	-1.34	13.25
	254 nm	4.14	-8.09	-1.87	9.27
CV_1	365 nm	4.51	-12.18	-0.50	12.99
	254 nm	4.18	-10.04	-1.35	10.96
CV_2	365 nm	2.07	-6.96	0.52	7.27
	254 nm	3.30	-9.20	-0.83	9.81
CV_3	365 nm	0.95	-6.09	0.41	6.18
	254 nm	3.65	-9.10	-1.28	9.89
CV_4	365 nm	0.34	-3.91	1.07	4.07
	254 nm	3.85	-9.02	-1.15	9.88

3.2. Washing durability

The washing durability of the samples treated with photocatalytic dispersions was determined by assessing the photocatalytic effect after 1 washing cycle by color measurement the results being shown in Table 3.

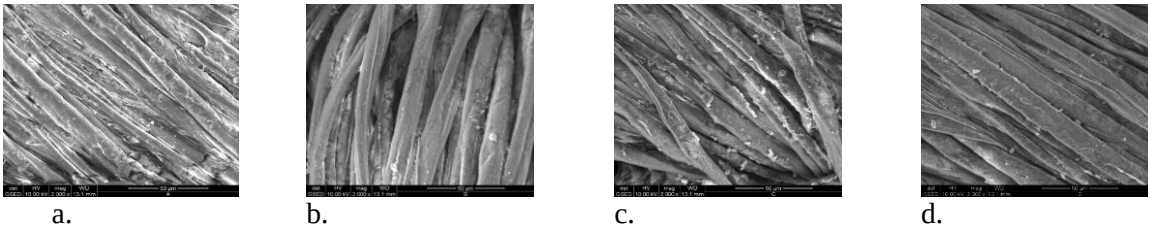
Table 3: *Color difference parameter values obtained for samples treated with photocatalytic dispersions*

Sample code	Colour difference parameters			
	Unwashed samples		Washed samples	
	DL*	DE*	DL*	DE*
AV_1	4.66	12.11	3.46	11.44
AV_2	6.17	15.76	5.59	14.74
AV_3	5.66	13.41	3.95	10.85
AV_4	8.51	20.29	4.59	12.77

From the analyzed batch is distinguished the treatment performed in concomitant phase with AERODISP W 740 X commercial dispersion and with the binder based on urethane polycarbonate (ITOBINDER U30 NEW), followed by the binder based on acrylic copolymer (ITOBINDER AG), the last from the batch in terms of fixation degree being the binder based on crosslinking urethane resin (ITOCOAT LJ25). The standard sample of the (code AV4) batch, realized without fixation binder, confirms the contribution to the chemical substances to the fixation of TiO_2 nanoparticles on the textile material, in this case the reduction of DL* between the unwashed and the washed sample being bigger, respectively a reduction with 4 units in absolte value, comparative with the realized samples in the presence of binders, for which the reduction of DL* value between the washed and unwashed sample is included between 1-2 absolute units.

3.3. Electron microscopy

Electronic images obtained at a magnification of x 2000 for textile materials treated with photocatalytic dispersions are shown in Figure 1.



a. b. c. d.

Fig. 1: *Electronic images recorded at a magnification X 2000 obtained for: a. –AV_1, b. – AV_2, c. –AV_3, d. – AV_4*

The electron microscopy has allowed only the evaluation of the grade distribution of TiO_2 particles on the fibers surface from the component of textile materials. Electronic images recorded for textile materials treated with TiO_2 based dispersions reveal that they are covered with a relatively uniform layer of particles, which are less agglomerated, of different shapes and sizes.

3.4. Energy-dispersive X-ray spectroscopy - EDX

Cuantification of the Ti content existing on the surface of textile materials treated with synthesized photocatalytic dispersions is shown in Table 4. In the case of textile materials treated with photocatalytic dispersion AERODISP W 740 X according to variant I (A batch) the bigger quantity of Ti was found for the sample which was considered standard for this batch, without addition of binders (code AV_4), correlating with the most pronounced photocatalytic effect found to this sample. The smallest content of Ti was found at the treated sample with acrylic copolymer ITOBINDER AG, for which were measured the smallest photocatalytic efficiency, materialized into the smallest value for DL* parameter.

Table 4: *Ti content existing on the surface of textile materials treated with photocatalytic dispersions*

Variant code	Ti content	
	Wt (%)	At (%)
AV_1	14.09	4.56
AV_2	26.19	9.36
AV_3	26.64	9.57
AV_4	27.05	9.82

5. CONCLUSIONS

Textile materials treated with AERODISP W 740 X dispersion in different experimental variants showed photocatalytic efficiency, this decrease's gradually with the diminution of the TiO_2 content from the liquor bath. The addition in the treatment bath of the chemical substances used in fixation of TiO_2 nanoparticles diminushes lesser or greater the photocatalytic efficiency of the treated samples with the photocatalytic dispersion, the biggest diminution of the photocatalytic effect obtaining in the case of variant with high content of photocatalytic dispersion (50 g/L AERODISP W 740 X) and the binder based on acrylic copolymer (sample AV_1). Electron microscopy revealed the presence of microparticles deposited on the surface of the textile material, in a relatively uniform layer of particles, which are less agglomerated, of different shapes and sizes. Samples treated with dispersions show a Ti content ranging between 14.09- 27.05%, the highest quantity of Ti being obtained for samples treated with the biggest content of TiO_2 without adding of binders (AV_4).

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ANNALS OF THE UNIVERSITY OF ORADEA
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MATHEMATICAL MODELLING OF THE SHIELDING EFFECTIVENESS FOR PES/STAINLESS STEEL FABRICS

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Abstract: *Textile screens for electromagnetic radiation represent a modern solution, due to their flexibility, lightweight and good mechanical resistance. Electromagnetic shielding is a must in various applications, while strict regulations are set for electromagnetic compatibility. Conductive fabrics are widely used for electronic equipment covers, RF suits or EMI protection tents. This paper aims to investigate the shielding effectiveness of conductive woven fabrics with stainless steel yarns at different weft distances [2,3,4,5 mm]. These conductive fabrics were investigated for their physical-mechanical properties (mass per surface unit, density on warp and weft direction and thickness), within the INCDTP accredited laboratories. The conductive fabrics as well as combinations thereof where tested for their shielding effectiveness accordingly to the standard ASTM ES 07, within the EMC laboratories of ICPE-CA. A signal generator, an amplifier, a TEM Cell and a spectrum analyser were used were used for this purpose. Graphs in logarithmic scale were issued for the shielding effectiveness analysis. Moreover, an experimental factorial plan was conceived for obtaining a mathematical model for the studied fabrics in relation to the weft distance between the conductive yarns. The coefficients of the mathematical model were obtained through the least squares regression method in Excel, while the response curve was designed in Matlab. The response curve enables the computation of intermediate values of the shielding effectiveness in relation to the distance between conductive yarns.*

Key words: *Electromagnetic compatibility (EMC), fabrics, conductive, shielding effectiveness, physical-mechanical properties, mathematical modelling*

1. INTRODUCTION

The shielding of electromagnetic radiation is an important issue in nowadays environment. Several research studies have been conducted in the domain of modelling conductive fabrics for electromagnetic shielding. The model of equivalent circuits of recurrent structures makes possible the determination of the equivalent impedance for a grid conductive fabric [1]. The inductive and capacitive character result in a RLC equivalent structure of the conductive fabric, whose electrical parameters were computed by mathematical regression, based on physical measurements values. The resulting RLC model has good values when compared to the physical measurements. The modelling of the electrical conductivity was studied for yarns [2], analysing the dependence of the electrical resistance R on the yarn length l. The methods for evaluating the shielding effectiveness of textile fabrics have been extensively studied [3]. The standards MIL-STD 285 and ASTM 4935 using an antenna-receiver system and respectively a TEM-cell were assessed in the testing of conductive

fabrics. A new method for testing the shielding effectiveness of PES-metal textile materials, doubled by a related simulation process, proved the justness of this testing method [4]. The testing method proposes a measurement device composed of transmitting antenna, textile material, waveguide, receiving antenna and carbon foam for insulation. Research studies in the field tackle the accomplishment of personal protection equipment (PPE) for protection against EM radiation [5]. The reflection and transmission coefficients of fabrics destined for PPE, were measured in relation to the frequency of electromagnetic radiation: the higher the content of conductive material, the higher the shielding effectiveness.

This paper aims to analyse different samples of conductive woven fabrics with stainless steel yarns. The samples have been especially produced for the study with different distances between the weft conductive yarns. The goal of the approach was to perform an optimization computation for identifying the adequate distance for the optimal shielding effectiveness of the fabrics.

2. MATERIALS AND METHODS

2.1 Materials

Four variants of woven fabrics were produced at the textile enterprise SC Majutex SA – Iasi. The woven fabrics are composed of PES and stainless steel yarns (Beckaert Bekinox BK) with the yarn count Nm50/2. The Bekinox BK yarn is a blended yarn with 80% cotton content and 20% Bekinox VS fibre (from 100% stainless steel). The woven fabrics were produced on a SOMET rapier weaving machine with the width of 1,90 m (Fig. 1). The woven fabrics have a twill weave. The four variants produced are presented in Table 1:

Table 1: *The four variants of the woven fabrics with relation to the sequence of the yarns*

	Variant 1	Variant 2	Variant 3	Variant 4
Weft Sequence PES / Bekinox BK	**1/1**	**2/1**	**3/1**	**4/1**

Fig. 1: *Rapier loom at SC Majutex SA – Iasi for weaving the fabrics*

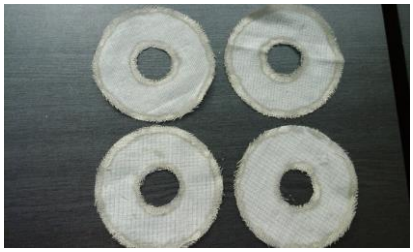

Fig. 2: *The fabric variants tailored accordingly to the standard ASTM ES07*

2.2 Methods

The physical-mechanical and electrical properties of the woven fabrics were investigated in INCDTP and ICPE-CA laboratories, accordingly to up-to-date standards. The data obtained for the physical-mechanical properties is presented in Table 2.

Table 2: *Physical-mechanical properties of the conductive fabric variants*

Physical-mechanical properties	Mass on surface unit [g/m^2]	Density [no yarns/10cm]		Fabric thickness [mm]
		Warp	Weft	
Standard	EN 12127:1999	SR EN 1049:2:2000		SR EN ISO 5084/2001
Variant 1	114	130	120	0,47

Variant 2	114	136	120	0,47
Variant 3	114	134	120	0,469
Variant 4	115	130	120	0,479

The standard ASTM ES07 was used for measuring the shielding effectiveness. A signal generator, an amplifier, a TEM Cell and a spectrum analyser were used were connected and the woven fabric variants were placed individually and in combinations within the TEM cell (Fig. 3).

Fig. 3: *Electrical device system for measuring the shielding effectiveness*

The experimental factorial plans were chosen for the mathematical modelling of the shielding effectiveness. The distance on vertical / horizontal direction between the stainless steel conductive yarns was set as input, independent factor and the shielding effectiveness was chosen as result, dependent factor. A mathematical polynomial model second degree was chosen [6]:

$$z_1 = a_0 + a_1*x + a_2*y + a_{12}*x* + a_{11}*x\text{^}2 + a_{22}*y\text{^}2 \quad \textbf{(1)}$$

where:
x = distance on vertical direction [mm]
y = distance on horizontal direction [mm]
z_1 = shielding effectiveness [dB]

3. RESULTS

The results of the shielding effectiveness measured accordingly to the standard ASTM ES 07 are presented in table 3.

Table 3: *Experimental results for shielding effectiveness*

No.	Screen structure	Shielding effectiveness Standard ASTM ES 07 (dB)							
		1 MHz	10 MHz	30 MHz	100 MHz	300 MHz	600 MHz	900 MHz	1 GHz
1	Variant 1.1	11.99	9.78	14.40	19.00	14.92	12.44	9.05	4.50
2	Variant 2.1	10.19	8.28	13.15	16.84	13.60	11.84	8.56	4.20
3	Variant 3.1	10.36	7.87	11.65	15.00	11.99	11.10	8.42	4.40
4	Variant 4.1	9.60	7.10	10.87	13.95	10.93	11.16	8.64	4.50
5	Variant 1.2	11.57	9.70	14.78	18.95	15.95	13.02	9.44	4.70
6	Variant 2.2	12.15	9.48	14.06	18.50	13.37	12.00	8.68	4.20
7	Variant 3.2	8.98	7.15	11.42	15.33	13.44	12.30	9.06	4.50
8	Variant 4.2	10.78	8.32	12.09	15.32	11.34	11.18	8.48	4.30
9	Variant 1 with	15.00	11.67	16.95	23.20	22.30	25.70	21.07	16.50

	Variant 1								
10	Variant 1 with Variant 2	14.66	11.96	17.40	22.10	20.70	24.00	20.40	15.33
11	Variant 1 with Variant 3	12.40	10.63	16.07	21.56	20.30	22.41	17.98	12.79
12	Variant 1 with Variant 4	13.28	10.79	15.66	20.85	19.30	22.60	20.18	15.53
13	Variant 2 with Variant 2	13.00	10.67	15.40	21.50	19.92	22.80	19.51	15.03
14	Variant 2 with Variant 3	13.15	10.52	15.63	20.90	18.82	22.22	19.62	14.96
15	Variant 2 with Variant 4	12.82	10.60	15.70	20.38	17.53	21.55	19.90	15.45
16	Variant 3 with Variant 3	12.79	9.80	14.42	19.15	17.60	21.10	18.58	13.87
17	Variant 3 with Variant 4	11.88	9.93	14.62	18.60	14.82	20.85	18.89	14.35
18	Variant 4 with Variant 4	12.66	9.94	14.36	17.70	15.35	19.44	18.65	14.53

4. DISCUSSION

4.1. Figures

The obtained results for the shielding effectiveness in dB were represented in a graph with logarithmic scale for the frequency (Fig. 4). The analysed frequency range was [1Mhz – 1 Ghz]. The four fabric variants were represented with different colours. Px corresponds to Variant x.

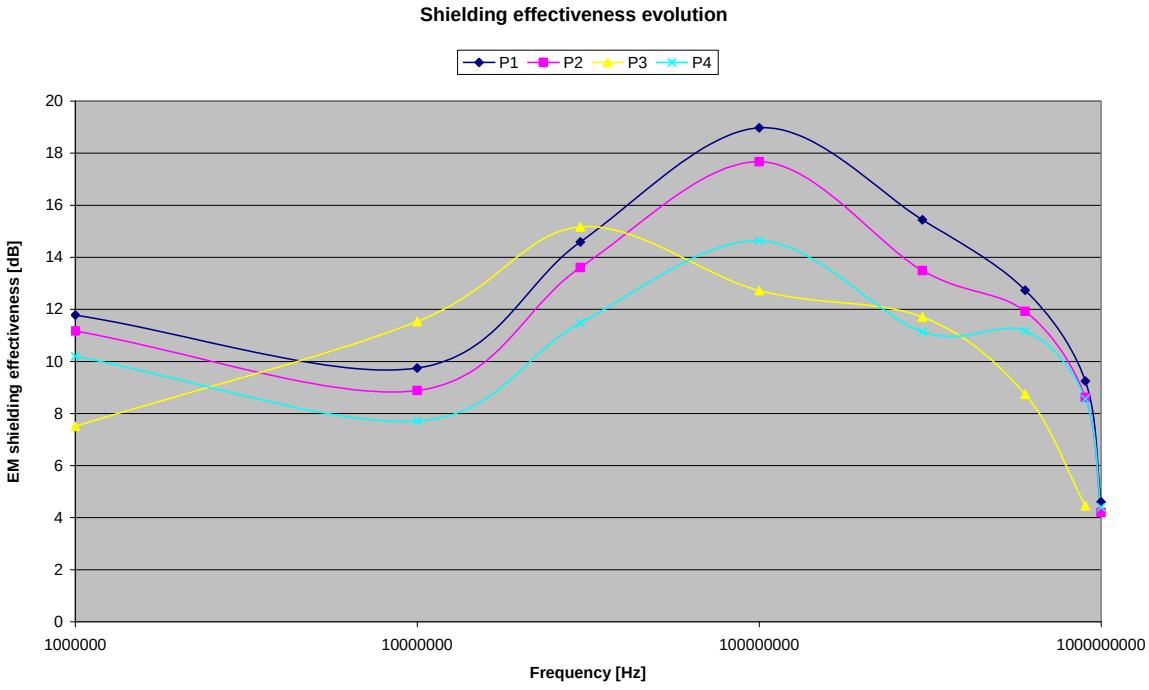

Fig. 4: *Shielding effectiveness in dB of the four fabric variants on logarithmic frequency scale*

4.2. Mathematical modelling

In order to analyse the evolution of the shielding effectiveness also for other, intermediate values of the distance between the conductive yarns, a mathematical modelling was proposed, accordingly to the factorial plans.

Table 4: Variation levels at 10 MHz

Variable	***X* [mm] – distance between conductive yarns horizontal direction**	***Y* [mm] – distance between conductive yarns vertical direction**	**Z – Shielding effectiveness [dB]**
Level			
Superior level +1	4 (P3)	4 (P3)	12.79
Basis level 0	3 (P2)	3 (P2)	13.00
Inferior level -1	2 (P1)	2 (P1)	15.00
Variation range Δ	1	1	

The mathematical modelling is going to be performed by means of an experimental matrix with three levels of variation (table 5). It follows a factorial plan of the type 3^2. The variables in Table 5 were encoded with the formula (2).

$$x = \frac{X_1 - X_m}{\Delta X} \quad \textbf{(2)}$$

Table 5: *The experimental matrix with three levels of variation*

	x	y	xy	x^2	y^2	z_1
a_0	a_1	a_2	a_{12}	a_{11}	a_{22}	
1	1	1	1	1	1	12.79
1	1	0	0	1	0	13.15
1	1	-1	-1	1	1	12.40
1	0	1	0	0	1	13.15
1	0	0	0	0	0	13.00
1	0	-1	0	0	1	14.66
1	-1	1	-1	1	1	12.40
1	-1	0	0	1	0	14.66
1	-1	-1	1	1	1	15.00

The proposed mathematical model has a polynomic form second degree (1). The computation of the coefficients by regression with the least squares method was performed in Excel, yielding the following results (Table 6):

Table 6 The coefficients of the polynomic form second degree

a_0	a_1	a_2	a_{12}	a_{11}	a_{22}
13.74	-0.62	-0.62	0.74	-0.2	-0.2

The expression of the function results in:

$z_1 = 13.74\text{-}0.62x\text{-}0.62y\text{+}0.74xy\text{-}0.2x\text{^}2\text{-}0.2y\text{^}2$ **(3)**

By decoding the variables, the following expression is obtained for the shielding effectiveness (4).

$$Z = 20.58 - 1.64X - 1.64Y + 0.74XY - 0.2X^2 - 0.2Y^2 \quad \textbf{(4)}$$

The response curve was performed in Matlab (Fig. 5).

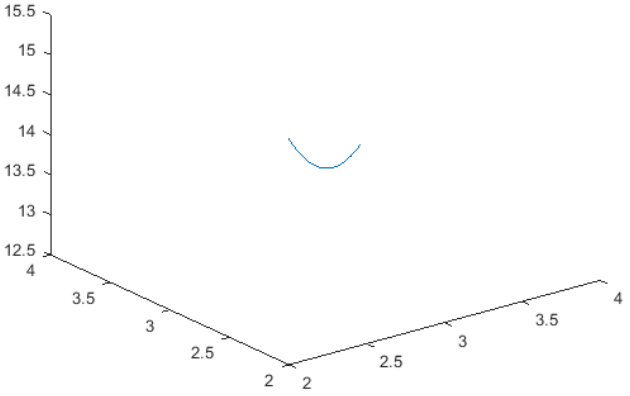

Fig. 5: *The response curve for the shielding effectiveness in relation to the distance between conductive yarns*

The response curve indicates a minimum point for the vertical / horizontal distances (X; Y) = (4.82; 4.82). For lower values of the distances the shielding effectiveness increases. This graphics shows the evolution of the shielding effectiveness for intermediate values of the distance between the conductive yarns of the shielding fabrics.

5. CONCLUSIONS

The electromagnetic shielding by means of textile materials is of great importance in the nowadays EM radiation polluted environment. Textile fabrics with conductive yarns represent a valuable alternative to usual EM screens, due to their flexibility. This paper approached a mathematical modelling of the shielding effectiveness produced by woven fabrics with different distances between the conductive stainless steel yarns. The obtained model achieves intermediate values and indicates an evolution of the shielding effectiveness.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PRODUCTION OF ESSENTIAL ORANGE OIL MICROCAPSULES: COMPARISON OF THE USE OF SURFACTANTS CETILTRIMETILAMONOUS BROMIDE AND POLYSORBATE 20 BY ELECTRONIC SCAN MICROSCOPY

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Abstract: *Commercial applications of microcapsules began to appear in the textile industry in the late 1990s increasing investments in research to develop functional tissues, with a special focus on value aggregation, coating them with various active substances for the development of innovative products and according to fashion. Microcapsules have been presented as an alternative with regard to the encapsulation of essential oils since it is one of the most effective methods to achieve the goal of controlled release. The orange essential oil has biocidal properties and has been used microencapsulated as an ecological botanical insecticide. The characteristics of microcapsules containing aromatic oils, such as morphology and particle size distribution, depend on the preparation conditions such as the type of emulsifier used and the viscosity of the core material. Thus, for the microcapsules to be effectively used for the development of innovative products in the textile industry, studies on their formulation and characterization are necessary. This article proposes to compare the use of cetyltrimethylammonium bromide and polysorbate surfactants by means of their morphology, by scanning electron microscopy analysis on the formulation of microcapsules whit melamine formaldehyde shell with core of orange essential oil (citrus sinensis) combined with a non-volatile oil Medium Chain Triglycerides produced by interfacial polymerization method. At the end, the microcapsules were analyzed by microcoscopies and the differences in microcapsule morphologies were observed according to the kind of surfactant used.*

Key words: *Microcapsules. Essential Orange Oil. Electronic Scan Microscopy. Textile.*

1. INTRODUCTION

In the textile industry, commercial applications of microcapsules began to appear in the 1990s, more specifically in 1999, with the launch of the first fabric with microcapsules applied onto textile fibers [1]. This has contributed to a significant increase in investment in research to develop functional fabrics, developing textile materials with specific properties, adding value to the products by coating them with active substances, resulting in innovative and fashionable products [1] [2] [3] [4]. Also, worth mentioning are studies on the controlled release of fragrances for the development

of textile products with long lasting fragrances, which is seen as a challenge for industries that use perfumes in their products, due to the great attraction of consumers [4] 5] [6] [7] [8]. Through microencapsulation it is possible to encapsulate a wide range of substances that impart different properties related to the nature of the product [4] [7], thus being able to combine core and shell materials, also giving visual, tactile and olfactory characteristics, but specifically in the sector Of textile finishes with fragrances has been an important commercial target and a challenge [3]. Therefore, the use of microcapsules has been presented as an alternative to achieve satisfactory results with regard to encapsulation of fragrances and active substances such as biocidal agents [2] [3] [9] [10] [11] [11] 12].

Orange essential oils have been used for medicinal purposes since the fourth century [13] [14]. The biocidal properties of citrus essential oils are well known and historically [11] [13] [14], as for example, antifungal [15] [16] and insecticides [16]. The orange essential oil (citrus sinensis) is a citric oil, and like all others of this nature, contains an extremely wide variety of compounds, being able to vary between 20 and 60, composed mainly of monoterpenes (limonene: 32-98%), , Sesquiterpene hydrocarbons, oxygen derivatives thereof, as well as aliphatic aldehydes, alcohols and esters [14] [18]. The antifungal capacity has been attributed mainly to the presence of limonene, linalool or citral [18]. As for insecticide properties, studies have shown that orange essential oil has its proven and proven insecticidal activities and is recognized as safe by the United States Food and Drug Administration (FDA) [17]. The orange essential oil also has strong activity against some insects and its components may be potential candidates for new botanic insecticides [17], because the oil, when microencapsulated can aid in the application, being an economically feasible, fast and effective method, besides leaving minimal residues [19]. Another advantage of the use of orange oil is that the crop of the genus Citrus, of which orange is a part, is the largest in the world (100 million cubic tons per year), oranges account for 60% of the total product volume [15]. After processing the oranges, approximately 45% are available as a sub-product and can create environmental problems, especially water pollution due to the presence of biomaterials such as essential oil, pectin and sugars [15]. In this case the use of the essential oil represents a decrease in the disposal of this material.

The use of microcapsules has been presented as an alternative with respect to the encapsulation of essential oils and other active substances. Using this microencapsulation technology, it is one of the most effective methods to achieve the goal of controlled release [5] [20]. To solve restrictions on the material to be encapsulated, the microencapsulation of aromatic oils plays important roles, for example: it captures the fragrance in its original form with minimal alteration and maximum retention; protects the fragrance from interaction with an uncontrolled environment and from premature release during storage; and completely releases the fragrance, when desired [1].

Therefore, special attention should be paid to the shell that envolve the core material, as this is the material that is susceptible to the outside and may increase the stability of the microcapsule. Preparing microcapsules of melamine formaldehyde (MF) resin for the aromatic oil shell material increases the durability of the perfume [8], in addition, the cured MF resin is non-toxic and can be used in both wet and dry environments [6]. Thus, MF resin has been extensively studied and applied in the elaboration of functional products, such as microcapsules containing essential oils, and due to its excellent performance, its fields of application are being expanded [6].

For the microemcapsulation of aromatic oils are used the chemical methods, among them, the interfacial polymerization [1] [6] [8] [21]. In interfacial polymerization many types of polymerization reactions can be induced to occur in interfaces resulting in microcapsules [8]. It is a widely used method that allows the manufacture of microcapsules from two immiscible liquids (oil / water emulsion) by forming thick polymer walls around liquid droplets [21].

The preparation conditions such as the type of emulsifier used and the viscosity of the core material directly influence the characteristics of the microcapsules containing aromatic oils such as morphology and particle size distribution [22], therefore, it is important to analyze the morphologies of the microcapsules. In this case, we can use the Scanning Electron Microscope (SEM), one of the most versatile instruments available for the observation and analysis of the microstructural characteristics of solid materials [23]. Among the main advantages of the SEM are to allow increases of 300.000 times or more, keeping the depth of field compatible with the observation of rough surface and provide information quickly on morphology [23]. Another advantage is the ease with which a particular region of interest in the sample can be chosen and located at low magnification [24]. Therefore, SEM is one of the most versatile instruments available for the observation and analysis of micro-structural characteristics of solid objects, this is mainly due to the high resolution that can be obtained when the samples are observed [23]. One of the most important characteristics of the SEM is the three-dimensional appearance given to the images of the samples, only possible because of their large depth of field, and the possibility of doing the small exam with a great depth of focus [23]. This ability to confer a three-dimensional appearance and the possibility of obtaining small increases with great depth of focus, which facilitates the morphological analysis of the microcapsules.
Thus, for the microcapsules to be effectively used for the development of innovative, functional and sensorial products in the textile industry, studies on its formulation and characterization are necessary, so this article proposes to compare the use of cetyltrimethylammonium bromide surfactants (CTAB) and polysorbate 20 (Tween 20) by means of its morphology, performed by scanning electron microscopy (SEM) analysis in the formulation of melamine formaldehyde (MF) shell microcapsules with orange essential oil nucleus (citrus sinensis) combined with a fixed oil medium-chain triglycerides (MCT) produced by interfacial polymerization method.

2. MATERIALS AND METHODS

Materials: Essential orange oil (*citrus sinensis*), surfactants CTAB and Tween 20, all was purchased from Sigma-Aldrich®.; MF; MCT was purchased from Delaware®. Preparation of microcapsules: Microcapsules containing essential orange oil combined with a MCT (1:1) and surfactants Tween 20 and CTAB with MF resin as shell material were synthesized by interfacial polymerization technology. To characterization of microcapsules: SEM FEI model Phenom (Fei, Oregon, USA).

The microcapsules were obtained by the interfacial polymerization method. To prepare the emulsion was placed in a beaker, deionized water with surfactant. The mixture was stirred on a mechanical stirrer (Fisatron 713D), after stirring the essential oil was added and brought to the ultrasound (Cole Parmer model CV33). The pH was adjusted to 4.5 using a solution of acetic acid. The emulsion was reserved. The prepolymer was prepared in another beaker containing deionized water and formaldehyde, after using a magnetic stirrer (TE-085) at a temperature of 70 ° C, while maintaining gentle agitation was added the melamine. The pH was adjusted to 8.5. The prepolymer was reserved.

For the preparation of the microcapsules the jacketed beaker containing the emulsion was connected to the thermostatic bath with a temperature of 70 ° C. This emulsion was subjected to a mechanical stirrer. During this stirring the prepolymer was slowly added to the emulsion. After addition of the prepolymer the mechanical stirrer timer was adjusted, also adjusting the pH to 9.0. After of shaking, the solution was placed in a centrifuge (Quimis, Tubes Centrifuge) at its maximum speed for phase separation. The microcapsules were filtered and washed with deionized water. After the microcapsules were taken to the desiccator (ARSEC). The obtained method was tested with

different surfactants, CTAB and Tween 20 in proportion (1:1) with essential oil. At the end of the production, the microcapsules were analyzed by microcoscopies and the differences in microcapsule morphologies were observed according to the kind of surfactant used.

3. RESULTS AND DISCUSSION

The conditions of preparation of the microcapsules, more specifically, the use of the two surfactants (CTAB and Tween 20) directly influenced the characteristics, according to the images obtained by SEM. In Figure 1, SEM images of the orange essential oil microcapsules with CTAB surfactant are ob- served. It is observed that the CTAB surfactant interacted well with the core material (orange essential oil), forming microcapsules of regular morphology, according to Figure A(C), that is, the formation of regular capsules, in addition, are evenly distributed in the sample, according to Figures 1(A) and 1 (B), indicating a satisfactory formation. In Figure 2, in SEM images of the orange essential oil microcapsules with the change of surfactant to Tween 20 and the same formulation of the previous production, it is observed that the surfactant Tween 20, unlike CTAB, did not interact well with the orange essential oil, forming irregular microcapsules, according to Figure 2(B), in addition, the microcapsules formed, according to Figure 2(C), present some pores, according to Figure 2(C), that can come from formation of foam in the emulsion. Unlike the previous sample, Figure 1, the microcapsules produced with Tween 20 surfactant, as in Figure 2(A), are not uniformly distributed in the sample, in addition to the formation of agglomerates of microcapsules, indicating an unsatisfactory formation.

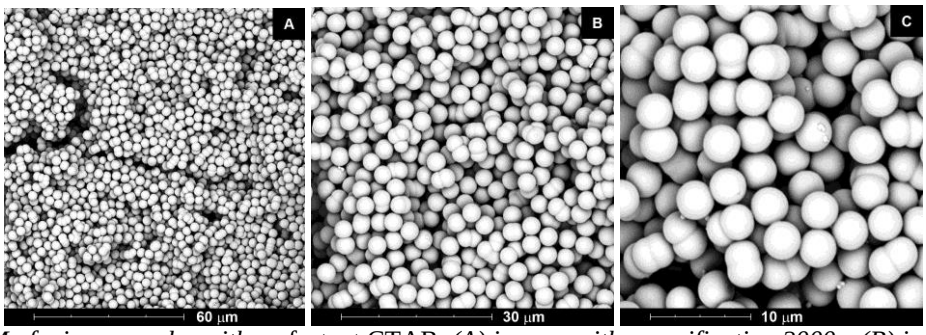

***Fig. 1**: SEM of microcapsules with* surfactant CTAB, *(A) images with magnification 2000x, (B) images with magnification 4000x and (C) images with magnification 8000x.*

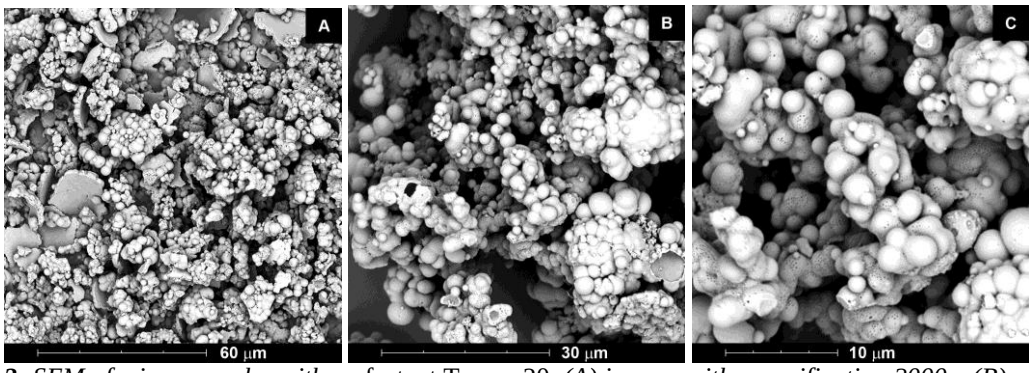

***Fig. 2**: SEM of microcapsules with* surfactant Tween 20, *(A) images with magnification 2000x, (B) images with magnification 4000x and (C) images with magnification 8000x.*

3. CONCLUSIONS

At the end of the work by comparing the images obtained by SEM with different magnifications, it was possible to observe the differences in the morphologies of the microcapsules according to the type of surfactant used.

The use of SEM allowed us to understand the influence that the use of different surfactants produced on the morphological characteristics of the analyzed microcapsules, emphasizing the importance of the analysis of microcapsule morphologies.

By means of SEM, it is possible to obtain magnifications of 2000 times, 4000 times and 8000 times, conserving the depth of field of the samples and providing information on their morphology in different regions of interest, both in larger planes (2000 times) and In more detail (8000 times), with three-dimensional appearance and great depth of focus, which facilitated the morphological analysis of the microcapsules.

Through the analyzes the morphological differences of the microcapsules related to the surfactant were realized. The CTAB, according to the images obtained by the SEM, interacted well with the core material (orange essential oil), forming microcapsules of regular morphology and evenly distributed in the sample, indicating a satisfactory formation. After modification of the surfactant type for Tween 20, it was observed that the surfactant Tween 20, unlike CTAB, did not interact well with the orange essential oil, irregularly forming microcapsules, in addition to the formation of pores, were not uniformly distributed in the sample, forming agglomerates of microcapsules, indicating an unsatisfactory formation.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PREDICTING DEMAND FOR COTTON YARNS

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Abstract: *Predicting demand for fashion products is crucial for textile manufacturers. In an attempt to both avoid out-of-stocks and minimize holding costs, different forecasting techniques are used by production managers. Both linear and non-linear time-series analysis techniques are suitable options for forecasting purposes. However, demand for fashion products presents a number of particular characteristics such as short life-cycles, short selling seasons, high impulse purchasing, high volatility, low predictability, tremendous product variety and a high number of stock-keeping-units. In this paper, we focus on predicting demand for cotton yarns using a non-linear forecasting technique that has been fruitfully used in many areas, namely, random forests. To this end, we first identify a number of explanatory variables to be used as a key input to forecasting using random forests. We consider explanatory variables usually labeled either as causal variables, when some correlation is expected between them and the forecasted variable, or as time-series features, when extracted from time-related attributes such as seasonality. Next, we evaluate the predictive power of each variable by means of out-of-sample accuracy measurement. We experiment on a real data set from a textile company in Spain. The numerical results show that simple time-series features present more predictive ability than other more sophisticated explanatory variables.*

Key words: *Time-series, random forests, trend, seasonality, futures contracts.*

1. INTRODUCTION

Eliciting the size of inventory buffers for fashion textile products is by no means straightforward. On the one hand, buffers help reduce the lack of synchronization between customers demand and production. On the other hand, a high amount of resources in terms of space and necessary funds are required to maintain stocks. It is also important to know when products are going to be demanded as a way to plan both purchases and production. As a result, predicting demand for products is a crucial task for production managers.

Time-series analysis is a well-developed research field [1]. A time-series is a sequence of observations taken in time sequentially, e.g., a monthly sequence of the quantity of cotton yarns shipped from a factory. The traditional time-series approach is concerned with the building of statistical linear models and their use for forecasting purposes. However, non-linear time-series analysis [2] provides a much wider class of forecasting models and relaxes the common constraints imposed by linear models such as the Gaussianity of forecasting errors.

Demand for fashion products presents a number of particular characteristics such as short life-cycles, short selling seasons, high impulse purchasing, high volatility, low predictability,

tremendous product variety and a high number of stock-keeping-units [3]. These facts make forecasting demand for fashion products a complex task that is not usually well captured by common linear approximations [4]. As a result, recent proposals in predicting demand for fashion products suggested non-linear forecasting models [4,5]. However, these works were based on predicting demand for fashion products based only on past observations.

In this paper, we follow a more general approach by: i) including a number of additional explanatory variables in the forecasting model; and ii) assessing the importance of each explanatory variable. To this end, we rely on random forests [6] in an attempt to capture possible non-linear patterns in forecasting demand for cotton yarns. A random forest is a forecasting technique based on an ensemble of slightly different decision trees. A decision tree is a non-linear model that splits the input space into subsets based on the value of a particular feature. This technique allows us to consider as many explanatory variables as desired such as currencies, cotton prices and any other time-series feature. In addition, random forests provide an assessment of the importance of the input variables used to estimate the model. From this assessment, we are able to identify those variables with more predictive ability and those with no predictive power.

Summarizing, we propose a method to analyze the importance of alternative explanatory variables in predicting demand for cotton yarns based on random forests. We first identify a number of tentative explanatory variables. Next, we use these variables to both estimate the random forest model and assess the importance of variables. In this step, we use a real data set from a textile company in Spain containing monthly demand quantities for cotton yarns from January 2012 to March 2017. Finally, we validate the model by computing the predictive accuracy of the model using a test data set not used in the estimation phase.

The results derived from a numerical example using our real world data set show that simple time-series features present more predictive ability than more sophisticated explanatory variables. These results imply that a number of costless time-series features can be explored as a first step to time-series forecasting.

The structure of this paper is as follows. In Section 2, we describe the methodology used. In Section 3, we present the results derived from a numerical example applying our methodology to a real world data set. Finally, in Section 4, we provide some concluding remarks.

2. METHODOLOGY

In this section, we describe the methodology used to both build and validate a random forest forecasting model for cotton yarns based on a number of explanatory variables.

2.1 Feature extraction

The notion of feature extraction is concerned with the process of identifying and selecting relevant explanatory variables for forecasting purposes. In this paper, an explanatory variable means any data x_i that can be used as an independent variable to predict the value of a dependent variable y by means of a given forecasting function f:

$$y = f(x_1, x_2, ..., x_n) + \varepsilon \quad \textbf{(1)}$$

where n is the number of different explanatory variables and ε is the prediction error. Some particular examples of explanatory variables that can be used for predicting demand for industrial textile products are the exchange rate for currencies involved in commercial transactions or the price of raw materials. We here refer to this class of explanatory variables as *causal variables* due to some expected correlation between the dependent and the independent variable.

An additional kind of explanatory variables available for forecasting when dealing with temporally annotated data is the concept of *time-series feature*, meaning any time-related attribute that can be used for forecasting. Classical time series analysis is based on past observations to produce forecasts (autoregression). Then, we say that past observations are time-series features. The number of time-series features is virtually infinite since we can obtain without much effort a wide variety of statistical attributes from a given time-series. Some time-series features are related to seasonality such as a categorical variable with the month, the week or the day when the observation is taken. Some other time-series features are related to trend attributes such as the rolling-mean of the last three observations. And some other time-series features are related to possible trend such as the variation observed in the last six observations.

Since we experiment on a monthly time-series of demand for cotton yarns, we here rely both on causal variables and time-series features to suggest a set of tentative explanatory variables as described in ***Table 1***.

Table 1: *Tentative explanatory variables*

x_i	Name	Description	Type
x_1	Rate	Average monthly exchange rate EUR/USD	Causal
x_2	Cotton	Average monthly quotation Cotton No. 2 Futures [7]	Causal
x_3	Month	Month of the year of each observations	Time-series
x_4	MA3	Moving average of the last 3 observations	Time-series
x_5	MA6	Moving average of the last 6 observations	Time-series
x_6	Var12	Variation in the last 12 observations	Time-series

2.2 Model selection and out-of-sample validation

We mentioned in the introduction that a random forest is a non-linear forecasting technique based on an ensemble of decision trees. Random forests provide an assessment of the importance of the input variables in terms of mean error decrease provided by each variable. We use this assessment to identify those variables with less predictive ability. To this end, we start with a time-series y with monthly demand for cotton yarns and a data set of explanatory variables x_1 to x_6 as described in ***Table 1***. Following the common out-of-sample model validation procedure [8], we proceed as follows:

1. Separate the entire data set in a training set with the first 80% of the observations and a test set with the remaining 20% for validation purposes. These data sets contain both the time-series y and the explanatory variables x_1 to x_6
2. Estimate the forecasting random forest model using data from the training set.
3. Remove variable x_i with the least predictive ability from the training set.
4. Repeat steps 2 and 3 until only one explanatory variable is left.
5. Select model with the minimum out-of-sample forecasting error e_{out} computed using only data from the test set as follows:

$$e_{out} = \frac{\sum_{\text{test}} (y - f)^2}{\sum_{\text{test}} (y - m)^2} \qquad \textbf{(2)}$$

where m is the average of time-series y over the training set. Note that the denominator in equation **(2)** is used as a normalization factor used to discard models with poorer accuracy than a trivial

forecast such as the mean *m* of past observations. Values of e_{out} above one implies that forecast *f* is worse than using the mean as a forecast.

By following the aforementioned steps we are able to select the set of variables to build the forecasting model with best performance in terms of out-of-sample forecasting accuracy. The out-of-sample method measures the generalization power of any forecasting model by computing the accuracy of the model using a data set that was not used to fit the model. This method is used to validate models in similar circumstances to a real deployment in practice. As an additional benchmark, we use the classical Holt-Winters method [9] for seasonal time-series forecasting in its additive formulation.

3. NUMERICAL EXAMPLE

In this section, we apply the methodology described in Section 2 in order to predict demand for cotton yarns using a real world data set from a textile company in Spain. Recall, that the initial data set contains 63 monthly observations for cotton yarns and a number of tentative explanatory variables described in Table 1. Then, following the procedure described in Section 2.2, we divide the whole data set in a training data set with 50 observations and a test set with 13 observations, equivalent to a 80-20% split. We begin estimating a model using all the available explanatory variables over the training set. Then, we progressively remove the variable with less predictive ability according to the importance assessment from the random forest model. At each step, we compute the out-of-sample prediction error by means of equation (2). The results derived from this procedure are summarized in Table 2.

Table 2: *Model selection*

Subset of variables	**Description**	**Out-of-sample error (e_{out})**
$x_1\ x_2\ x_3\ x_4\ x_5\ x_6$	Rate, Cotton, Month, MA3, MA6, Var12	0.205± 0.009
$x_2\ x_3\ x_4\ x_5\ x_6$	Cotton, Month, MA3, MA6, Var12	0.242± 0.020
$x_3\ x_4\ x_5\ x_6$	Month, MA3, MA6, Var12	0.219± 0.014
$x_3\ x_5\ x_6$	Month, MA6, Var12	0.225± 0.017
$x_3\ x_5$	Month, MA6	0.190± 0.012
x_3	Month	0.512± 0.010
-	Additive Holt-Winters method	0.265± 0.000

Due to its particular construction, random forests produce forecasts that are also random. Thus, we perform 100 replicates of the forecasting process to compute its average out-of-sample error and its standard deviation. Note that higher than one out-of-sample errors mean that the particular model performs worse than the mean as a trivial forecast. The results summarized in Table 2 show that even though the causal variables considered in this example do not damage the accuracy of the model, their predictive ability is low. Indeed, both the exchange rate EUR/USD and the cotton quotation are the first removed variables under our proposed procedure for model selection due to their low importance in the model.

As a benchmark, we also present the out-of-sample error achieved by the additive Holt-Winters method for time-series forecasting [9]. In this numerical example, random forests outperform the Holt-Winters method with the exception of the model considering only the month as explanatory variable. Furthermore, the random forest model using the month and the moving average of six months produced the best out-of-sample error results. As a result, we select this model

to predict the future behavior of the demand for cotton yarns. Both the real observations and the forecasts obtained with this model for the test set are depicted in **Fig. 1.** For confidentiality reasons, quantities are normalized by multiplying the original time-series by a correction factor. These results show good generalization power, hence validating the model for forecasting purposes.

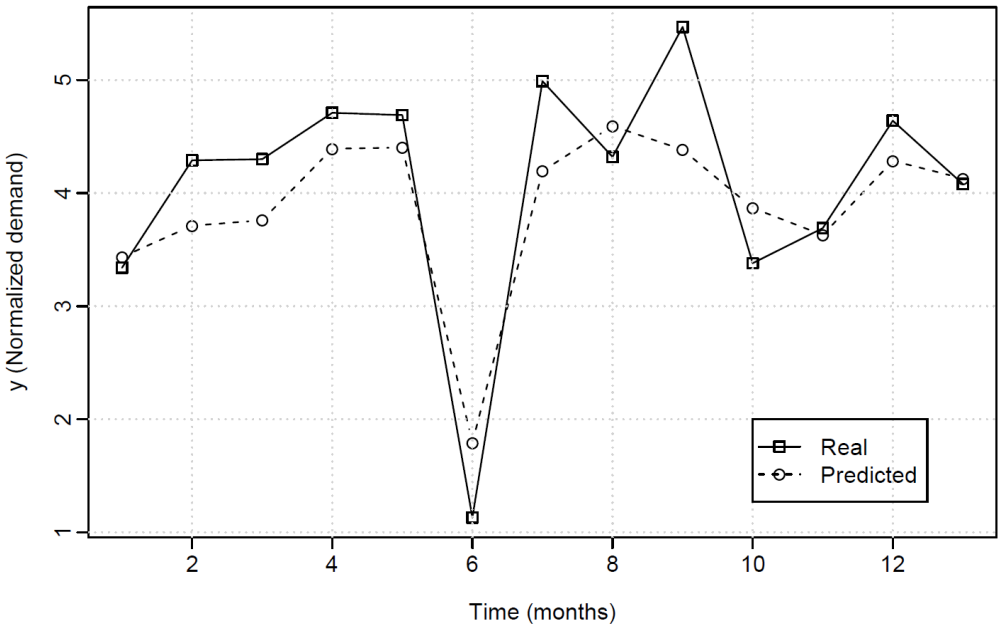

Fig. 1*: Real and predicted demand for cotton yarns over the test set*

4. CONCLUSIONS

In the textile and fashion industry, a flexible forecasting technique is crucial for planning and commercial purposes. In this sense, random forests represent a suitable technique due to both its ability to capture non-linear patterns and the possibility to consider multiple explanatory variables. These explanatory variables are usually labeled either as causal variables, when some correlation is expected, or as time-series features, when extracted from time-related attributes such as seasonality.

In this paper, we rely on random forests to propose a simple methodology to select and validate tentative forecasting models by means of the out-of-sample accuracy measurement procedure. The results derived from a numerical example using our real world data set show that simple time-series features present more predictive ability than more sophisticated explanatory variables. These results imply that a number of costless time-series features can be explored as a first step to time-series forecasting.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A REVIEW ON TEXTILES IN SPACE PROTECTION EQUIPMENTS

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Abstract: *Astronauts need the lander for decelerate and bridle the speed when they land on the space surface slowly. This lander could be controlled velocity magnitude in any direction or orientation and provide protection. The landers consist of airbags and parachutes. The airbag is a type of vehicle safety device, have a soft cushioning and is an occupant restraint system. The parachute provides to slow the motion of an object through an atmosphere by the hauling. Space protection equipments must have some properties because of astronaut's entry, descend and landing in safely. Textiles in airbags provide these properties especially which are light weight, low gas permeability, high strength, low cost, low temperature flexibility and low coefficient of friction. For textiles in parachutes must have properties such as smooth, porosity, air permeability, high strength, cost-effective, stability light weight and good in drag and lift. Airbags and parachutes in space protection equipment's are improved in systems provide easy stability. Recently, inflatable technologies for space protection equipments plays a fundamental role in building re-entry capsule. It can be performed a variety of pre-flight analyses to ensure the success of the tests of protection systems from day to day. In this review, space protection systems, their textile materials and properties, their advantages and disadvantages are presented.*

Key words: *Airbag, Parachute, Space lander, Bridle, Protection*

1.INTRODUCTION

Space is defined as located the remaining portion of the universe infinite emptiness, outside the earth's atmosphere and between celestial bodies. For space exploration, space travel must be organized. Space travel generally begins with rocket firing on the earth, passing to gravity, go out of atmosphere and then return after a while. After space travel, astronauts need a safe entry, descent and landing for returning to earth. So, they need to use space protection equipments such as airbags and parachutes.

2.AIRBAG

An airbag is a type of vehicle safety device, have a soft cushioning and is an occupant restraint system. The airbag module inflates extremely rapidly then quickly deflates during a

collision and in this way, it prevents impact-caused injuries [1]. Airbags should have a chemical explosion to inflate the airbags immediately. The chemicals used such as the nitrogen gas finally inflates the airbags in 30-40 milliseconds [2].

2.1. Textiles Used in Airbag

Airbags fabrics must have some characteristic properties such as low air permeability, light fabric weight, low fabric thickness and high fabric breaking strength and breaking extension [3]. Generally, [3], [4], [5], [6] airbag fabrics are made of a synthetic yarn. The airbags used in are mostly a rubberized polyamide fabric because of low level of air permeability. Instead of polyamide yarns, it can also be used polyesters, vinyl polymers, polyolefins, rayon, polyoxymethylene, polysulfones, carbon fibers, glass fibers, ceramic fibers and metal fibers which must be rubberized. Rubberizing production is very important because it makes the fabrication of the airbag complicated and expensive, and increases the space required by the folded airbag [3]. Mostly used rubberizing polyamide yarns for the airbag fabric woven from nylon 6, 6 ranging from 420 to 840 deniers [5], [6]. The fabric which is used to make passenger airbag is normally uncoated and its weight is about 170 and 220g/m² [6], [7]. Airbag fabrics are generally woven, with the construction of either 840 X 840 D, 98 X 98 /dm plain weave, 60″ width or 420 X 420 D, 193 X 193 /dm plain weave, 60″ width [5]. Initially, airbags were coated by neoprene rubber, but recently silicon coated and uncoated varieties have been used in a lot because of both lighter and thinner to fold up into a compact pack [6], [7]. Coated airbags are preferred for driver seats because of slow wearing off, good resistance for burn, easily to cut and sewn, air porosity precisely controlled. Non-coated fabrics are lighter, low in cost, softer, smaller package and easier for recyclability [5], [6], [7].

2.2. Airbags Used in Space Protection Equipments

The Mars Pathfinder (MPF) airbag system firstly was landed in 1997 and landing was achieved with a combination of bridle-mounted retro-rockets and an airbag impact attenuation system [9]. Airbags must be strong enough for descent to land on rocks or rough terrain and must be inflated in seconds before contact to surface [10]. MPF airbag system consisted of four separate airbags, each with six lobes (hold the airbag to lander) (see in Figure 1) and a gas generator [11], [12]. Connection between lobs is important, because it provides to landing forces for keeping the airbag system flexible and responsive to ground pressure. Materials in MPF airbags must have some characteristic properties to reliable fabrication processes for assembly. (see in Table 1). Airbag fabrics are generally [9], [10], [11], [12] produced from high strength of Vectran HS. Vectran with liquid crystal polymer has a better property for flex-crack/abrasion resistance. For the Vectran HS fabric, Kevlar 29, Technoro T-240 and Spectra 1000 can be used. The bridle consisted of a Kevlar tether [9], [10], [11. For the non-coating fabric structure, it is generally suggested to use an adaptable fabric [9], [12], [13] which is suitable for a smooth topography, has lightest gas retaining coating with a 50 × 50 plain weave of 200 denier in fineness (details in Table 2). For coating material, the low temperature silicone is selected [9], [13] because of constrain from gas with a thin coating and provide to lend itself well to assembly processes [9].

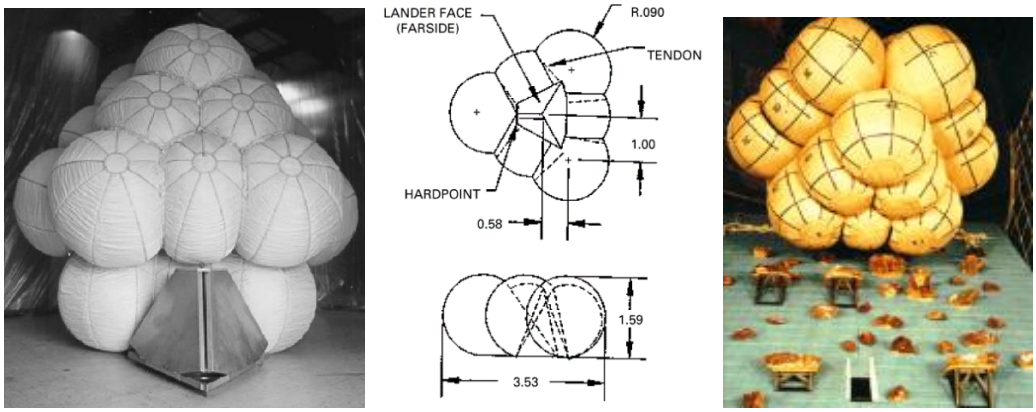

Fig. 1: *MPF airbag six lobes, MPF geometry and drop test in MPF airbags [9],[10,[11],[12]*

Table 1: *Fabric for MPF Airbag*

Fabric requirements of MPF Airbag	
Light weight	Low temperature flexibility
High tensile strength	Retention of strength after flex/crease
High tear strength	Low coefficient of friction
Low gas permeability	Low cost

Table 2: *Fabric Construction of MPF Airbag*

Type of MPF Airbag	**Fabric Construction**	
	Coated	**Non-coated**
Yarn Type	Vectran	Vectran
Yarn Denier	400-750	200
Weave	50x50 plain	
Tensile (lbs/inch)	485	485
Weight (oz/yd^2)	4,3	2,7

3. PARACHUTE

A parachute provides to slow the motion of an object through an atmosphere by the hauling [14]. There are three principal stages in a parachute drop: deployment, inflation, and descent. The deployment means that eliminating of the payload from the aircraft and ends when the suspension lines and canopy could be transferred from deployment bag [15]. Parachutes rocket burns to motor in 3,5 seconds before launching the flare and flare burns for about 40 seconds while slowly descending [16].

3.1. Textiles Used in Parachute

Parachute fabrics must have some characteristic properties such as smooth, porosity, air permeability, high strength, cost-effective, stability light in weight, good in drag and lift [15], [16], [17], [18]. For parachute design, actuating and sensing technologies for feasibility of implementation are improved. These systems provide that very high mechanical flexibility, light weight, excellent bond between parachute canopy and sensor and very high strain limit [18]. Parachutes are usually made from silk or most commonly nylon [14]. Because the silk is so expensive for the use in parachute canopy, other fibres can be used either in whole or in admixture with silk [17] Nylon

parachute fabrics are generally in 50-75 µm thickness [19]. Parachute fabrics could be woven [17] or knitted [20] structure. Parachute woven fabric has both adjacent warp and weft threads where a binder thread interlaces arbitrarily with other threads so it could be increase the permeability and tearing resistance of the fabric [17]. Parachute knitted fabric make from a combination of metallized polyester ribbons and synthetic plastic polymeric filaments knitted together. Polyester ribbons have a metallic coating thereon and metallic coating is aluminum [20].

3.2. Parachutes Used in Space Protection Equipments

Orion's parachute system helps to slow the spacecraft down during entry, descent and landing and ensure a safe landing for astronauts returning to earth [21], [22] Parachute loads are used with atmospheric density, velocity, parachute drag area, and mass. Parachutes must be produced with a high strength material and must be reasonably lightweight so it can be fit in well to a very small area. Before the space travel, they must be pressure packed and folded several times. Parachutes generally [21], [22] are made from Kevlar or Nylon fibers. For parachute's bridle Zylon and Kevlar fibers are used. Zylon bridles are sewn specifically in a webbing pattern, provides deployment and increased stability [21]. Parachutes are in four types which have different gauges, materials and properties (details in Table 3) (see in Figure 2)

Table 3: *Types of Orion Parachute Systems [22]*

Types of Orion Parachute System	Gauge	Material	Speed
1.Forward Bay Cover Parachutes	7 feet in diameter and 8 lbs.	100% Kevlar	475 feet per second
2.Drogue Parachutes	23 feet in diameter and 80 lbs.	Kevlar/Nylon hybrid material	450 feet per second
3.Pilot Parachutes	11 feet in diameter and 11 lbs.	Kevlar/Nylon hybrid material	190 feet per second
4.Main Parachutes	116 feet in diameter and 310 lbs.	Kevlar/Nylon hybrid material	265 feet per second

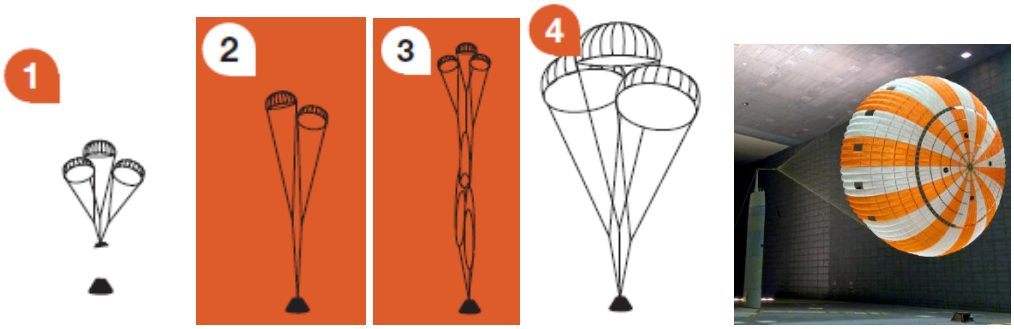

Fig. 2: *Types of Orion Parachute Systems and Parachute Testing [22]*

4.ADVANTAGES AND DISADVANTAGES OF SPACE PROTECTION EQUIPMENTS

Airbags and parachutes in space protection equipment's are improved in systems provide easy stability. The engineers performed a variety of pre-flight analyses to ensure the success of the tests of protection systems [23]. Recently, inflatable technologies for space protection equipments plays a fundamental role in building re-entry capsule [24]. These technologies have advantages such as low volume and mass, easily reconfiguring [24], high strength, good resistance [5],[18]. However, inflatable re-entry capsule has some disadvantages about design process such as aero-thermodynamics, material sciences, shield design, multi-body mechanics, inflatable structures blow up simulation and stress analysis. In re-entry and descent times, high stress in capsule can be affect easily to design. Structure of the re-entry capsule could be deformed and stressd when it imposed to loads, stiffness and strength [24].

5. CONCLUSIONS

Airbags and parachutes in which space protection equipments have offered highly important criteria for space travel because of safe entry, descent and landing. Textiles in space protection equipments must have light weight, high strength, low cost, flexibility, stability, foldable and good resistance to provide successful performance. Their performances can be improved by using advanced textiles and designs in airbags and parachutes from day to day.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ROMANIAN TRADITIONAL MOTIF ELEMENT OF MODERNITY IN CLOTHING

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Abstract: *In this paper are presented the phases for improving from an aesthetic point of view a clothing item, the T-shirt for women using software design patterns, computerised graphics and textile different modern technologies including: industrial embroidery, digital printing, sublimation.*
In the first phase a documentation was prepared in the University of Oradea and traditional motif was selected from a collection comprising a number of Romanian traditional motifs from different parts of the country and were reintepreted and stylized whilst preserving the symbolism and color range specified to the area. For the styling phase was used CorelDraw vector graphics program that allows changing the shape, size and color of the drawings without affecting the identity of the pattern. The embroidery was done using BERNINA Embroidery Software Designer Plus Software. This software allows you to export the model to any domestic or industrial embroidery machine regardless of brand. Finally we observed the resistance of the printed and embroided model to various: elasticity, resistance to abrasion and a sensory analysis on the preservation of color. After testing we noticed the imprint resistance applied to the fabric, resulting in a quality that makes possible to keep the Romanian traditional motif from generation to generation.

Key words: *Apparel, printing, CorelDraw, BERNINA Embroidery Software Designer Plus.*

1. INTRODUCTION

One reason for the comparatively slow growth of digital printing on textiles may be related to the extreme demands of the textile applications.

Other challenges:

There are many types of synthetic and natural fibers, each with its own ink compatibility characteristics, in addition to dealing with a fabric that is stretchable and flexible, it is often a highly porous and textured surface.

Use requirements include light fastness, water fastness (sweat, too) through finishing operations and often outdoor use, heavy wear, abrasion, and cleaning.

The fabric not only has to look good but to feel good too, fabric has much greater sorbency, requiring many times the ink volume compared with printing on papers. [1]

2. THE EXPERIMENTAL PART

In this paper are presented the phases for improving from am aesthetic point of view a clothing item, a T-shirt for women respectively, with a Romanian traditional model using a computerised graphics software, CorelDraw [2] [3] respectively and an imprinting rubber system of the model. After the printing phase we passed onto embroiding the model on the T-shirt with the help of the embroidery machine [4] [5] [6] [7]. We also tested the strength of the printed and embroided model by washing. The T-shirt was washed several times, dried and ironed. A sensory analysis on the preservation of color was performed (a comparative analysis with the elastin sample) to see if the substance with which it was printed did not degrade or crack, and a pilling test was performed by a repeated number of abrasive discs with an abrasive disc that lets us know if the quality of the model has not been affected.

The documentation part was done at the University of Oradea and the traditional motif was selected from a collection that includes a series of Romanian traditional motifs from different parts of the country **Fig. 1**.

The proper motif was stylized and re-interpreted, but the shape features were preserved (diamonds, rectangles, triangles), composition (the way the modules combine with each other) in order to maintain the degree of authenticity of the motif. Graphical model processing was done in the CorelDraw program **Fig. 2**.

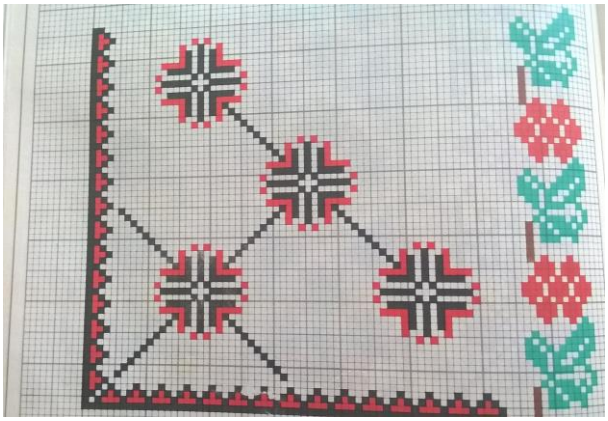

***Fig. 1**: Model selection*

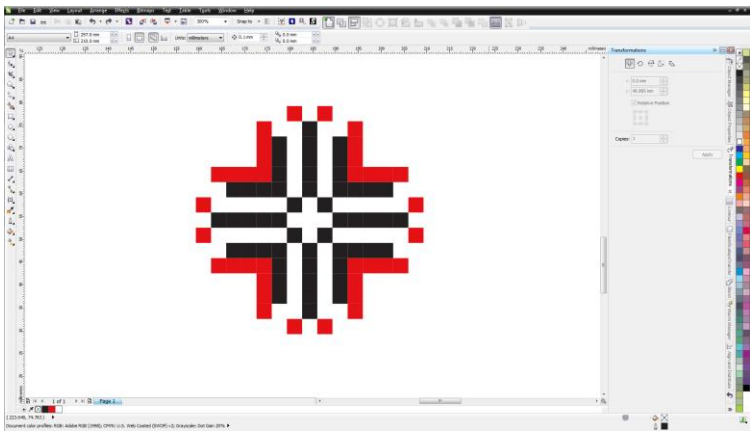

***Fig. 2**: Model processing in CorelDraw*

The motif has been stylized in several sizes and chromatic combinations, and then one of these variants has been chosen, followed by the digitization of the motif using the CorelDRAW graphic program.

T-shirt printing was done with a thermal press and JET-ST transfer sheet.

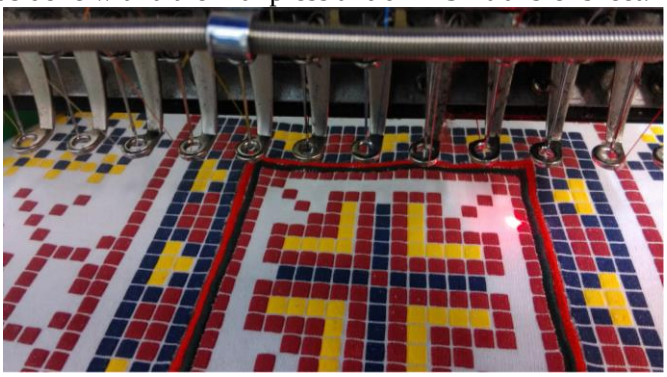

***Fig. 3**: Happy embroidery machine [8]*

After the digitization phase, we passed onto embroiding the model on the T-shirt with the Happy embroidery machine **Fig.3** from S.C. CONFIDEX S.R.L Oradea. [8]

The embroidered pattern was made using the BERNINA Embroidery Software Designer Plus software. The software used to create the embroidery on the T-shirt also incorporates CorelDraw Graphics Suite X6 professional software (Corel PHOTO-PAINTTM, PowerTRACETM, Corel Website CreatorTM, Corel CONNECTTM, PhotoZoom Pro 2 and ConceptShareTM), which helps us create the desired model in vectorial variant. Transforming into embroidery model is easy with a simple click. This software allows you to export the model to any type of embroidery machine. [2] [8]

***Fig.4**. Comparative analysis with elastin sample*

3. CONCLUSIONS

Traditional Romanian motifs can be applied on different textile supports using modern technologies while preserving their degree of authenticity. These modern technologies allow a mix of old and new, combining the creative features with the technological ones, and can be stylized and reinterpreted in various graphic programs, embroidery programs that retain the shape and size of the designs and the chromatic palette.

As a result of the tests, we have noticed a strength of the imprinted model on the textile fabric, which leads to a quality that makes it possible to keep the traditional Romanian motive from generation to generation.

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ANNALS OF THE UNIVERSITY OF ORADEA
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EFFECTS OF THE FATIGUE PROCESS UPON THE STRUCTURE OF A BICONSTITUENT FIBER

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Abstract: *Knowing the processes that take place in the macromolecular and morphological structure following repeated mechanical stresses, during the technological processing of chemical fibres and yarns is mostly important for the specialists in the field. This aspect is also motivated by the fact that, due to the viscoelasticity of the thextile fibres, during stresses, especial the tensile ones, with small forces but repeated at short times, fatigue appears represented by structural changes, difficult to be noticed, and in the most severe cases of stress destruction occurs.*
During the fatigue process in the fibre there are several non homogeneous deformations especially in the microcavities and areas where the structure has imperfections. Thus, modified isolated structures will be obtained, representing the primary destruction of the fabric by forming micro-fissures that progress rapidly by propagation, affecting the fibre in several areas, and in the end it results in the tearing of the fibres.
The action of the mechanical forces upon the fibre triggers several chemical reactions that result in the breaking of the chemical bonds and the birth of free macroradicals, the concentration of which will depend on the intensity of stresses. These aspects of the fatigue process will influence correspondingly the fibre's physicochemical and chemical properties.
This paper reports the experimental results regarding the effect of some cyclical stresses with constant force on the main properties of the textured filament yarn made of Polyethylene terephthalate (PET) and Polybutylene terephthalate (PBT) with a fibrillar matrix structure, of 110/32 dtex.

Key words: *viscoelasticity, biconstituent, polyethylene terephthalate, polybutylene terephthalate, extension, stress*

1. INTRODUCTION

This work represents the experimental results of a study the effect of some cyclical stresses with constant force on the main properties of the textured filament yarn made of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) with a fibrillar matrix structure (inslands-in-the-sea), of 110/32 dtex.

In the case of the bioconstituent yarn, the chemical and morphological structure is different, i.e. the matrix is made of polyethylene terephthalate (PET) whose chain structure is more rigid, and the fibrils are made of polybutylene terephthalate (PBT) whose structure unit has an aliphatic element (butylene) with a higher flexibility, thus being suitable for a better orientation and organization during the elongation stresses. In the same time, the different weighting of the two elements, as well as their non homogenous distribution in the yarn, also contribute to the evolution of the mechanical characteristics but not always in the same direction [1], [2].

2. RESULTS AND DISCUSSIONS

The fatigue of the abovementioned yarn was achieved by cyclical stresses for loading-unloading (at InstronMechanical Testing Machine) with constant forces for the elastic field (2 forces of 60 and 100 cN/yarn), postelastic field (1 force of 150 cN/yarn) and two forces of 250 and 300 cN/yarn for the final area of the effort-elongation curve (Fig.1).

For each stress force, loading-unloading cycles were executed for four time lengths: 1, 2, 4 and 8 minutes, followed by a 3-minute relaxation, after which the effort-elongation curves were registered until tearing on the same device. The average values of the parameters that characterize the effort-elongation curves compares to the control sample (effort-elongation curve of the unstressed yarn) show that, compared to the control sample (M), the efforts executed with the first four stressing forces lead to a rigidity of the yarn by increasing the initial module (E_1) for stresses lasting for up to 4 minutes, after which it decreases and it stays higher than the control sample (Fig.1). Under the highest stress (300 cN), the elasticity module grows only until 2 minutes of stress, after which it decreases noticeably, still remaining higher than the control sample's.

This aspect shows a change in structure, firstly of the orientation of macromolecular chains in the amorphous and transitory areas [3], and secondly, when the duration of stressing forces are higher, changes are more spectacular, as a result of the orientation of crystallites. Simultaneously, in addition to the breaking of secondary forces and of some chemical bonds, whose energy was defeated by the mechanical one, resulting in the formation of free macroradicals [4], [5].

Thus, if we look in figure 2 at the evolution of the elastic effort (δe) compared to the stress force for different durations, we notice that it grows compared to the control sample only during the 1st stress phase (60 cN) up to 4 minutes, after which it decreases. During the second stress phase (100 cN) (also in the elastic field, but closer to the passage towards viscoelasticity), the elastic stress decreases for all the effort length, but not too much compares to the control sample.

Instead, for the other stress areas, the elastic stress decrease significantly compared to the control sample, even for a stress period of 1 minute.

Therefore we conclude that structure changes are significant in the cases where stress forces exceed the elastic limit.

A considerable change appears in the yielding deformation (ε_c) that decreases continuously and considerably for the small stress forces (fig. 3). Under these conditions it is estimated that although the yielding effort decreases, the corresponding deformation decreases even more and the post-elastic area of the yarn becomes rigid.

Following the values of the yield stress (δ_c) under the same testing conditions, we notice that it decreases slightly during the first two loading phases up to 1 minute, after which it grows rapidly for the 100 cN force up to 4 minutes of stress and then it decreases again. The same tendency is seen in the other stress forces, but with values much lower compared to the first two stress phases, and the decrease of the stress starts earlier, after 2-minute stress (fig. 4).

The tearing limit (δ_r and ε_r) varies within contradictory limits, with a tendency to decrease the specific effort compared to the control sample for the stress conditions in the elastic field, more pronounced at the maximum effort duration (fig. 5) and (fig. 6) and its increase upon high stresses of 250 and 300 cN (fig. 7) and (fig. 8).

The mechanic work specific to deformation of the curves recorded after stresses decreases compared to the control sample and is continuously decreases as the stress intensifies. In such circumstances, the yarn will have an ever smaller capacity to render the stored elastic energy and the energy dissipated into the fabric will lead to the breaking of valence bonds and to the appearance of the fatigue process [6].

By following the optical birefringence performed on the requested yarn samples, with growing forces at minimum and maximum duration (1 and 8 minutes), a slight orientation towards the control sample is noticed at the 60 cN stress, and a more prominent one at 100 and 150 cN stresses. This orientation takes place in the amorphous and transitional areas of the yarn, while at high stresses of 250 and 300 cN the increased values of birefringence are due to the orientation of the crystallites. However it is noticed that orientation decreases under these forces for long stress durations compared to the short ones, as proof of the destruction of the regularity of morphological formations and conformation changes at the level of smaller or larger segments of the macromolecular chains [7].

It can be easily observed that during the fatigue process in the fibre there are several non homogeneous deformations especially in the microcavities and areas where the structure has imperfections. Thus, modified isolated structures will be obtained, representing the primary destruction of the fabric by forming micro-fissures that progress rapidly by propagation, affecting the fibre in several areas, and in the end it results in the tearing of the fibres.

Therefore, the action of the mechanical forces upon the fibre triggers several chemical reactions that result in the breaking of the chemical bonds and the birth of free macroradicals, the concentration of which will depend on the intensity of stresses.

These aspects of the fatigue process will influence correspondingly the fibre's physicochemical and chemical properties.

3. CONCLUSIONS

By correlating all the analyzed parameters under the stress conditions discussed above, the result is as below:

- the subsequent application of cyclical elongation forces in the elastic field, during short times, lead to the improvement of the mechanical characteristics of the yarn, but during long times, the fatigue effects appear;
- by adding to the stress intensifying forces that exceed the elastic field, structural changes are obvious. Thus, the ever enhanced process of yarn rigidity, especially in the postelastic area, reveals the same morphological changes with effects on the yarn's properties;
- analysing the fatigue process inside a fabric, only after its breaking final values, are not always satisfactory because during stresses there are complex processes with different directions whose overlapping lead to the fact that tearing does not truly reflect the fatigue mechanism;
- the fair interpretation of the fatigue process of fibres and yarns creates the premises for avoiding the progressive destruction during long static stresses and, therefore, for preserving their integrity, in order to reduce to a minimum the number of macroradicals and, as a consequence, of the mechanical-chemical processes taking place before the final destruction - tearing.

As a result of this study, due to the viscoelasticity of the textile fibres, during stresses, especial the tensile ones, with small forces but repeated at short times, fatigue appears represented by structural changes, difficult to be noticed, and in the most severe cases of stress destruction occurs.

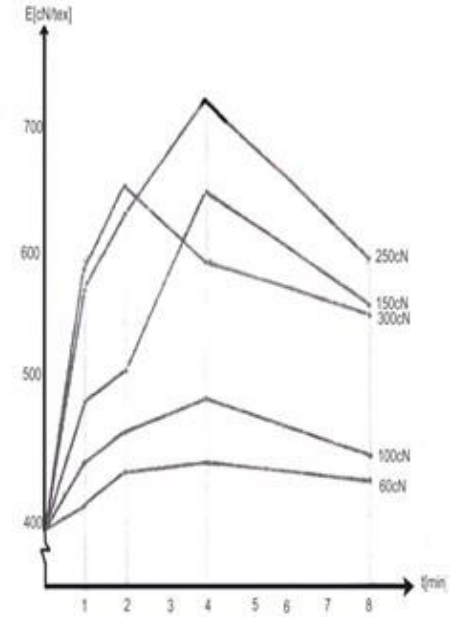

Fig. 1:*Effect of time and load level in the E-moduls*

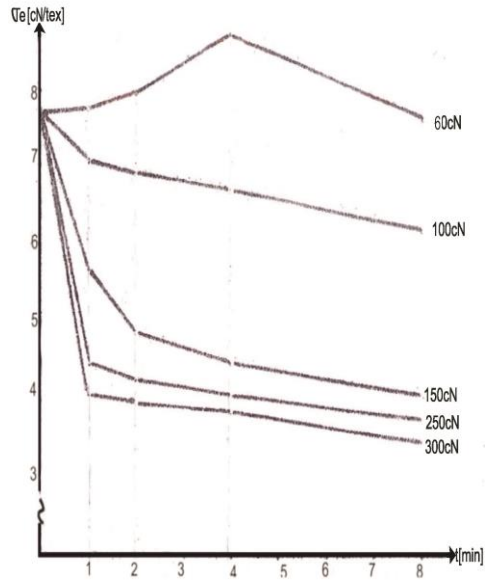

Fig. 2:*Effect of time and load level in the elastic stress*

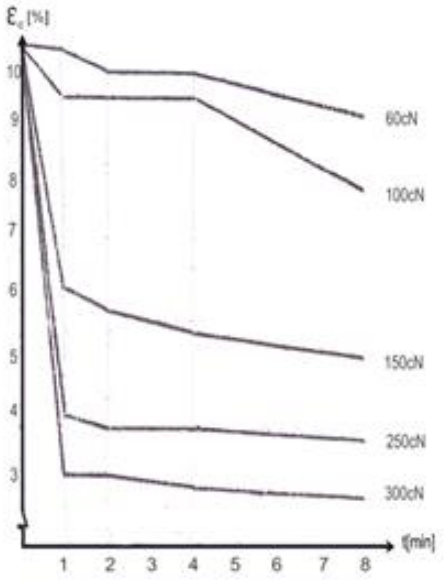

Fig. 3:*Effect of time and load level in the yield strain*

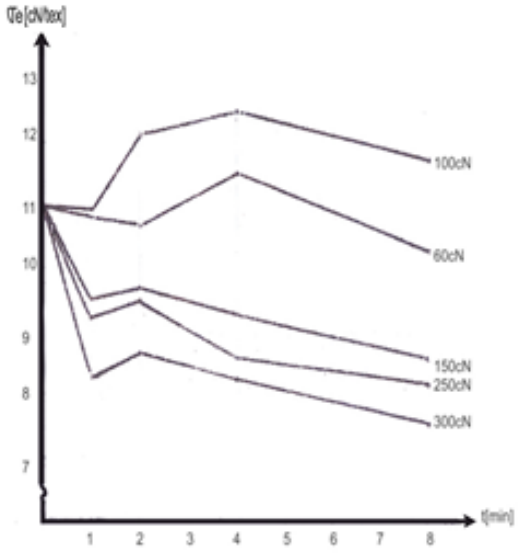

Fig. 4:*Effect of time and load level in the yield stress*

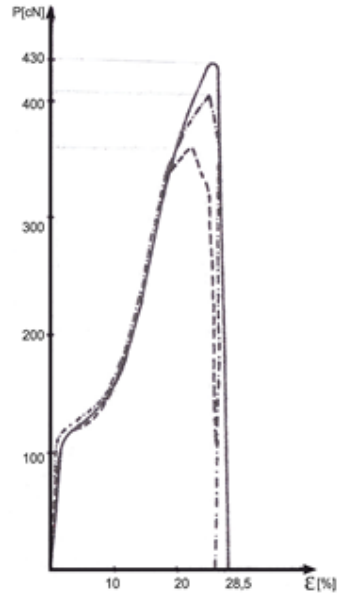

Fig. 5:*Load elongation curves at P=60cN*
Legend:
control stample
loaded stample 1 min
loaded stample 8 min

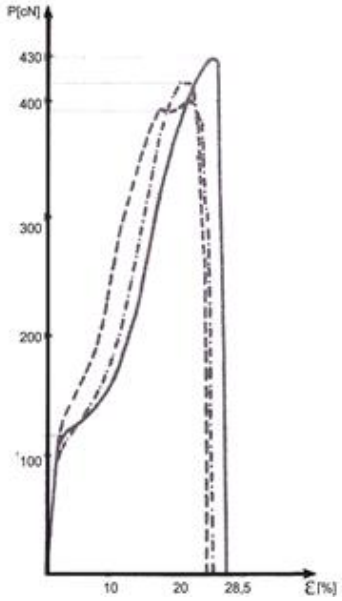

Fig. 6:*Load elongation curves at P=100cN*
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loaded stample 8 min

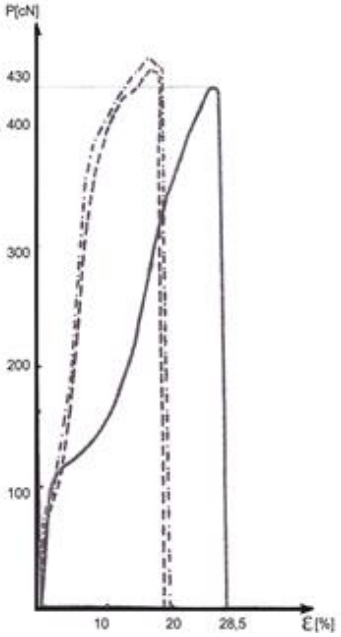

Fig. 7:*Load elongation curves at P=250cN*
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loaded stample 1 min
loaded stample 8 min

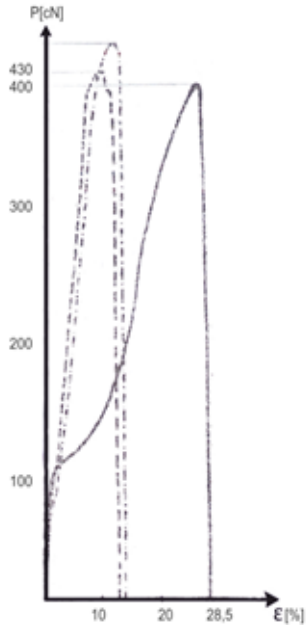

Fig. 8:*Load elongation curves at P=300cN*
Legend:
control stample
loaded stample 1 min
loaded stample 8 min

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ANNALS OF THE UNIVERSITY OF ORADEA
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THE "TREE OF LIFE" SYMBOL IN JEWELLERY

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Abstract: *History and tradition play a very important role in the development of a society. Designed objects were and are adorned with signs and symbols holding various messages and aesthetic particularities. These objects have the ability of spreading emotions through their shape, material, finishing or graphic and are made using different materials, techniques and technologies. By particularising a sign one must take into account its orientation towards certain objects regarding the significance, the culture and the historical period. The sacred geometry, a sum of shapes with religious and cultural values, can be analysed from a scientific, philosophical, aesthetic and mystic point of view. The origin, the nature and the relationship between these shapes are considered to be determined by the surrounding universe. The symbol is an intermediary which favours the communication from the visible reality to the invisible, non-figurative one. One of the shapes with a symbol value, frequently used, is the tree of life. The tree of life is a symbol dating from the Neolithic, but still applied nowadays. Bearing information and witness of the history of a civilisation, the "Tree of life" symbol inspired the artisans and artists from different cultures, being graphically readapted, both due to the technology development, as well as to the society's maturation. The present paper presents the evolution of the "tree of life" sign, the manner in which it followed the history and civilisation flow, the diversity of objects adorned with it through various working techniques, as well as its evolution through new interpretations in the jewellery design applications. The paper presents the experiment of making a silver pendant with the "Tree of life" symbol, reinterpreted and made using a 3D program.*

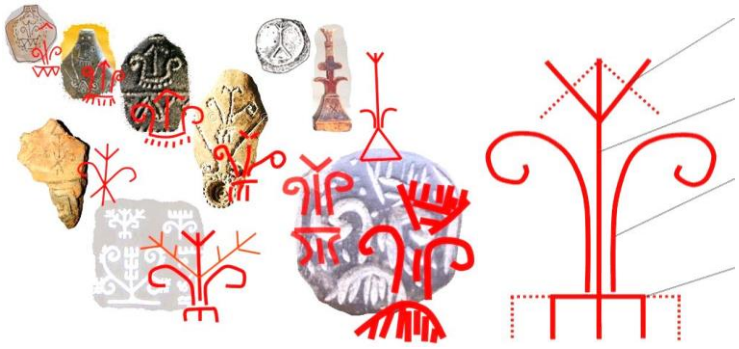
Key words: *sign, technologies, material, product, silver.*

1. INTRODUCTION

The tree symbol dates from the 1st century B.C. The tree of life shown on wood, stone, metal, embroideries, fabrics, knitting and tapestry, in object and textile graphics, has emphasized into images the symbols of basic elements, traditional in ancient cult doctrines. The sacred tree becomes a symbol without losing its formal-concrete attributes (the palm-tree and the date palm at Mesopotamians, the oak tree at Scandinavians, Asvattha and ryagrodha at Hindu, etc.), after certain mental step were surpassed and the symbol is detached from the concrete shapes, becoming sketchy and abstract [1]. In **Fig. 1, Fig. 2, Fig. 3, Fig. 4, Fig. 5** one can notice the diversity and the continuity of the "Tree of life" symbol as inspiration source. Along the evolution of human society, this symbol was used as a decorative element on charms, fabrics, clothes, vessels, jewellery, showing its potential through the richness of its messages. History presents the graphic, geometric

evolution of the "Tree of life" symbol, but also the way in which it can be found on various personal use, household or religious objects.

The tree of life originating from the Neolithic of Ancient Europe is made of 3 regenerating symbols, shown in **Fig. 1**: the *"V" symbol* of the Great Goddess, the *bucranium-uterus* and the *tooth comb–brush*. All these symbols have the purpose of amplifying the sacred significance in a certain order which was maintained throughout time. This representation of the tree of life can be seen on female anthropomorphic statuettes discovered in the necropolis from the Bronze era culture (Gârla Mare, Mehedinți county and Orsoia, Montana in Bulgaria).



a. b.

Fig. 1: a. *Ancient objects with the "Tree of life" symbol;* ***b.*** *The scheme with the "Tree of life" which comprises the 3 regenerating symbols [2, 6]*

a. b. c. d. e.

Fig. 2: a. *The Thracian tree of life, southern Oltenia, 5th – 4th century B.C.;* ***b.*** *The Thracian tree of life, northern Bulgaria, 4th century B.C.;* ***c.*** *The Etruscan tree of life, Italy, 4th century B.C.;* ***d.*** *The Greek tree of life, Greece, 6th century B.C.;* ***e.*** *The tree of life from Bardar [2]*

2. GENERAL INFORMATION

2.1 The symbol's evolution

The "Tree of life" symbol can be found on the territory of different peoples. Archeologic discoveries prove the existence of this symbol **Fig. 2** in many cultures, from the oldest times. In **Fig. 2. e**, the symbol of life from Bardar, life and its spring meet in a single sign. The angle with the tip towards the earth is situated in the circled ear of the column. The birth axle is shown as pairs of flower shaped rhombuses. The self-recognition axle, situated on the next level, is shown as being a growing fruit and the theme axle, marked at the base through a circle containing three oblique parallel lines, situated between the "S" sign, represents a symbol of a rich and eternal earthly life, of the whole eternity. This symbol archaically describes the entire existence. The tree symbol made by

incision, fretwork, embroidery, knitting, fabrics, in textile and ceramics graphics, metallic ornaments and not only, emphasizes the basic elements of the ancient cult doctrines, creating at the same time the technical profile that existed in a certain historical period, **Fig. 3**. The sign's evolution represents a global phenomenon based on the development of technologies and the society's maturation.

a. b. c. d. e. f.

Fig. 3: *a. b. The "Tree of life" woven and represented on carpets (Rădăuți); c. d. The "Tree of life" on embroideries; e. Coat with interpretations of the symbol; f. The "Tree of life" represented on a Moldavian painted plate [2]*

a. b. c. d. e.

Fig. 4: *Precious metal objects with the "Tree of life" symbol:* ***a.*** *The "Tree of life" on the silver fibula, Ostrovul Mare, 4th century B.C.;* ***b.*** *The "Tree of life" on the gold bracelet, Sarmisegetuza Regia, 2nd – 1st century B.C.;* ***c.*** *The "Tree of life" on the silver bracelet, Valisoara;* ***d.*** *The "Tree of life" in the shape of a fir tree on a gold ring, Romania, 2nd century A.C.;* ***e.*** *The "Tree of life" in the shape of a fir tree on a gold ring, 1st – 2nd century A.C. [2, 6]*

2.2 Using the "Tree of life" symbol in the field of jewellery

The symbol can be found in the adornment of various objects, offering aesthetical and material value to them. Since ancient times to the present moment, the symbol is applied, in various interpretations, on different jewels, **Fig. 4** and **Fig. 5**. The development of technologies has allowed these symbols to be transposed by designers into an aesthetically reinterpreted manner, with a focus on the guide mark's quality. The area of artistic possibilities of interpreting and reproducing the details of a symbol is getting broader, the artist having the advantage of 3D technologies, **Fig. 5. b, c, d**.

a. b. c. d.

Fig. 5: a. *The "Tree of life" in the shape of a fir tree multiplied on silver helmet plated with gold, Agighiol; b. c. d. The "Tree of life" in different contemporary stylistic interpretations, applied on silver [2, 6]*

3. TECHNOLOGIES USED IN JEWELLERY DESIGN

Fig. 6*: The way of making a silver pendant with the "Tree of life" symbol. The symbol is made by the designer Negru Diana in relief (in two graphic variants)*

3.1. The jewel as expression of the relationship between symbol, material, technology

Jewellery designers have aesthetically exploited the sacred symbols. By associating the symbol's power with the qualities of the precious metal (silver), elements with a common history trail [3], the designer creates jewellery with an aesthetic impact, psychological qualities and material value, capitalizing both the symbol's graphic, as well as the aesthetic, mystical, septic and technologic qualities of silver. Creating a piece of jewellery means choosing: the design, the material, the semi-finished goods and the fabrication process. The objective is obtaining pieces with aesthetic surfaces of high quality, having an aesthetically and technically controlled rugosity, and with a good mechanic toughness. The technologies used in jewellery processing must ensure a material and manual labour economy, a pleasant aesthetic look without defects or traces of processing [4, 5]. The elements of detail designed by the jewellery designer, with various

significations and symbols, are reproduced through working techniques and materials with different colours and structures, having the ability to generate aesthetic creations (through size, materiality, lustre, contrast) compatible with the outfit, emphasizing the user's personality.

Nowadays, the fabrication process of jewellery represents a combination of traditional manual methods and modern techniques, fact which allows processing, finishing and fixings with a high degree of precision and accuracy. The used materials are precious metals or common metals.

3.2 Traditional processing technologies

Processing a piece of jewellery through classic methods is made by splinting, cold or hot plastic deformation and casting. Currently, manual processing (which requires a long period of time, a big quantity of material and hard manual labour) makes complex jewellery design difficult in order to satisfy the sophisticated requirements of customers.

3.3 Modern processing technologies

3D printing is a simple and fast method of making an object. Through fast prototyping, the ideas, sketches, 2D planes and 3D models can become real objects in a very short time. Unlike traditional methods of fabrication, 3D printing allows the designer to quickly visualise the concept, to offer micro geometric details which aesthetically improve the jewel's macro geometry. [7] The designer's role in creating jewellery represents its transformation from a market product into an art object. The modern processing technologies offer the possibility to make details, processing, welds, mounting and finishing hard to equal through manual processing. After the concept, the computer model with fine details, difficult to realise with traditional tools, the master model is then made from a special epoxydic wax made on a 3D micronic machine, afterwards following the making of the moulds, the casting with programable machinery and the finishing.

3.4 The steps of making a piece of jewellery with the "Tree of life" symbol

The steps of making a jewel concept with the "Tree of life" symbol, are presented in **Fig. 6**: generating the ideas; choosing the best solution; the 3D project (through the 3Design Cad, 3D Rhino Gold, Matrix programs); conceiving and creating the wax master model (in which the models are fixed) on the "printer"; its setting into a metal cylinder over which a paste is placed using vacuum, paste which solidifies and copies the details of the wax models, resulting a multi mould; the placing of the metal cylinders in a computerized oven programmed at a sequential baking cycle at high temperatures for melting the wax, obtaining the details of wax models impregnated on the negative; the casting of the silver at high pressure and controlled temperatures; the cooling of the metal cylinder after casting in water bath (water jet of min. 120-160 bars), resulting the autocleaning of the hardened paste cylinder through drying and baking (due to hot water bubbling); cleaning the slag generated by the incandescent metal, in a pickling solution, followed by a supplementary cleaning in an ultrasound bath; after pickling, the precious metal trees are prepared to be introduced in the technological steps of processing through debiting, micro-splinting, micro-locksmith, micro-finishing and polishing (automatized, semi-automatized and manual). **The modern processing techniques of jewellery** used in this study have numerous **advantages**: cost reduction, design optimization, personalisation opportunity, lowering the production time, material economy, promoting the principle of sustainability, recycling and planned recovery. The process of fast prototyping helps in: improving the communication manner regarding the development of new products, the shortage of the design cycle, superior quality, model precision, elimination of errors, innovation, the optimization of the collaboration between clients, designers and marketing.

Fig. 7: *The Tree of life in various stylistic interpretations, applied on silver, designer Negru Diana*

For the experiment regarding the application of the stylised "Tree of life" on a piece of jewellery, the designer tried to transpose the aesthetic detail stylised differently, on different geometric shapes presented in **Fig. 7.** The resulted models, in which micro geometry and macro geometry, the precision of 3D technologies and the proprieties of the metal material, the silver, confirm the aesthetic and technic requirements. The designed and 3D produced pendants, with full and empty detail elements, geometric shapes with closed or open outlines, outline with connection rays which are bigger or smaller to sharp angles, as well as imprints or engravings applied on different depths, in positive or negative relief, express the aesthetic quality and technique accuracy.

4. CONCLUSIONS

Applied from ancient times on different interpretations, the tree of life was, is and will remain an inspiration symbol with an aesthetic value, proving cultural continuity, the technical level of a certain historical period and the existence of globalisation. Updated and reinterpreted, made of various materials, through various technologies with different aesthetic effects of the surfaces, the symbol shows the aesthetic refinement and the technologic support capable of expressing the quality of the concept of design. Full and empty, in positive or negative relief, through shiny or mate surfaces, using different materials and technologies, the designer generates various objects with aesthetic value which can express messages to the society. The paper points out the efficiency and the importance of 3D technologies in the jewellery design. Using a Neolithic inspiration source, having as objective the satisfaction of the modern client (styled and educated) and having state-of-the-art technologies, the designer can create jewellery with a potential of transmitting emotional messages in a short time, ensuring the concept's quality.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

INVESTIGATION OF DIFFERENT REDUCING AGENTS OF AZO DYES FROM TEXTILE MATERIALS

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Abstract: *Toxicology of textiles is a subject of increasing interest, because of the presence of dangerous compounds in clothes generated from dyeing and finishing processes. In order to protect human health, numerous regulations (Oeko Tex Standard 100, REACH Regulation) limit the presence of dangerous chemicals, such as aromatic amines, generated by reductive cleavage of azo dyes, by no more than 30 mg/kg of textile material. The objective of this work was to investigate different methods of azo dyes reduction from colored textile specimens, in order to determine the procedure with the highest selectivity and sensibility. Aromatic amines are generated by chemical degradation achieved by the cleavage of the azo linkage using reducing agents.Different alternatives to sodium dithionite, reducing agent recommended by standard method ISO/FDIS 14362-1 were tested, such as: sodium sulfite and tin chloride. Also, xylene extraction, the common procedure for synthetic fibers was also performed for cotton, dyed with azo dye Direct Blue 6, in order to assess the reliability of common simultaneously extraction and reduction of direct dyes from natural fibres. Sodium ditionite remains the popular choice for reducing agent, since it provides efficient cleavage of azo linkage, generating specifically carcinogenic amines. Both liquid and gas chromatography analytical techniques were used for precise quantitative determination of generated compounds.*

Key words: *carcinogenic amines, azo dyes extraction, ecotoxicology, liquid and gas chromatography*

1. INTRODUCTION

Worldwide consumer standards have changed over the years, due to continuous improvement of people's living standards. Even in textile industry, the preferences are headed towards ecological, non-toxic and environmentally friendly textile products. The focus regarding ecotextiles is primarly on materials that may come into direct or prolonged contact with the human skin or oral cavity, such as clothing, bedding, towels, wigs, hats, nappies and other sanitary products, etc. Regulations as Oeko Tex Standard 100 [1] and REACH [2] limit the usage of azo dyes in textile and leather products due to their risk associated with tumours of the urinary bladder and carcinoma of the renal pelvis [3]. The maximum limit established in textile materials for aromatic amines, generated by reductive cleavage of azo dyes, is 30 mg/kg. The main goal of this paper was investigation of different methods of azo dyes reduction from colored textile specimens, in order to determine the procedure with the highest selectivity and sensibility. Aromatic amines are generated by chemical degradation achieved by the cleavage of the azo linkage using reducing agents [4]. Different alternatives to sodium dithionite, reducing agent recommended by standard method ISO/FDIS 14362-1[5] were tested, such as: sodium sulfite and tin chloride [6, 7]. Also, xylene

extraction, the common procedure for synthetic fibers was also performed for cotton, dyed with azo dye Direct Blue 6, in order to assess the reliability of common simultaneously extraction and reduction of direct dyes from natural fibres.

2. EXPERIMENTAL PART

2.1 Materials

Textile material: knitted cotton 188g/m2 weight; 0.927 mm thickness.

Chemical reagents:

- Xylene, mixture of izomers (Sigma Aldrich)
- Sodium sulfite (Merck)
- Tin chloride (Merck)
- Acetonitrile, ultrapure water, methanol form Sigma Aldrich (Germany).
- Analytical standard of 24 aromatic amine from Sigma-Aldrich and Dr. Ehrenstorfer GmbH (Germany) -> for quantitative determination using calibration curve.

2.2 Method

The cotton knit was dyed using equipment RedKrome REDP - Ugolini. Dyeing recipe is described as follows: Direct Blue 6 dye, 3% mass concentration and NaCl solution 20 g/L were maintained at 98ºC for 60 min (**Fig.1**);

- the material was rinsed as follows: at temp. 70ºC- for 15 min
  at temp. 40ºC- for 15 min
  at temp. 20ºC - for 15 min

Fig. 1: *Cotton knit dyed with azoic dye Direct Blue 6*

For aromatic amines determination from textile azo dyes, standard method ISO/FDIS 14362-1 has been applied, alterations of this method being specified in the following. Four textile samples were cut into narrow strips and weighed, as to obtain about 1 g of material/each sample; they were treated as follows:

Sample 1: dye extraction in xylene (although the procedure is specific only to synthetic fibres, we were interested to determinate the extraction products obtined in case of a natural fibre).

Textile material was hung by a inert hook to a refrigerent and introduced into 50 mL round-bottom flask; dyed textile sample was kept in a refrigerent above 25 ml extraction solvent (xylene) for 40 minutes, droplets leaking from the fabric became colorless; the organic extract was allowed to cool down to room temperature, and then the solvent was evaporated in a rotary evaporator for extract concentration (**Fig. 2**); the azo bond cleavage was performed using reducing agent sodium dithionite, 200 mg/mL.

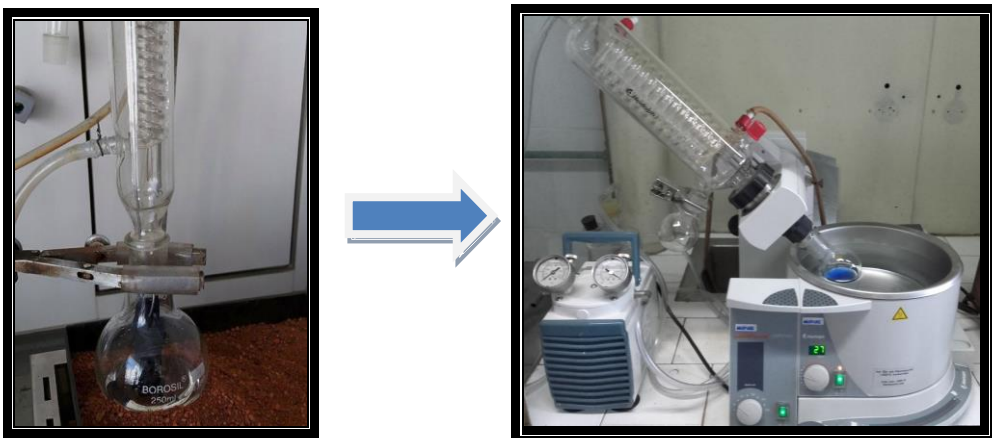

***Fig. 2**. Extraction unit for the extraction of dye and rotary evaporator*

Sample 2: direct dye reduction and cleavage of azo bond, using sodium dithionite, 200 mg/mL
Sample 3: direct dye reduction and cleavage of azo bond, using tin chloride, 200 mg/mL
Sample 4: direct dye reduction and cleavage of azo bond, using sodium sulfite, 200 mg/mL

2.3 Qualitative and quantitative determination of aromatic amines

Instrumentation

HPLC separation was performed on Agilent 1100 LC System using an Agilent Zorbax Eclipse XDB C18 column with detection on Agilent MWD 1100. GC separation was performed on Agilent 6890 GC System coupled with Agilent 5973N transmission quadrupole mass spectrometer, using standard method ISO/FDIS 14362-1.

3. RESULTS

Sample 1

In case of Sample 1, that was subjected to extraction procedure, no aromatic amines were obtained (**Fig. 3, Table 1**), only radicals of azo dyes (alpha-methyl-benzenemethanol, 2-methyl-benzaldehyde) were generated, which means that for natural textiles there is no need for dye extraction, this type of samples can be directly subjected to reductive cleavage of azo bonding.

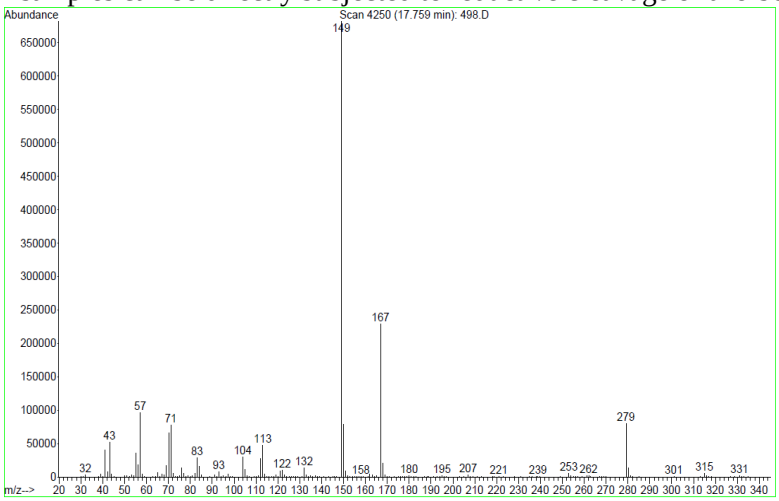

***Fig.3:** Mass spectrum of Sample 1*

Table 1: *Compounds identification using NIST database*

Compound	Area (%)	Name	CAS #
1.	22.88	alpha-methyl-benzenemethanol	001445-91-6
2.	67.04	2-methyl-benzaldehyde	000529-20-4
3.	10.07	3-methylbenzyl alchool	000587-03-1

Sample 2

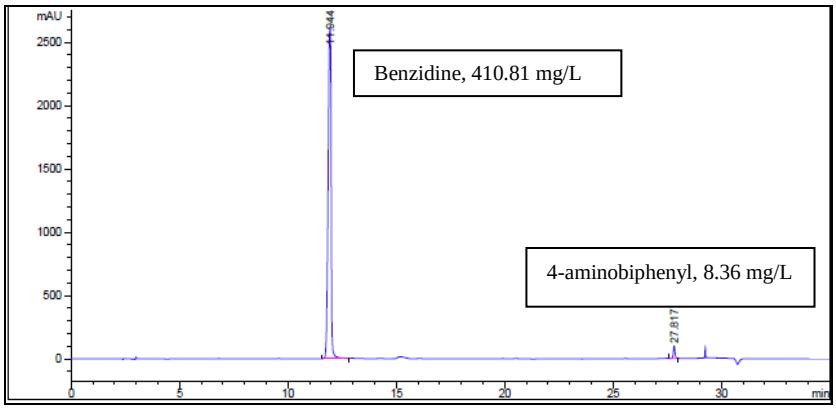

Fig. 4: *HPLC chromatogram of Sample 2*

For sample 2, results indicate a high amount of aromatic amines resulted from degradation of azoic dye, benzidine and 4-aminobiphenyl (Fig. 4); HPLC quantitative results were also confirmed by GC-MS technique (Fig. 5).

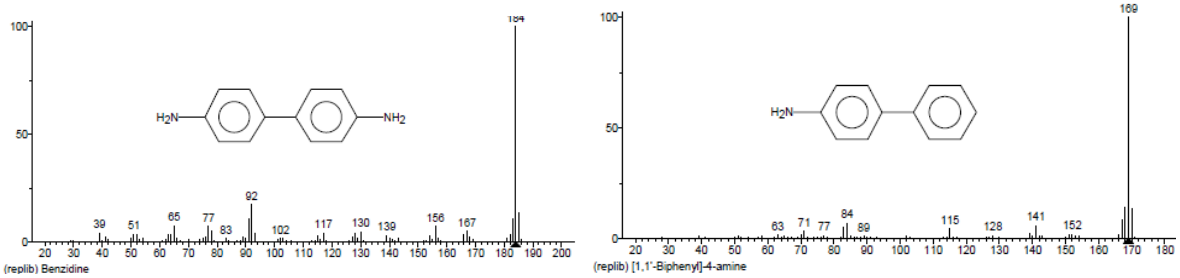

Fig. 5: *NIST confirmation by GC-MS of benzidine and 4-aminobiphenyl*

Sample 3

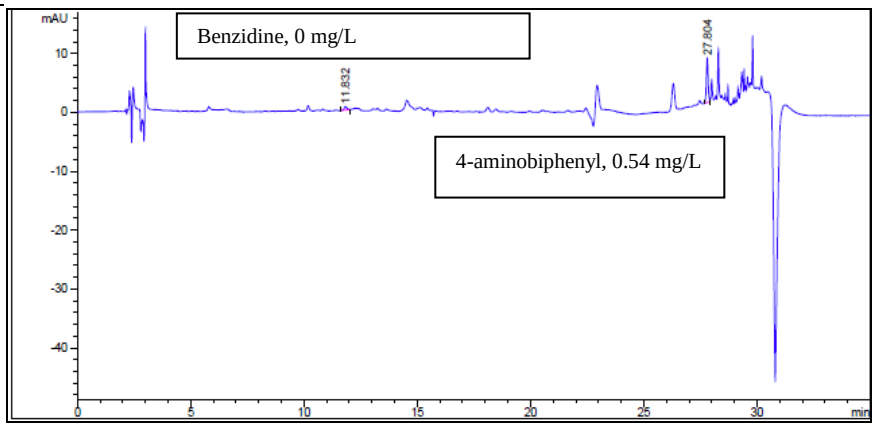

Fig.6: *HPLC chromatogram of Sample 3*

Tin chloride, reducing agent used for cleavage of azo bonding proved to be inefficient in degradation of Direct Blue 6 in aromatic amines (Fig. 6).

Sample 4

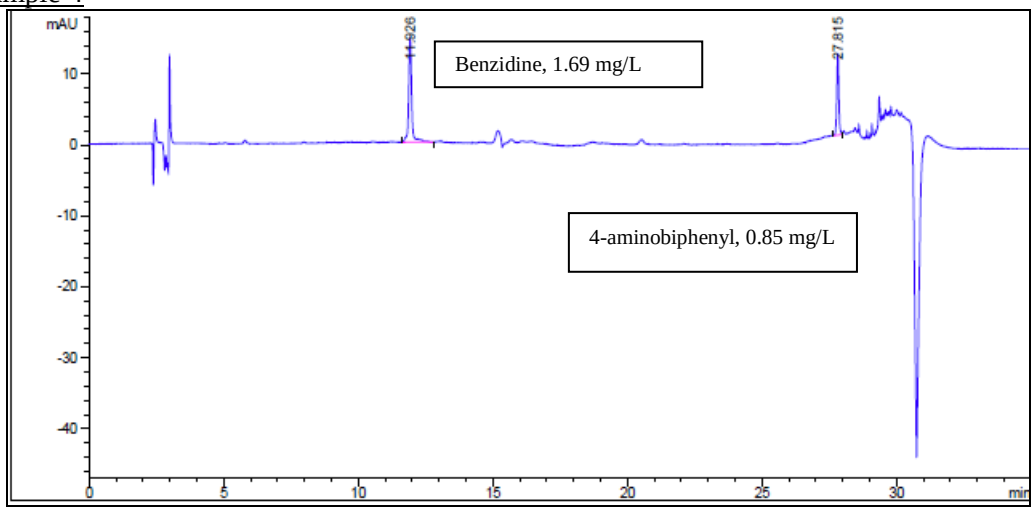

Fig.7: *HPLC chromatogram of Sample 4*

Sodium sulfite, however, managed to reduce the colorant to benzidine and 4-aminobyphenil, but in smaller quantities compared to sodium dithionite (Fig. 7).

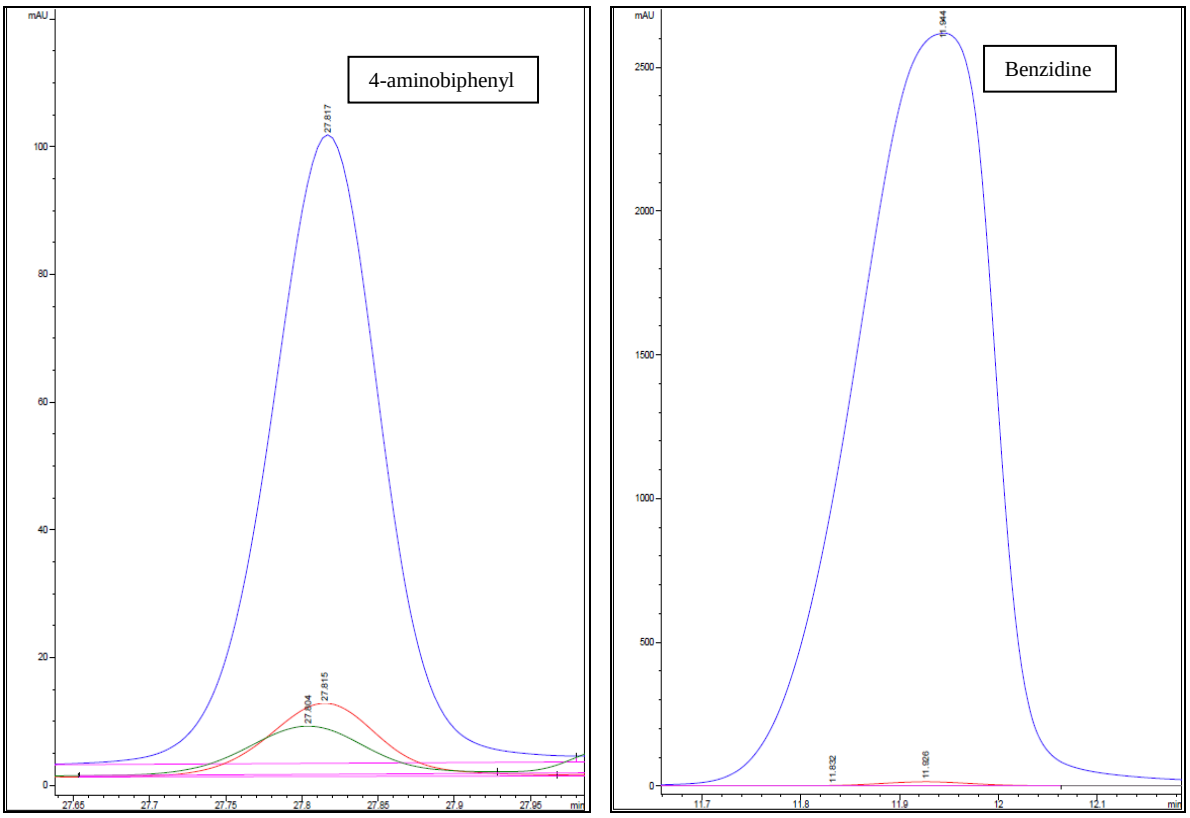

Fig.8: *Overlaid HPLC chromatograms of 4-aminobiphenyl (left) and benzidine (right) in samples 2 (blue), 3 (red) and 4 (green)*

4. CONCLUSIONS

Detection of right amount of carcinogenic amines can be made if complete degradation of azo dye is realized, cleavage of azo bonding being possible only with efficient reducing agents; sodium dithionite proved to totally degrade dye solution and form easily detectable aromatic amines.

ACKNOWLEDGEMENTS

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

AN INVESTIGATION ON PROPERTIES OF SIRO-SPUN YARNS

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Abstract: *Conventional ring spinning is known as traditional spinning system and it is most widely used system in textile industry. Despite being the most prevalent system and supplying approximately 60% of short-staple yarn production, there are still some limitations as lower production rate, longer production flow and higher production costs. That is why, researches in textiles started to accelerate to develop alternative spinning systems. Siro-spun spinning system which is an important type of twist spinning, had been developed with the aim of reducing yarn manufacturing costs by eliminating plying and twisting processes in the production flow. The main principle of Siro-spun spinning is to feed two parallel fibre strands in drafting zone and allow these two fibre strands twist together on each other when they leave the front roller. In this study, it was aimed to compare the properties of two ply yarns produced by ring spinning system and Siro-spun spinning system. For this purpose, properties of Ne 40/2 yarns made of cotton, Tencel, polyester and micro Modal were analysed. Results showed that Siro-spun yarns have lower hairiness and unevenness than ring-spun yarns, besides mechanical properties of both spinning systems are approximate. Besides the advantages in terms of production costs, it can be also concluded that Siro-spun spinning system is a strong alternative of conventional system in terms of many yarn characteristics.*

Key words: *Siro-spun spinning, twist spinning, plied yarn, micro Modal*

1. INTRODUCTION

Doubling and twisting processes which are used in conventional spinning technology are generally applied by low productive and low efficient machines. Besides; the fact that the twisting and winding processes are performed by the same element, causes some technological limitations. These limitations triggered new investigations and new developments on spinning technology. One of them is called twist spinning.

It can be modified a conventional ring-spun machine to a twist spinning machine easily by changing and adding couple of machine parts. As we can eliminate doubling and twisting processes, twist spinning technology provides us numerous important advantages such as lower energy and machine costs, lower investments and expenses [1].

Siro-spun spinning is one of the most widely used spinning technology invented by CSIRO and IWS in early 80's [2]. The main principle in Siro-spun is, two parallel fibre strands are drafted simultaneously in the drafting zone. These two fibre strands twist together on each other when they leave the front roller [3].

The most important difference between ring-spun plied yarns and Siro-spun yarns is the twist directions of single yarns which forms two ply Siro-spun yarns and the final twist direction of Siro-spun yarns are same. It means if Z twisted single yarn has been used to form a Siro-spun yarn,

the final twist direction will be also Z as shown in Figure 1. That is why Siro-spun yarns have lower hairiness and smaller yarn diameter. According to Figure 2, the fibres of plied yarn with unidirectional twist produced by the twisting machine are orientated at right angles to the axis of the folded yarn. However, with Siro-spun yarns, fibres always have an incline to the axis of the plied yarn [4]. This orientation difference makes ring-spun yarns more voluminous and hairy.

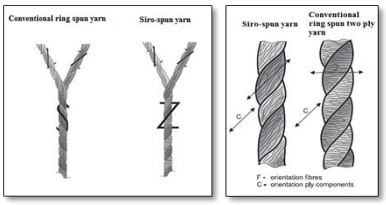

Fig. 1: *Twist directions and fibre orientations of conventional ring-spun yarns and Siro-spun yarns [4]*

In literature, there are many studies on properties of Siro-spun spinning and the comparison between ring spinning and Siro-spinning. Mansour and Tawfik [5] studied on the technology of Siro-spun spinning and its working principle by comparing yarn strength level of Siro-spun yarns and ring-spun yarns. Sun and Cheng [6] compared yarn structures of cotton Siro-spun yarns and ring-spun yarns according to their longitudinal and cross sectional view. Bedez Üte and Kadaoğlu [7] produced ring and Siro-spun viscose yarns in different yarn counts, twist multipliers and strand spacings to investigate effects of multiplicity in production parameters to yarn properties and aimed to compare strength and hairiness of viscose ring and Siro-spun yarns. In the end of this research it was seen that, Siro-spun yarns have lower hairiness and to obtain the maximum level of strength, it is proven to use the optimum stand spacing between two fibre strands.

Siro-spun spinning allows the textile industry to use a wide range of raw material and provides a production in a large variety yarn counts. In addition, we can easily obtain mouline yarns and serve new fabric qualities to the market by using the advantage of feeding two strand at the same time of Siro-spun spinning.

Establishing and adopting innovations instead of conventional systems is a highly costly investment all over the world and has a commercial risk, too. This new system called Siro-spun spinning technology, aims to increase both speed and efficiency of production with some machine parts that can be mounted on the ring spinning machine without requiring a new system to be reconstruct.

2. EXPERIMENTAL

In this study 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester two-plied ring-spun yarns and Siro-spun yarns were used. The yarn counts of Siro-spun and ring-spun yarns are Ne 40/2 for all raw materials. First of all, Ne 40/1 ring-spun yarns in Z twist have been produced by using 1000 TPM. After the application of doubling process the final yarn count of ring two ply yarns became Ne 40/2 in S twist and the last obtained twist amount became 500 TPM for all components. Secondly, Ne 40/2 Siro-spun yarns in Z twist have been produced by using 500TPM.

Table 1 shows linear density and cut length values of raw materials used in this study.

Table 1: *Properties of raw materials used*

Raw material	Linear Density (dtex)	Cut Lenght (mm)
Cotton	1,4	29,5
Tencel	1,3	38
Polyester	1,3	38
Micro Modal	1,0	38

All samples were conditioned in standard atmosphere (65% RH and 20±2°C) and tested according to machine specifications. To compare the physical, structural and mechanical properties of Siro-spun yarns and two-plied yarns such as unevenness, hairiness, imperfections, breaking force and elongation, Uster Tester 5 and Uster Tensorapid were used. Hairiness values (H, sh, S3, S1+2) were tested by Uster Tester 5 S800 and Uster Zweigle Hairiness Tester 5. Lawson Hemphill CTT tester was used to measure friction properties between yarn-to-metal, yarn-to-ceramic and yarn-to-yarn.

3. RESULTS AND DISCUSSIONS

Properties of 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester two-plied and Siro-spun yarns were statically analysed by using ANOVA at $\alpha = 0.05$ and examined by graphs for confidence interval at 95%.

3.1.Hairiness

According to the test results of Uster Tester 5 S800 (H, sh), hairiness values of Siro-spun yarns are lower than ring-spun yarns also in all raw material groups (Figure 2). Besides, according to the test results of Uster Zweigle Hairiness Tester 5 (S3, S1+2), Siro-spun yarns in all raw material types have approximate values of ring-spun yarns (Table 2). A general analyse of the effects of spinning system on hairiness of yarns shows that spinning technology is statistically important for H and sh hairiness values in all raw material groups. S3 and S1+2 values are not statistically important for cotton, Tencel and polyester yarns but important for micro Modal yarns. Table 2 shows the results of analysis of variance.

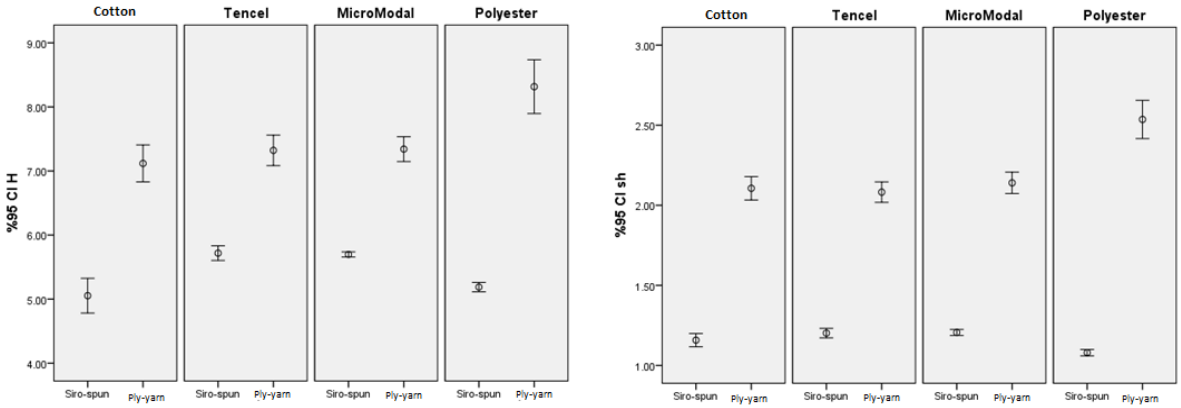

Fig. 2: *Hairiness values of 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester ring and Siro-spun yarns (H, sh)*

Table 2: *Significance (p) levels from ANOVA table for hairiness values*

Raw Material	Significance (p)			
	H	sh	S3	S1+2
Cotton	0,000	0,000	0,603	0,340
Tencel	0,000	0,000	0,627	0,132
Micro Modal	0,000	0,000	0,001	0,000
Polyester	0,000	0,000	0,260	0,486

3.2.Unevenness

Comparing unevenness values of two-plied and Siro-spun yarns shows that unevenness values of Siro-spun yarns in 100% Tencel, 100% micro Modal and 100% polyester are lower than ring-spun yarns and 100% cotton Siro-spun yarns have also a very similar test results with ring-spun yarns which can be entitled as competitive. Graphs are given for this values in Figure 3. ANOVA results also show that, spinning technology is statistically significant for unevenness values of Tencel and micro Modal yarns but unappreciable for cotton and polyester.

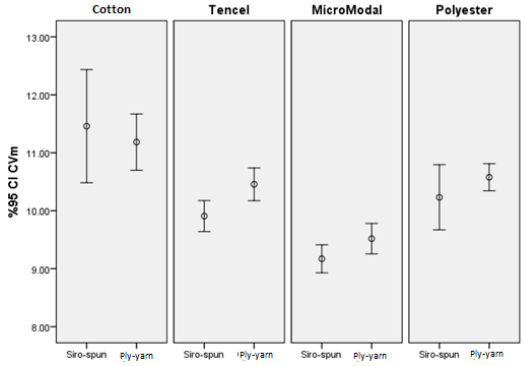

Fig. 3: *Unevenness (%CVm) values of 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester ring and Siro-spun yarns*

3.3 Imperfections

Thin places (-50% /km), thick places (+50% /km) and neps (+200% /km) were measured by Uster Tester 5 S800. Figure 4 shows the graph for confidence intervals at 95% which belong to imperfection values. ANOVA data shows us that spinning technology isn't statistically significant for imperfection values of thin places (-50% /km). Besides, we can generally determine that values of thick places (+50% /km) and neps (+200% /km) are relatively higher for Siro-spun yarns. The most possible reason for this situation could be the uncontrolled strand transportation in the drafting zone while producing the Siro yarns. In addition, Tyagi and his colleagues explain the reason of higher neps quantity as; using more dense fibres in Siro-spinning can be a cause of having more neps on Siro-spun yarns [8].

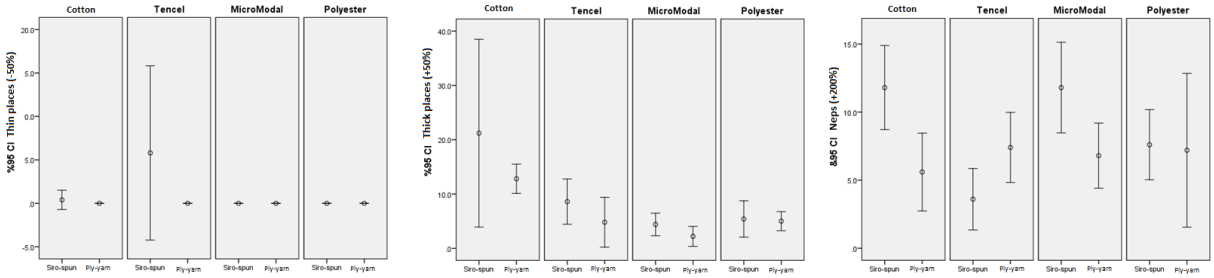

Fig. 4: *Thin places (-50%/km), thick places (+50%/km) and neps (+200%/km) values of 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester ring and Siro-spun yarns*

3.4 Mechanical Properties

In order to compare mechanical properties of yarns, breaking force (cN) and breaking elongation (%) were measured by Uster Tensorapid. ANOVA results show that spinning technology is important for all raw material groups for breaking force. Besides, breaking elongation is statistically significant for 100% Tencel, 100% micro Modal and 100% polyester but not significant

for 100% cotton. Although breaking force of polyester Siro-spun yarns are higher, ring-spun yarns shows higher values for other raw materials. Furthermore, breaking elongation values of cotton, polyester and micro Modal Siro-spun yarns are higher than values of conventional ring-spun yarns. Results are illustrated in Figure 5.

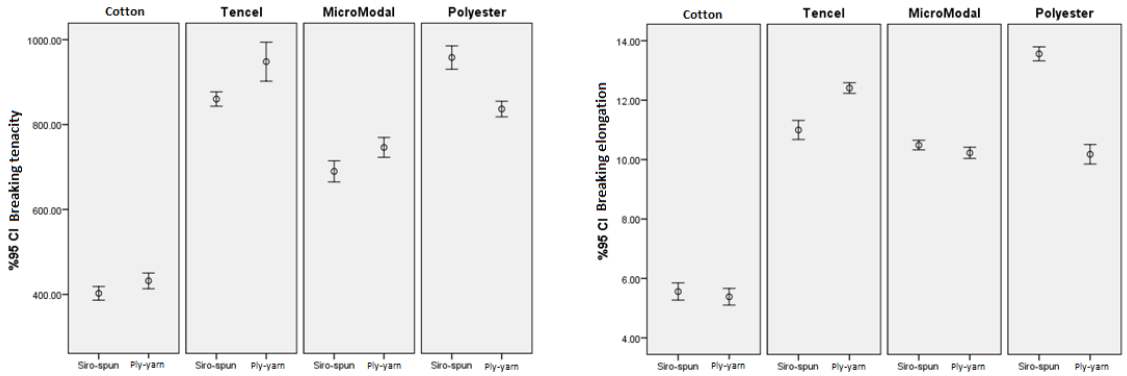

Fig.5: *Breaking force (cN) and breaking elongation (%) values of 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester ring and Siro-spun yarns*

3.5 Friction Properties

To analyse yarn friction properties, tests were performed under three main topics such as yarn-to-yarn, yarn-to-metal and yarn-to-ceramic friction properties. Yarn-to-yarn friction properties were calculated by using Equation 1. Equation 2 was used to calculate yarn-to-metal and yarn-to-ceramic friction properties. Figure 6 shows us, ring-spun yarns and Siro-spun yarns have quite approximate values for yarn-to-metal and yarn-to-ceramic friction. Nevertheless, Siro-spun yarns in all raw material groups show superior values compared to ring-spun yarns in yarn to yarn friction. This result could be concluded as lower value of yarn-to-yarn friction cause lower hairiness level.

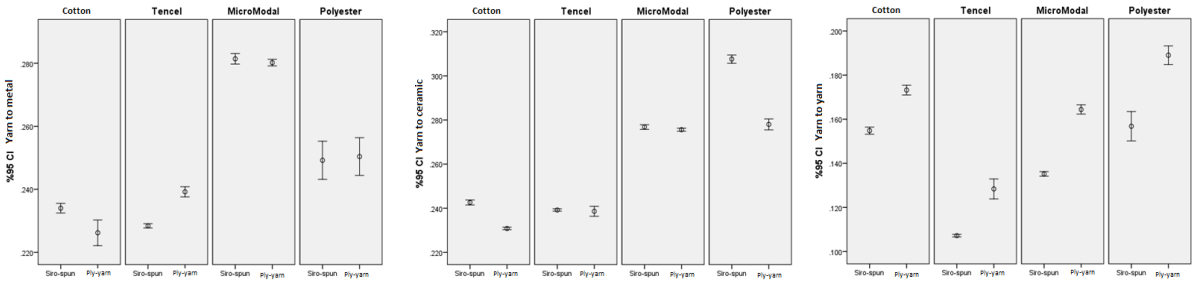

Fig. 6: *Yarn-to-yarn, yarn-to-metal and yarn-to-ceramic friction properties values of 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester ring and Siro-spun yarns*

4. EQUATIONS

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

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

5. CONCLUSIONS

In this study 100% cotton, 100% Tencel, 100% micro Modal and 100% polyester ring-spun yarns and Siro-spun yarns were used. It was aimed to compare the Siro-spun and two ply ring-spun yarns in terms of physical, structural and mechanical properties such as unevenness, hairiness, imperfections, breaking force, elongation and friction. Results showed that all hairiness values (H, sh, S3, S1+2) of Siro-spun yarns considering all raw material groups have lower hairiness degree.

For unevenness and imperfection values, results showed us that cotton and polyester Siro and ring-spun yarns have approximate values which makes Siro-spinning a good alternative of ring spinning. In addition, it can be easily found that Siro-spinning has an improving effect on unevenness values of micro Modal and Tencel yarns. Siro-spun yarns and ring-spun yarns have quite approximate quantities of thin places and thick places. Besides cotton and micro Modal ring-spun yarns have lower neps quantities.

In cotton, Tencel and micro Modal Siro-spun yarns, the values of breaking strength is lower than those of ring-spun yarns, but the difference can be ignored for yarn production where strength is not on the priority. In 100% polyester fibers, the tensile strength and breaking extension values of Siro-spun yarns are higher than ring-spun yarns. For Tencel and micro Modal fibers, the Siro-spinning system can be interpreted as a good alternative to the ring spinning system in terms of mechanical properties.

Siro-spun and ring-spun yarns in all material groups shows similar properties in yarn-to-metal friction except Tencel and in yarn-to-ceramic friction except polyester. Polyester Siro-spun yarn has higher coefficient of yarn-to-ceramic friction and Tencel Siro-spun yarn has lower coefficient of yarn-to-metal friction. In all material types, Siro-spinning system has a certain advantage on yarn-to-yarn friction which is a crucial parameter on yarn formation and fabric weaving.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

NATURAL FIBRE COMPOSITES: A REVIEW ON FLAX FIBRES

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Abstract: *In the composite industry, generally glass and carbon fibres are most widely used materials because of their high strength to weight ratio. On the other hand, in recent years, the use of natural fibres as reinforcement in composites have shown some esteem due to their properties such as light weight, low cost, recyclability, biodegradability and an increasing requirement for developing sustainable materials. Some of these natural fibres, such as jute, flax is cost-effective and can be much more in demand due to their specific mechanical properties comparable to the glass fibres. This study focuses on natural fibre composites (NFCs) in which polymeric resins are used as matrix materials. NFCs materials have at least one primary component originated from a biological source. Here, fundamentals of NFC materials are presented according to the reinforcement preforms, matrix resins, which are thermosets or thermoplastics, composite manufacturing techniques and characterization. Since NFCs based on renewable resources can provide feasible low-cost structural components and eco-friendly alternatives to conventional structural materials for many applications such as equipment housings, roofing and in large diameter piping. This review is especially carried out in more detail on the flax fibres which are the recently emerged offers for automotive industry. Additionally, fibre/matrix interfaces of these studies are reported.*

Key words: *NFCs, green composites, flax, mechanical properties, automotive.*

1. INTRODUCTION

Natural fibre composites (NFCs) are composing from reinforced fibres which are derived from renewable and carbon dioxide neutral resources such as wood or plants. NFC composites are generally used where a moderate strength are required i.e. housings, roofing, in large diameter piping for low-cost housing [1]. Natural materials have some advantages such as they are renewable, reasonably cheap, biodegradable and ecologically freindly. More recently sustainable mobility is also important; for instance, European Parliament and the Council reduced the deposition fraction of a vehicle from 15% (2005) to 5% (2015). However, natural fibres have disadvantages too; for example, they show variations in both fibre geometry and in physical properties, have lower mechanical properties, poor interfacial adhesion and incompatibility with hydrophobic matrix resin systems [2]. For this reason, researchers are willing to improve those advantages of NFCs on the reinforced composites such as in automotive industry and other applications. This can be seen in some studies [3],[4],[5] where natural fibres such as sisal,bamboo, jute, flax and wool were used to attain good tensile properties comparable to glass fibres.

This review emphasizes on NFCs in which polymeric resins are used as matrix materials. As is known, NFCs materials have at least one major component derived from a biological origin. The

natural fbres can be used as the reinforcement fibres either long (i.e. flax, hemp, kenaf, jute, ramie and sisal) or short (i.e. wood, wool,) from the fibre processing and/or recycled fibres [6]. The matrix materials can be derived from biomaterials such as various epoxidized plant oils and soy protein [7]. The major ones of the NFC materials are made from a combination of natural fibres and polymeric matrices.

NFCs can be produced with traditional composite fabrication methods such as resin transfer moulding (RTM), vacuum infusion, compression moulding, a direct extrusion and compounding, injection moulding. These different manufacturing techniques can affect various properties on the resulted composite materials. The properties of NFCs, thus, can be modified for various types of applications by choosing appropriate fibres, matrix resins (thermosets or thermoplastics), additives and production method. NFCs can replace the traditional application areas of fibreglass reinforced plastics (FRP) and thermoplastic composites (TPC) by choosing the proper natural reinforcement fibre and its matrix resin. The most common thermoset resins are epoxy, polyester, vinylester, polyamide, polyurethane and phenolics (see Table 1).

Table 1: *Unfilled thermosetting resin properties [8]*

Resin	Density (g/cm^3)	Tensile Modulus (GPa)	Tensile Strength (MPa)
Epoxy	1.2-1.4	2.5-5.0	50-110
Phenolic	1.2-1.4	2.7-4.1	35-60
Polyester	1.1-1.4	1.6-4.1	35-95
Acrylated epoxidized soybean oil/styrene	1.0-1.2	1.0-1.6	15-21

Lately, NFCs are fabricated with bio-based thermosetting resins such as soybean triglycerids. Petrovic et al. 2004 [9] and O'Donnell et al. [10] studied natural fibre/acrylated epoxidized soybean oil composites which are known as bio-based green composites. However, one of the disadvantages may be their component life which may be lower if compared to FRP components. Therefore, it is necessary to obtain better component life, performance and sustainable materials in the future studies. For example, in automotive components, natural fibres can be chosen such as flax, ramie as a replacement of glass fibres. Some of these NFCs i.e. flax and bamboo fibre composites are introduced at the below sections.

2. FLAX FIBRE

As mentioned earlier, natural fibres are used to replace glass fibres [11],[12]; for instance it is estimated that approximately 830,000 tonnes of natural fibres will be consumed by 2020 and hence the total reinforcement materials may go up to 28% [13]. As they are cost effective with low density they will find various places for many engineering applications in the future. Before moving to flax fibre composites, a summary on flax fibre is given below.

Flax is a plant fibre which belongs to *linaceae family* and is one of the widely utilised natural fibres. Records from Babylonia and Anatolia from 3000 BC show that flax was cultivated in Ancient Egypt for its seeds and for linseed oil; it is also one of the oldest to be extracted, spun and woven into textiles where was found in graves in Egypt dating back to 5000 BC [14]. Flax fibres are produced in the stems of flax bast plant and are a cellulose polymer. As its structure is more crystalline than cotton it is therefore stronger too. Flax is also stiffer to handle and is more easily wrinkled than cotton. Length of a flax plant ranges up to 100 cm which has strong fibres along its stem with average fibre diameter 10-25 μm [15]. The micro-structure of a flax fibre is complex due to the hierarchical organisation at different length scale and different materials present in variable

proportions (Fig.1). From the Fig.1, it can be seen that the thickest cell wall is S2. This wall contains numerous crystalline cellulose micro-fibrils and amorphous hemicellulose which are oriented at 10^{o} with the fibre axis that gives the high tensile strength to the flax [16].

Flax fibre consists of cellulose, hemicelluloses, wax, lignin and pectin in different quantities where reported by many authors [17], [18]. This variation of proportions in the constituents of flax fibres is due to the plant variety, agriculture variables i.e. soil quantity, weathering conditions, level of plant maturity, quality of retting process [19]. However, it is well known that flax is rich in cellulose for about 70% of the total chemical composition and this makes it possible to be used as reinforcement in composites. As for the natural fibres such as flax, the main disadvantage is their hydrophilic nature which lowers the compatibility with hydrophobic polymeric matrices during the composite production. On the other hand, natural fibres have low mechanical properties; flax fibres do show better mechanical properties than the most natural ones; especially when retting is done to improve its mechanical properties. Flax looks much agnate to cotton fibre except in pigment intensity [20].

2.1. Flax Fibre Composites

Flax fibre reinforced composites are not only considered in the form of monofilament configuration [21], [22] they can be also processed into mats [23], [24], rovings [25], [26], yarns [27], and fabrics [28], [29] in composites. A series of manufacturing techniques have been developed to produce composites, such as film stacking [24], hand lay-up [5], vacuum infusion, filament winding [27], compression moulding [21], [22], resin transfer moulding (RTM) [23], [26], injection moulding [21] and pultrusion [25].

Flax fibre composites are being used such as in the forms of panels, tubes, sandwich plates, to replace the wooden fittings, fixtures, furniture, and noise insulating panels in the last decade. There is also an increasing demand from automotive companies for materials both with sound reduction capability and lower weight for fuel efficiency. NFCs have excellent sound absorbing efficiency and are more shatter resistant and have better energy management features than glass fibre reinforced composites. In automotive parts, bio-composites not only reduce the mass of the component but also lower the energy needed for production by 80% [30]. Although flax fibres have potential to replace glass fibres as reinforcement in composite, their main disadvantage is the variability in their properties. Environmental effects such as high relative humidity can degrade the tensile properties of these fibres. However, an appropriate chemical curing, i.e. Silane (Si), can increase the breaking strength and strain of the flax fibres (see Fig.2) [31].

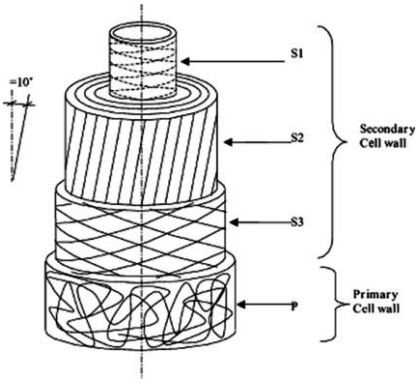

Fig.1: *Flax fibre cell [16]*

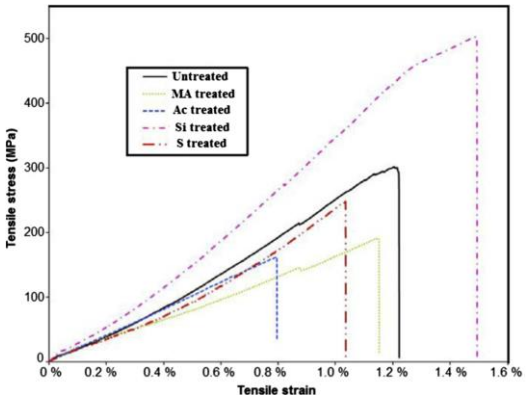

Fig.2: *Stress-strain diagram of untreated and chemical treated flax fibres [31]*

Also, the tensile properties of flax fibres are not consistent along its length. Their tensile strength and modulus can decrease with an increase in fibre length, fibre diameter and gauge length. Therefore, because of flax fibres at the mid-span and tip in the stem have high content of cellulose [32], it is suggested to use as raw materials for flax fibre reinforced composites.

Before using flax fibre as a reinforced material, another important object is fibre surface condition which is critical for interfacial bond between fibre and matrix. Hence, alkali treatment is beneficial to clean the fibre surface, modify the chemistry on the surface, lower the moisture uptake and increase the surface roughness prior to the composite production [5] (see Fig.3. and Fig.4.). It was observed that dewaxed flax fibre reinforced composites exhibited better impact energy absorption capability when compared to untreated flax fibre reinforced composites.

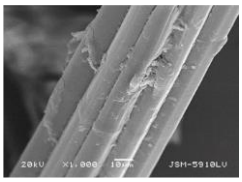

Fig.3: *Dewaxed flax fibre (X1000) [5]*

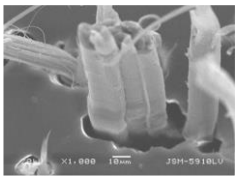

Fig.4: *Izod impact test of untreated flax fibre reinforced composite (X1000) [5]*

3. GREEN COMPOSITES FOR AUTOMOTIVE INDUSTRY

Automotive industry has been pioneer for the long NFCs. Comparing to glass, natural fibres with low density reduces vehicle weight and consequently lowers fuel consumption. It is estimated that no more than 50 kg of natural fibres can be used in a car. This corresponds to a reduction of about 10 kg if glass fibre composites are replaced with natural fibre composites in an automobile. If the weight of a car can be reduced by 10 to 20 kg, the effect on the environment will be significant. The European car production is about 55000000 cars/year. This indicates that more or less 1000000 metric tons of natural fibre materials are targeted for the consumption in the automotive industry.

Today, beside flax, other plant-based fibres i.e. hemp, sisal, jute are also used to produce various parts in automotives; for example, door and trunk panels, headliners, floor panels, dashboards, insulations. NFCs can also be formed in various degrees of strength and rigidity.

Compression moulding is one of the simple production methods for the automotive industry and can take advantage of non-woven mats that can be impregnated with thermoplastics or thermosets. Recently, the automotive industry has also shown a lot of interest in injection mould NFCs for lower cost interior or exterior panels. Germany is the leader in the green composites and the German auto manufacturers have taken the initiative to introduce NFCs for interior and exterior applications. As am example, the first commercial inner door panel was made of 35% Baypreg F semi-rigid (PUR) elastomer from Bayer and 65% of a blend of flax, hemp and sisal [33].

4. CONCLUSIONS

NFCs with an appropriate matrices exhibit promising mechanical properties such as in flax fibre reinforced composites. A major limitation of using flax fibres as reinforcement in composites is their inconsistency. However, this may overcome if appropriate alkali treatment is carried out prior to composite production; therefore, a good fibre/matrix interfacial bonding can be achieved and thereby the tensile properties can be improved. Also, the selection of suitable manufacturing process and physical/chemical modification is very important, i.e. NaOH for bleaching and/or cleaning the surface of the plant fibre to improve its mechanical properties of the flax composites. Flax

composites have the potential to be the next generation materials for structural application for automotive industry and for other consumer applications. Imminent studies on flax composites can be attentive to understand environmental assessment, durability, improving the mechanical properties and moisture resistance. We also believe that, novel manufacturing processes and surface modification methods can be developed in the future.

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ANNALS OF THE UNIVERSITY OF ORADEA
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EFFECT OF REACTION CONDITIONS ON THE HYDROLYSIS OF WOOL KERATINS

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Abstract: *Every year millions of tons of keratinous wastes are generated worldwide, therefore from an economic and environmental point of view, it is worthwhile developing processes to use and reuse these resources. Many different procedures and methods can be applied to obtain keratin hydrolysates. Microwave heating is based upon the ability of a particular substance to absorb microwave energy and convert the electromagnetic energy to heat (kinetic energy). An extension of this is application in the field of proteomics (the study of proteins and in particular their structure and function). Large complex proteins can be broken into smaller parts by using microwave heating. This work aimed to perform microwave-assisted hydrolysis of wool keratin wastes in different experimental conditions, and compare it with a conventional method of alkaline hydrolysis, in order to study the efficiency of the treatment induced by this field on the reaction products, subsequently analyzed by specific methods. It was studied the influence of the reaction conditions (reaction time and working recipe) on the keratin hydrolysis yield, and also were analysed the structural changes induced by hydrolysis. A significant reduction of reaction time concurrent with a higher hydrolysis yield was obtained by microwave hydrolysis regardless of the alkali mixtures used; better results were obtained for 60 min treatment. IR analysis performed highlight the structural modifications induced by hydrolysis conditions, the process carried out by means of microwaves leading to a lower degradation of hydrolysis products.*

Keywords: *alkaline hydrolysis, microwave heating, keratin hydrolysates, IR analysis.*

1. INTRODUCTION

Keratin proteins are the major components of hair, feathers, wool and horns and represent an important source of renewable raw materials for many applications. Generally, the organic wastes produced from protein materials, can be processed by different physical or physical chemical methods for obtaining products with various utilizations: nutrients for agriculture [1-2], cosmetics (salves and creams based on keratin) [3], geotextiles, thermal and phonic insulating construction materials [4], nanofibrous materials with various applications for coatings, batteries, sensors, tissue engineering, medical textiles [5], etc. There are also studies for using protein residues of wool, feather and hair in mixtures for obtaining fiber-cement plates [6,7]. One group of promising candidates is the wool keratin wastes, which have the biodegradability and biocompatibility to support cell growth [8].

Every year millions of tons of keratinous wastes are generated worldwide, therefore from an economic and environmental point of view, it is worthwhile developing processes to use and reuse these resources. Wool contains up to 95% by weight of pure keratin, but this has high stability, distinctive physical properties and resistance to chemical attacks due to the presence of inter and intra-molecular disulfide bonds of cysteine amino acids in the wool structure. The cross-linking of the protein chains in wool due to disulfide bonds and inter and intra molecular hydrogen bonding results into the higher stability and lower solubility of keratin. Due to its non-reactive character and strong resilience, keratin can be processed only with great difficulty; for this reason it has to be partly hydrolyzed.

Many different procedures and methods can be applied to obtain keratin hydrolysates. Hydrolysis can be carried out in different process conditions, with different chemical agents. The traditional degradation is usually achieved by thermal hydrolysis in dilute acid or base, or by enzymatic hydrolysis. The decomposition products are almost entirely α-amino acids. [9] Keratin can be extracted by cleavage of the cystine disulfide bonds with reducing agents, such as thiols, to form cysteine, or by sulfitolysis with sodium sulfite to form cysteine and cysteine-S sulfonate or using oxidizing agents, such as peracetic acid, to form sulfonic acid [10]. However, the reductive or oxidative agents used for S-S cleavage, namely sulfites, thiols or peroxides, are harmful, often toxic and difficult to handle. Besides, the treatments result in severe degradation of the protein structure of keratin with reduction of the molecular weight and loss of mechanical properties. More recently, green hydrolysis processes, such as treatments with superheated water and by steam explosion, have been proposed with the aim of avoiding the use of harmful, often toxic, agents. Wool fibers were submitted to green hydrolysis with superheated water in a microwave reactor, in view of potential valorization of keratin-based wastes [11-13].

The microwave region of the electromagnetic spectrum is classified as that between 0.3 and 300 gigahertz (GHz). Microwaves, like all electromagnetic radiation, comprise oscillating electric and magnetic fields. Microwave heating is based upon the ability of a particular substance to absorb microwave energy and convert the electromagnetic energy to heat (kinetic energy). An extension of this is application in the field of proteomics (the study of proteins and in particular their structure and function). Large complex proteins can be broken into smaller parts by using microwave heating. By knowing the constitution of these smaller parts, it is possible to piece together the sequence of the original protein [14].

This work aimed to perform microwave-assisted hydrolysis of wool keratin wastes in different experimental conditions, and compare it with a conventional method of alkaline hydrolysis [16], in order to study the efficiency of the treatment induced by this field on the reaction products, subsequently analyzed by specific methods. It was studied the influence of the reaction conditions (reaction time and working recipe) on the keratin hydrolysis yield, and also the structural changes induced by hydrolysis were highlighted by IR analysis.

2. EXPERIMENTAL

In order to conduct the laboratory experiments, the following substances have been used: HCl (Merck), NaOH (grains), CH_3COOH, Na_2CO_3, NH_4OH, trichloroethylene, nonionic surfactant, isopropyl alcohol, ethyl alcohol, acetone, distilled water, pH indicator paper, and coarse wool waste.

The apparatuses used consisted of: thermostatic controlled stove, 750 W microwave oven, reaction vessels, centrifuge, IR-ATR spectroscopy using a DIGILAB–SCIMITAR Series FTS 2000 spectrometer with ZnSe crystal, 750÷4000 cm^{-1} range, 4 cm^{-1} resolution. For wool degreasing a classic Soxhlet installation was used.

In the first stage, wool wastes were subjected to dirt cleaning, then the fibers were cleaned and degreased in a solution of 3% Na_2CO_3 followed by an additional treatment with 0.1% nonionic surfactant solution. Then, the material thus treated was subjected to a final scouring with trichloroethylene in a Soxhlet apparatus for 8 hours; the resulting fibers were dried in a thermostatic controlled stove at 30ºC, then washed with a mixture of water: ethanol (1:1, v/v) and dried again at 25ºC for 24 hours. Subsequently, wool fibers were cut to 1÷2 mm in length in order to subject them to alkaline hydrolysis in different alkaline mixtures. Then wool samples with a weight of 5 g each have been held for 2 hours for prior swelling in 200 ml of the treatment mixture. In these experiments two hydrolysis solutions were used: a) 0.5N NaOH: isopropyl alcohol (3:1, v/v); b) 0.5N NH_4OH: isopropyl alcohol (3:1, v/v). The use of isopropyl alcohol is meant to facilitate a more rapid swelling of the protein matrix of wool.

In a first experimental variant, alkaline hydrolysis was performed with the two solutions in mild conditions (at 60ºC for 3 hours, according [15]); in the second, alkaline hydrolysis was conducted in a microwave oven (fig. 1). Thus, a glass bowl with 5 g of sample in the treatment mixture was put in a crystallizer with 300 ml of distilled water, for heat absorption purposes. The samples was treated under the following conditions: working cycles of 1 min with 30" break, total time 30 and 60 min, respectively, power 750 Watts, frequency 2,45 GHz. After the completion of the alkali hydrolysis, the samples were cooled to 25ºC, and then subjected to decantation/filtration for solide residue removal. The liquide phase was treated with a solution of HCl: distilled water (1:1, v/v) in order to precipitate the protein mixture, finding a wool pH_{iz} = 5. After the separation of the precipitates by centrifuging for 20 minutes with a rotational speed of 8000 rpm, the resulting supernatants were washed three times with a mixture of acetone: ethanol (1:1, v/v) followed by drying in a stove at 25ºC for 24 hours. The sequence of operations for obtaining keratin hidrolysates is shown in fig. 2. Hydrolyzed powder resulted from the liquid phase is shown in fig. 3.

3. RESULTS AND DISCUSSIONS

The extraction yield was determined by the following equation:

$$Y = \frac{W_h}{W_i} 100 \quad (1)$$

where Y is the extraction yield (%), W_h is the weight (mg) of the dried hydrolyzed powder and W_i is the weight (mg) of the initial sample in the dry state. The results obtained for the extraction yield are shown in fig. 4.

From fig. 4 it can be seen that the best values in terms of hydrolysis efficiency were obtained for the samples treated with the mixture of NaOH: isopropyl alcohol, both for the normal hydrolysis treatment and for the hydrolysis carried out by means of microwaves, comparing to the samples hydrolyzed in the same conditions but in alkaline medium using NH_4OH. This is due to increased swelling capacity of this mixture and also to pronounced disulfide bridges breaking in NaOH medium. NH_4OH has weaker basicity and lower swelling capacity and therefore lower access to the two areas (inner and outer) of the keratin matrix, but even in these conditions the yields obtained are satisfactory. Microwaves enhance hydrolysis processes concurrent with the significant reduction of reaction time regardless of the alkali agent used in mixtures. The best results for microwave-assisted hydrolysis yields were obtained for a reaction time of 60 min.

Fig. 1: *Reaction wessel inside of the microwave oven*

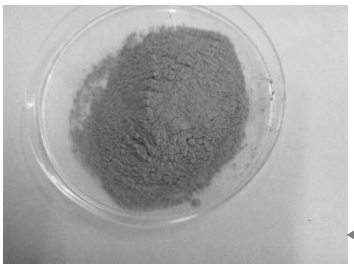


Fig. 3: *Hydrolyzed powder*

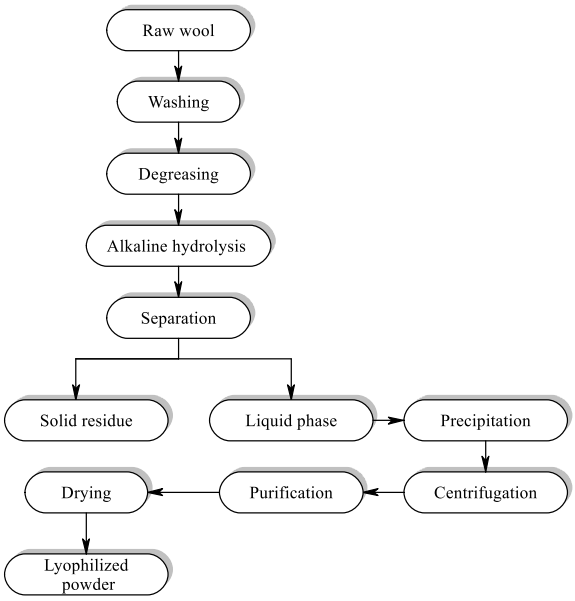
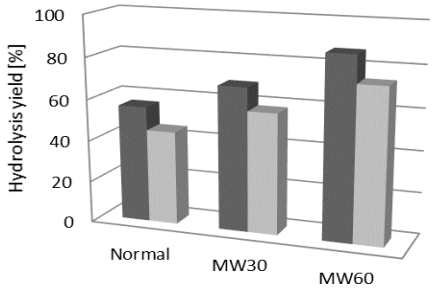


Fig. 2: *The operations flow for obtaining keratin hydrolysates*



	Normal	MW30	MW60
NaOH:isopropyl alcohol	56	69	87
NH4OH:isopropyl alcohol	45	58	74

Fig.4: *Dependence of hydrolysis yield on reaction conditions (Normal: conventional alkaline hydrolysis; MW30 and MW60: microwave-assisted hydrolysis at 30 min and 60 min, respectively).*

Spectral analysis

IR spectra of keratin hydrolysates in different alkaline media along with a control wool sample are shown in the fig. 5 and 6.

In the fig. 5 and 6 the spectra of control sample, show characteristic adsorption bands due mainly to the peptide bonds (-CO-NH-). Amide A and B are found at 3250–3300 cm^{-1}, connected with the N-H stretching vibrations and at ~ 2900 cm^{-1}, respectively, related to stretching modes of the C-H alkyl chains. The region between 1700-1500 cm^{-1} contains the most intense features in the IR spectrum, arising from the amide groups, predominantly from protein structures such as amide I band at ~1650 cm^{-1}, mainly due to the C=0 stretching vibration coupled to the in-plane bending of the N-H and stretching of C-N bonds; amide II band much weaker at ~ 1540 cm^{-1}, due to the coupled N-H in-plane bending and C-N stretching vibrations; and amide III which appears as a weak band at

1240-1260 cm^{-1} resulting from an in-phase combination of C-N stretching and N-H in-plane bending, with some contribution of C-C stretching and C=O bending vibrations.

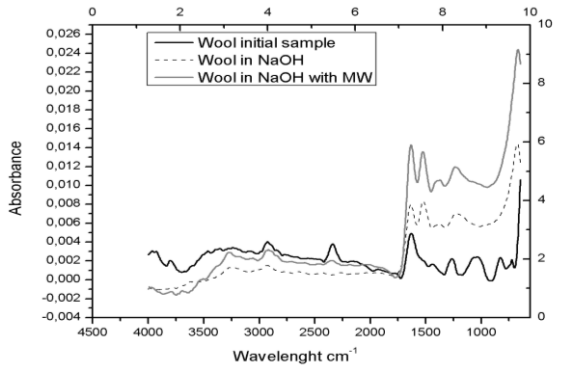


Fig. 5: *IR spectra of keratin hydrolysates in NaOH and in NaOH with microwave, 60 min.*

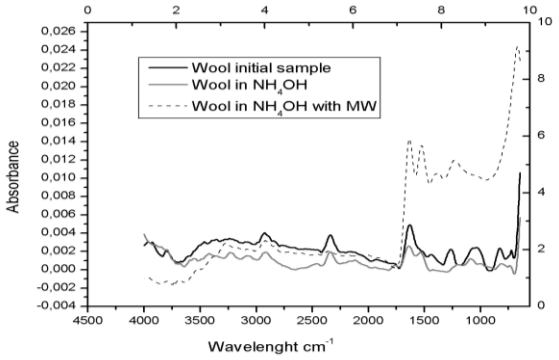


Fig. 6: *IR spectra of keratin hydrolysates treated in NH_4OH and in NH_4OH with microwave, 60 min*

In the spectra of all keratins extracted by hydrolysis, the signal strength in some areas decreases, and wool treated normally in NaOH mixture shows the most attenuated signal, which is due to the degradation of hydrolyzed keratin; the hydrolysis carried out by means of microwaves leads to a lower degradation. The amide I, II and III are the most sensitive probes for the conformational changes in the proteins. The literature [16] suggests that every chemical interference within a keratin fiber leads to a decrease in the share of a-helix as compared with a raw, untreated sample. The amide I adsorption which is known to be sensitive to the secondary structure of polypeptides shows a lower signal intensity for all treated samples, much more attenuated for the normal treated samples; this could be atributted to conformational changes in secondary structure, with a decrease in the α-helix structure, possible accompanied by an increase in the random-coil structure. What is interesting to note is that unlike this attenuation of the vibration of amide I, the signal in the spectral region of the amide II reveals no decrease in hydrolysate samples, which could be determined by a reforming of the α-helix of the amide II after treatment. Amide III remains relatively stable during microwaves hydrolysis. The intense peaks at ~ 1200 cm^{-1}, observed in the infrared spectrum of all keratin treated samples, are related, respectively, to the asymmetric and symmetric S-O stretching vibrations of the cysteine-S-sulfonate residues (bunte salts), formed through the reaction of cystine with sulfites during the hydrolysis of protein from wool. It can also be noted changes in the intensity of the characteristic peaks and of the surfaces in the area of the respective peaks at the wavelength 650 cm^{-1} which is characteristic for C–S bonds. Thus, it can clearly be seen the presence of this peak at the control samples. The alkali: alcohol mixtures treatment strongly affects the disulfide bridges, contributing to their partial dissolution or complete break during the treatment, highlighted on graphic by strong decrease of the peak intensity or even by its disappearance.

4. CONCLUSIONS

1. Hydrolysis yield of wool samples shows that the best results are obtained for the samples hydrolyzed in NaOH, both for the conventional hydrolysis treatment and for the alkaline hydrolysis carried out by means of microwaves, comparing to the samples hydrolyzed in the same conditions but in alkaline medium using NH_4OH.

2. A significant reduction of reaction time concurrent with a higher hydrolysis yield was obtained by microwave hydrolysis regardless of the alkali mixtures used; better results were obtained for 60 min treatment.
3. Even if microwave-assisted hydrolysis using NH_4OH mixtures results in lower reaction yield, it has the advantage that prevents the contamination of the protein hydrolysates, in contrast to hydrolysis in NaOH media that requires additional purification steps.
4. IR analysis highlights the structural modifications induced by hydrolysis conditions, the process carried out by means of microwaves leading to a lower degradation of hydrolysis products.
5. Further studies are considered in order to determine the molecular weights of keratin hydrolysates obtained in different conditions and to identify the possible applications fields.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ECOLABELS FOR LEATHER AND LEATHER PRODUCTS

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Abstract: *Nowadays, there is an increasing demand for consumer goods ecolabelling, coming from consumers concern for adverse environmental impacts of industrial pollution and manufacturers need to protect their existing markets and to expand into new ones. Ecolabels are used to guarantee the purchaser a product meets certain minimum standards relating to its environmental impact during production, use or disposal, and to distinguish the product from competitors in a positive way. In order to be awarded an ecolabel, a product must be certified according to a set of requirements or criteria, with regard to environmental, health and quality aspects. Leather industry and leather products trade hold a significant share of the worldwide economy and leather sector is vital for the economies of many developing countries. Though, leather processing is recognized as a highly polluting activity. Principles and practice of pollution control and prevention in tanning industry are well-known, and ecolabelling appears as an advanced tool to address the sector environmental issues. The emergence of ecolabels in the leather sector proves the commitment of tanneries and leather goods manufacturers for increasing their environmental performance and the consumers move towards more green purchasing patterns. It is the aim of this paper to shortly present the main ecolabels in use on the market of leather and leather products, the key parameters that define an eco-friendly leather, and the benefits and disadvantages of ecolabelling in the leather sector.*

Key words: *eco-leather, tanning industry, environment, ecolabelling, green purchasing*

1. INTRODUCTION

Ecolabelling is a worldwide voluntary or mandatory labelling system for consumer products, designed to help costumers to select and encourage manufacturers to make products with low environmental impact. An ecolabel provides brief information on environmental-related product qualities and certifies that the product is manufactured using eco-friendly materials, does not contain hazardous chemicals that may affect the consumer's health, and is safe to use and dispose of.

Ecolabelling essentially relies on symbolic differentiation, which means that the ecolabel indicates that a particular product has a quality that makes it different, in a positive way, from other products, and is environmentally preferable within a specific product category [1].

There are many different ecolabelling schemes in operation around the world, each covering different ranges of environmental criteria. Ecolabels are based on two types of criteria: a) product-related, and: b) production process-related, The most comprehensive ecolabelling scheme is based on Life-Cycle Assessment (LCA), which assess the environmental effects of products from "cradle-to-grave", but there are serious difficulties in its implementation [2].

The leather and leather products industry play a prominent role in the world's economy, with an estimated global trade value of more than US$90 billion per year [3]. The leather industry is vital especially in developing countries, but suffers from a negative image because it produces extensive pollution.The legislative bodies have enforced certain measures to determine the economic actors to adopt environmentally friendly technologies and reduce pollution at different stages of production. These measures include the introduction of ecolabelling, which appears as an advanced tool to address the sector environmental issues.

It is the aim of this paper to shortly present the main ecolabels in use for leather and leather products within the global ecolabelling concept, the key parameters and criteria that define an eco-friendly leather, and the benefits and disadvantages of ecolabelling in the leather sector.

2. ECOLABELS FOR LEATHER AND LEATHER PRODUCTS

2.1. What is an eco-leather and key parameters defining an eco-leather.

The term "eco-leather" refers to genuine leather distinguished from ordinary leather by two main characteristics: (1) is manufactured in tanneries that comply with an environmental management system, and make use of green or clean technologies with lower environmental impact than the conventional ones; (2) presents a minimal health hazard potential for the final consumer; such leather is also called "eco-friendly" or "environmentally preferred". The key elements that define the eco-friendly leather are given in **Fig. 1.**

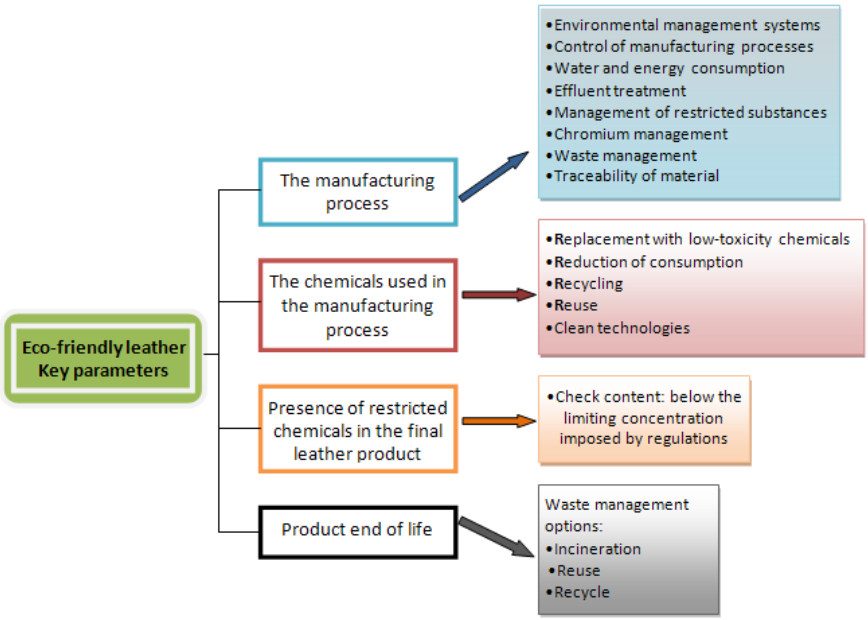

***Fig. 1**: Key parameters that define an eco-leather*

2.2. Ecolabels in use and compliance criteria for leather and leather products

The eco-friendliness of leather or leather products can be certified and recognized by consumer by means of ecolabels and marks awarded to tanneries or leather products manufacturers. The most dependable ecolabels and marks available on the global market of leather and leather

products are given in **Table 1**. The most credible labels are awarded by an impartial third party, such a testing institute, which are responsible for monitoring the compliance and issuing the ecolabel.

The **EU Ecolabel** criteria for footwear products include the following:

- Raw materials of natural origin, sustainably managed;
- Reduced water consumption and effluents polluting charge during the tanning stage processes:
  - The Chemical Oxygen Demand (COD) value in waste water from leather tanning sites, when discharged to surface waters after treatment, shall not exceed 200 mg/l;
  - The total chromium (Cr) concentration in tannery wastewater after treatment shall not exceed 1.0 mg/l.
- Minimised use of hazardous substances:
  - For shoes containing Cr-tanned leather, there shall be no Cr (VI) in the final product;
  - Residual concentrations of As, Cd or Pb in the end product must be lower than 0.2 mg/kg;
  - The amount of formaldehyde in the footwear shall not exceed 20 mg/kg;
  - The total use of VOCs in the final footwear production shall not exceed 18.0 g VOCs/pair.
- Footwear should not contain any electrical or electronic components;
- Leather used in products intended for children under three years of age shall be subject to the restriction on chromium-based tanning;
- Wear durability;
- The use of recycled materials for packaging.

The EU Ecolabel for footwear was revised in 2016 and new criteria were proposed, which address the "hot spots" of the life cycle and the labour conditions at final assembly sites. It is also important to consider harmonising the EU Ecolabel for footwear with other labels and schemes in order to reposition the EU Ecolabel within the market and to lower the administrative burden for both applicants and awarding authorities.

The **EcoSure** leathermark is designed as a credible marketing tool to aid the sourcing of leather and to demonstrate environmental compliance at point of sale. It is part of the Sure leathermarks family, which also comprises the LeatherSure, QualitySure, ConsumerSure and MetalSure trade marks [7]. Each individual mark denotes a different level of assurance, which allows them to be used as stand alone certification marks or in combination as a suite to demonstrate a holistic view of responsibility and compliance.

The **Naturleder IVN** mark is based on the assessment of all stages of the production chain, beginning with the raw material and including sales and usage of the finished leather (not the finished product). A meaningful savings of resources, environmental and health protection in both the production and usage as well as user-friendly design are benchmarks for this evaluation.

The **Nordic Swan Ecolabel** is a voluntary ecolabelling scheme that evaluates a product's impact on the environment throughout the whole life cycle. Ecolabelled hides/skins and leather fulfil a range of ***environmental, health,*** and ***quality*** requirements, but the use of chemicals during production are central to the criteria. The companies that administrate the Nordic ecolabelling schemes are from Finland, Denmark, Norway, Iceland, and Sweden.

The **Leather Standard by OEKO-TEX®** is a worldwide consistent, independent testing and certification system for leather and leather articles of all levels of production. Examples of articles that can be certified are: semifinished and finished leather, leather fiber material, garments of all types, accessories, leather gloves, leather handbags, leather covers, upholstery etc.

The **Environmental Choise New Zealand (ECNZ)** and the **Good Environmental Choise Australia (GECA)** use the life cycle approach to identify environmental issues across the whole life of a product or service. Certification criteria for leather are mainly related to the presence of heavy metals in the final product and to the treatment of tannery wastewater.

The India's **Ecomark** is awarded on the basis of compliance with both environmental and

Table 1: *Ecolables in use for leather and leather goods*

Ecolabel or mark name	Symbol	Awarding organization/ Country	Covered products	Ref.
EU Ecolabel		European Commision (EU) EU Ecolabelling Board	All categories of footwear	[4]
Nordic Swan Ecolabel		The Nordic Council of Ministers	Hides, skins, leather, leather products	[5]
Oeko-Tex® Confidence in Leather – Leather Standard- Leather goods tested for harmful substances		International Association for Research and Testing in the Field of Textile and Leather Ecology	Leather and leather articles of all levels of production	[6]
EcoSure Mark		BLC Leather Technology Center and Leather Working Group, UK	Leather and leather products	[7]
NATURLEDER IVN		Internationaler Verband der Naturtextilwirtschaft e.V. (IVN),Germany	Finished leather	[8]
SG Mark		Prüf- und Forschungsinstitut Pirmasens (PFI Group), Germany	Leather and fur products	[9]
Environmental Choise New Zealand (ECNZ)		The New Zealand Ecolabelling Trust	Skins and Leather	[10]
Good Environmental Choise Australia (GECA)		Good Environmental Choice Australia Ltd	Skins and leather	[11]
ECOMARK		Ministry of Environment and Forests India	Leather and leather products	[2]

product quality criteria. Ecomark's lack of success in India can be explained by low awareness of environmental issues amongst industries and consumers, and consumers reluctance to pay extra money for products with reduced impact on the environment.

The **SG Mark** (where SG stands for "Schadstoffgeprüft", meaning "tested for hazardous compounds") can only be awarded to those products which satisfy the stringent limit values and pollutant parameters listed in the SG catalogue of test criteria, and to ISO 9001 certified companies. For the consumer, the presence of the SG Mark on a leather product communicates a message of particular care taken by the manufacturer. It means that dyes which can release carcinogenic amines, carcinogenic and allergenic dyes, Cr(VI) and organotin compounds cannot be detected and that the formaldehyde content lies below the admissible limits. The amount of soluble heavy metals with a hazardous or sensitizing action meets strict limit values, so the product has no health hazard. Articles intended for use by young children are subject to particularly stringent requirements.

2.4. Ecolabels benefits and issues in the leather sector

Ecolabels offer three major benefits. Firstly, *for consumers*, they are an accesible, recognizable and trustworthy guide to leather products that were manufactured by eco-friendly technologies and present low health hazard. This is related to chemical auxiliaries left in leather, mainly to the hexavalent chromium. Chromium-tanned leather footwear, which releases >3 ppm Cr(VI), may pose a risk of sensitizing and eliciting allergic dermatitis. Chromium was identified in 95% of leather footwear products, and Cr(VI) concentration reached levels higher than 10 ppm or even 62 ppm [12]. Ecolabeled footwear guarantee Cr(VI)content lower than the exposure limit, which is beneficial mainly for children.

Secondly, *for manufacturers*, ecolabels offer a point of difference in the consumer's eyes and a competitive advantage over companies that do not make shifts towards environmental responsibility. Moreover, leather manufacturers committed for gaining an ecolabel must comply to severe environmental regulations and management procedures; for the long term, this would have positive effects for the bussines.

Thirdly**,** *labels encourage a general raising of environmental performance*, even among products that aren't labeled, because if environmentally friendly products sell better, all manufacturers have an incentive to produce similar products, and standards rise overall.

Use of ecolables may have disadvantages, as well. The *biggest problem* is that manufacturers may be tempted to make exaggerated or misleading claims, which deceive consumers into thinking products are better than they really are. Instead of raising standards, the result is confusion among consumers and a systematic undermining of genuine eco-friendly products.

A second problem is failure of ecolabelling implementation, related to both consumers and economical actors behaviour. Lack of consumers' environmental awareness produces lack of demand for environmentally friendly product and low willingness to pay extra for products with reduced impact on the environment will lead to low success of ecolabelling, mainly in developing countries. For the customers majority, price is the most critical consideration and environmental concerns do not play a role in their choice of products. It seems that ecolabelling is a marketing tool that works better in developed countries. Furthermore, companies feel that the expensive and laborious procedures involved in gaining an ecolabel are not justified by potential advantages in terms of increased profitability and market share. Manufacturers are required to pay for the application, testing, licensing fee, and renewal costs involved in certification. Some estimates indicate that these costs can increase the price of ecolabelled products by 15 % [13] .

The differences between ecolabels criteria and their negative impacts on the interstate trade, mainly to the developing countries detriment, are largely described by Alam [2], particularized for the Indian Ecomark *vs* the EU Ecolabel for footwear.

3. CONCLUSIONS

In the current climate of environmental awareness, there is a requirement to understand the environmental credentials of leather goods and the leathermaking process. Ecolabelling schemes for the leather industry aim to promote the sale of leather products having a reduced environmental impact, minimal risk of allergic reactions from process chemicals, and safe disposal choices.

A number of both developed and developing countries have introduced these labels to influence consumers and industry to behave in an environmentally responsible manner.

Inconsistency between certification criteria amongst different ecolabels schemes can raise trade barriers for leather and leather products, mainly between developed and developing countries. Ecolabels harmonization, which could solve this issue, still remains a debate subject.

Ecolabelling in leather industry is developing an "in progress work " and have the acceptance of an increasing number of consumers.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

DIVERSIFICATION OF A SAFETY FOOTWEAR PRODUCT

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Abstract: *Product diversification is a usual strategy of footwear producers. As a requirement related to competitiveness in this domain, diversification can be done by practical application of some criteria. Considering this aspect, the paper proposes a research on the diversification in the case of a safety footwear product by modifying its component patterns, while keeping the initial shape of the product. Thus, starting from a safety shoe model, diversification was performed by changing the configuration in the joining area of two patterns of the product.*
By joining the tongue with the bellows tongue, the upper with the quarter, the heel counter with the quarter and the collar and heel counter with quarter has resulted a family of models characterized by a reduction of the number of patterns in the product. The size of the set presents a significant influence on the theoretical nesting factor and implicitly on the size of the wastes. The analysis of the resulting new model types lead to highlighting the influence of the patterns number of the uppers and the area of the set on the usage index of the leather surface when cutting the parts and on the specific consumption.

Key words: *manufacturing, footwear, nesting factor, waste, usage index, specific consumption*

1. INTRODUCTION

In the process of footwear manufacturing the improved use of materials has a great significance on the manufacture price decrease.

From an organizational and economical point of view, the diversification of a footwear collection involves a series of possible problems as it implies the repetition of major activities whenever the model changes at a certain step. Some of them (such as product design and making of the afferent cutting devices) are time-consuming and expensive, especially when carried out by classical means and methods [1].

As a result, in footwear design, automated systems such as CAD systems (computer aided design) are being used as they allow an automatic control of this activity, the footwear design being conjugated with certain activities such as CAM (computer aided manufacturing) [2].

The precision of execution for the basic designs, the cutting patterns, the accuracy of grading for obtaining the whole size range of patterns are just some of the advantages that design systems available on the market can offer to footwear designers.

Considering these aspects a safety shoe model was designed in AutoCAD software and a family of models was furthermore developed by changing the configuration in the joining area of some

patterns. [2]. The family of models so constituted, decreases the number of patterns and implicitly the specific consumptions during cutting of parts on leather surface.

2. PRESENTATION AND DESIGN OF THE BASIC MODEL

The basic model was taken from a footwear company and designed in AutoCad pattern making software.

Model information

Safety shoe
Size range: 36-48
Materiales: uppers – natural box leather
lining - 3D knit
Individual Sole
Construction : tubular and cemented

Starting from the mean forme of the shoe last the basic drawing was made, considering the design particularities of the model [2, 3], figure 1.

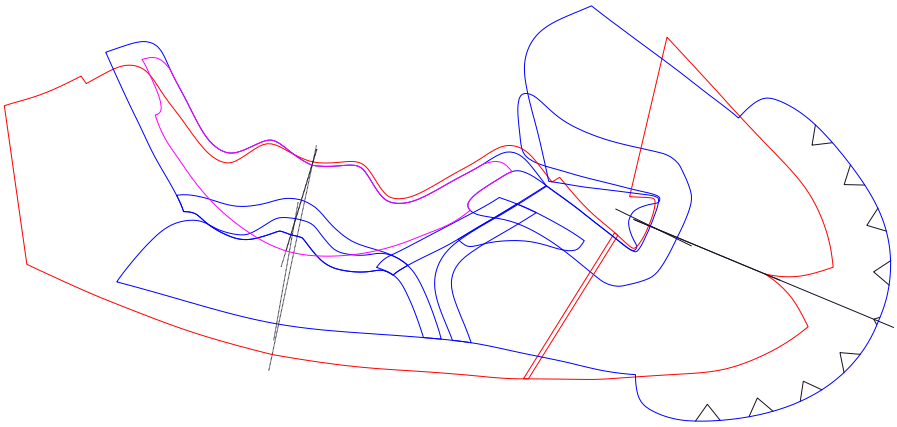
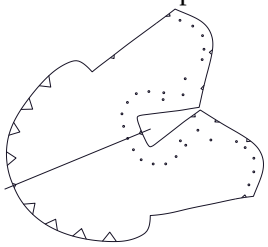
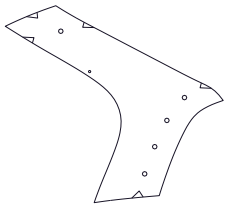
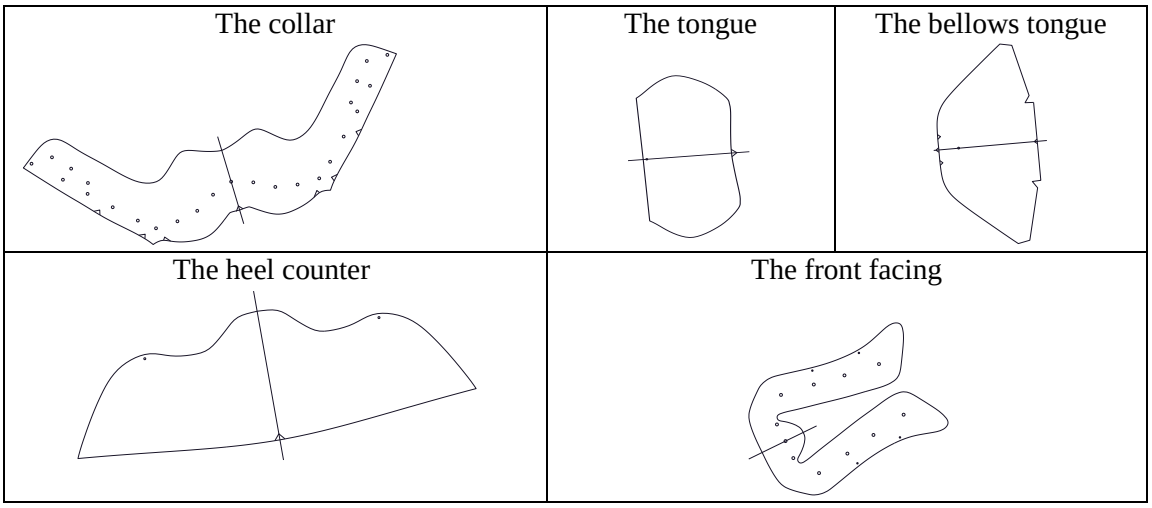


Fig. 1: *The master pattern of the uppers*

The structure of the outer subassembly (product uppers) are illustrated in table 1.

***Table 1**: The outer patterns of the model*

The patterns of the outer subassembly	
The vamp	The quarter
	



3. THEORETICAL CALCULATION OF LEATHER CONSUMPTION FOR THE BASIC MODEL

In table 2 are presented the values of the nesting factors for each pattern of the footwear product as well as the average nesting factor [4].

Table 2: *Nesting factor of component patterns*

No.	Pattern name	Nr. of similar patterns in set	Area(dm^2)		Area of the parallelogram (dm^2)		Perimeter (dm)		Nesting factor (Fa) (%)
			Pattern	Similar pattern	Pattern	Similar pattern	Pattern	Similar pattern	
1	vamp	2	4.072	8.144	4.466	8.932	10.16	20.32	91.18(%)
2	quarter	4	0.281	1.124	0.327	1.308	2.98	11.92	85.93(%)
3	heel counter	2	0.857	1.714	0.928	1.856	4.48	8.96	92.35(%)
4	collar	2	1.192	2.384	1.433	2.866	6.83	13.66	83.18(%)
5	front facing	2	0.668	1.336	0.875	1.75	5.94	11.88	76.34(%)
6	bellows tongue	2	1.576	3.152	1.622	3.244	5.31	10.62	97.16(%)
7	tongue	2	0.501	1.002	0.522	1.044	2.81	5.62	95.98(%)
Total		ns= 16		As= 18.86		Aps= 21.00		Ps= 82.98	

$$\overline{F_A} = \frac{A_s}{A_{ps}} \cdot 100 = \frac{18.86}{21} \cdot 100 = 89.81\%$$

For a clearer vue of how the calculation is done, table 3 shows the elements and relations for determining the specific consumption for the basic model [4, 5].

Table 3: *Elements and relations calculus for establishing the specific consumption [6]*

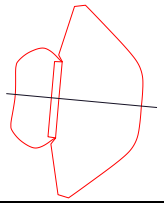
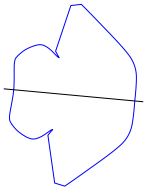
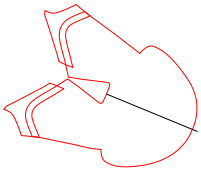
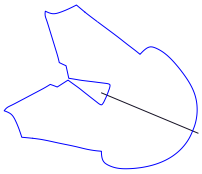
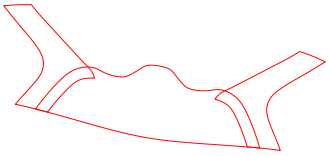
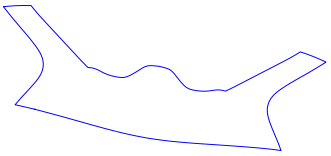
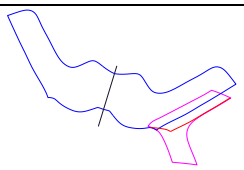
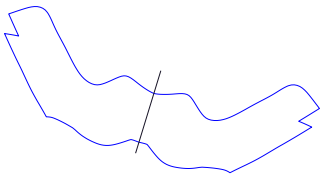
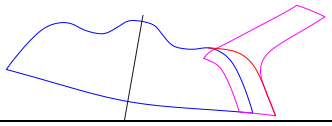
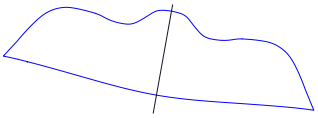
Element, significance	**Calcul formula**	**Measuring units**	**Value**
n, number of patterns			16
A_s, pattern's surface area		dm^2	18.86
A_{ps}, area sum of parallelograms that include the set patterns		dm^2	21.00
$\overline{F_A}$, nesting factor	$\overline{F_a} = \frac{\sum A_r}{\sum A_p} = \frac{A_s}{A_{ps}} \cdot 100$	%	89,81
a_{Dn} , normal wastes area	$a_{DN} = 100 - \overline{F}_A$	%	10,19
$\overline{A_S}$, sum of set's areas	$\overline{A}_S = \frac{A_S}{n}$	dm^2	1.18
$\overline{A_p}$, area of leather		dm^2	160
f_a , area factor	$f_A = \frac{\overline{A_p}}{\overline{A_S}}$		135.59
a, coefficient for flexible leathers			39
$\sqrt[4]{f_A}$, area factor			3.41
a_{Dm+Dt} , area of marginal and patterns wastes	$a_{Dm+Dt} = \frac{a}{\sqrt[4]{f_A}}$	%	11.43
P_s, set perimeter		dm	82.92
p, width of the between patterns		dm	0,02
a_{Dp} , area of wastes between patterns	$a_{Dp} = \frac{p \cdot P_S}{2 \cdot A_S} \cdot 100$	%	4.32
a_{DT} , total wastes area	$a_{DT} = a_{Dn} + a_{Dp} + a_{Dm+DT}$	%	25.94
I_U , leather utilization index	$100 - a_{DT} = 100 - (a_{Dn} + a_{Dm+t} + a_{Dp})$	%	74.06
C_S , specific consumption	$C_S = \frac{A_S}{I_U} \cdot I_C \cdot 100$; Ic=1	dm^2	25.46

4. ANALYSIS OF THE NEW TYPES OF MODELS

The family of models was obtained by creating distinctive types of models through changing the configuration in the joining area of two patterns.

With this regard, the different types of model were established by joining the tongue with the bellows tongue, the heel counter with the quarter and the collar + the heel counter with quarter; the configuration of modified patterns is shown in table 4.

Table 4: *Modifying the patterns for obtaining new models*

Model types	Initial joining of the patterns	Modified joining of patterns
Model M1 joining the tongue with the bellows tongue		
Model M2 joining the vamp with the quarter		
Model M3 joining the heel counter with the quarter		
Model M4 extending the collar and the heel counter, by including the quarter		
		

In table 5 is presented the comparative analysis of the new proposed models.

Table 5: *The wastes values, usage indices on the surface of the leather and of the consumption norms*

	U.M	Mb	M1	M2	M3	M4
ns		16	14	12	12	12
As	dm^2	18.86	18.72	18.43	18.63	18.36
Aps	dm^2	21.00	21.77	20.48	21.24	20.99
Ps	dm^2	81.44	79.28	73.42	77.48	73.36
$\overline{F_A}$	%	89.81	86.19	89.99	87.71	87.47
Dn	%	10.19	13.81	10.01	12.29	12.53
Dm+t	%	11.43	11.78	12.20	12.22	12.18
Dp	%	4.32	4.24	3.98	4.16	4.00
D_T	%	25.94	29.83	26.19	28.69	28.71
I_U	%	74.06	70.17	73.81	71.31	71.29
C_S	dm^2/pair	25.46	26.68	24.97	26.12	25.76

Analyzing the values obtained we notice a reduction of the number of patterns from the set and thus implicitly the set area.

In the new family of models, the usage index of leather when cutting the upper patterns varies in function of the selected model, being influenced by the configuration of the patterns and the set size.

Marginal and printing wastes increase by reducing the number of patterns from the product composition, when using the leather with a constant surface area (160dm^2). On the other hand, the waste is reduced by reducing the number of patterns of the set.

5. CONCLUSIONS

Nowadays it is a must for shoe manufacturers to pre determine the consumption of materials required for a particular design and to control the consumption of material. So, it is necessary to calculate the amount of material required in the case of diversification. By changing the configuration of patterns in the joining area, by adding a pattern to another pattern respectively, the reference set size is decreased, having a significant influence exerted on the size of normal marginal waste, between patterns and by bridges.

The best option in terms of specific consumption is M2 model type or the version in which the quarter was joined with the vamp.

The modification of the upper resulted in a consumption norm of 24.97 dm^2 / pair. Compared to the basic model we achieved a reduction of standard consumption with the 0.49 dm^2 / pair.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE USE OF VEGETABLE FILLERS AS REINFORCEMENT MATERIAL IN SBR BASED BIO-COMPOSITES

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Abstract: *The use of natural fillers as reinforcement material in the production of composite materials has gained extra attention in recent years from the environmental point of view. For this purpose, the use of vegetable fillers as a potential reinforcement material in elastomeric composites was investigated for the production of footwear sole material. In this study the acorn cups and the waste of acorn obtained after the tannin extraction was used as the reinforcement materials for styrene-butadiene rubber based composites. Acorn cups and pulps (acorn wastes) with different ratio (2, 4 and 6 wt%) were compounded with SBR by Banbury and the preparation of the composites with different filler loadings was performed via compression molding. The thermal characteristics of the bio-composites produced for the footwear sole were investigated in terms of Differential Scanning Calorimeter (DSC), and Thermogravimetric (TGA) analyses. The results revealed that different concentrations of vegetable fillers had no significant effect on DSC results and the highest TGA results were obtained by the use of 2% acorn cups as a reinforcement material. Besides, the homogenous dispersion of vegetable fillers within the elastomer matrix was achieved successfully and the obtained bio-composite materials were found to be a good candidate to be a bio based sole material in footwear production.*

Key words: *Bio-composite, acorn cup, acorn waste, DSC, TGA*

1. INTRODUCTION

In footwear production, various materials with different properties are used for providing foot comfort, wear hygiene in addition to ensure firmness and aesthetic properties. Footwear consists of two main parts as upper and sole, while upper leather covers the top and sides of the foot, sole makes the contact with the surface and is produced from polymer, rubber, neolit and leather. Sole is known as one of the important component of footwear and should be durable and flexible [1].

Sole leather provides different characteristics to footwear and is considered as a healthy and lightweight material with high air permeability properties. However, low abrasion resistance, low slip resistance, high water absorption and high prices are the drawbacks [2, 3]. Natural rubber soles costs high but it has high abrasion, slip and chemical resistance properties [3]. Polymeric materials

used in sole production, such as poly vinil chloride (PVC), ethylene vinyl acetate (EVA), styrene-butadiene rubber (SBR) and polyurethane (PU), have different softness, flexibility, abrasion and chemical resistance as well as slip resistance properties and all of these features still couldn't be catch on a single sole material [4-8].

The use of natural fillers as reinforcement material in the production of composite sole materials has gained attention due to the decrease in the production costs and to provide higher mechanical and strength properties. Although various studies have been carried out on the utilization of natural fillers such as rice husk, jute, cotton and cellulose fibers [9] as a reinforcement material, up to date according to our knowledge this will be the first study about acorn cups and waste of acorns used as reinforcement materials for the production of footwear sole. Considering the rubber sole materials, some studies have been found regarding composite sole production such as bambu fibers reinforcement for the rubber sole production [10] and wastes of shoe production utilized in rubber sole [11].

For this purpose, the use of vegetable fillers as a potential reinforcement material in elastomeric composites for the production of footwear sole material was investigated. Acorn cups and the waste of acorn obtained after the tannin extraction was used as the reinforcement materials for styrene-butadiene rubber (SBR) based composites. Acorn cups and pulps (acorn wastes) with different ratio (2, 4 and 6 wt%) were compounded with SBR by Banbury and the preparation of the composites with different filler loadings was performed via compression molding. The effect of different filler ratios on the thermal characteristics of the bio-composites produced for the footwear sole were investigated in terms of Differential Scanning Calorimeter (DSC), and Thermogravimetric (TGA) analyses.

2. MATERIAL AND METHOD

2.1 Material

In this study, acorn cups and the waste of acorn were used as the reinforcement materials for the styrene-butadiene rubber (SBR) based composites. The acorn cups and acorn wastes were supplied from AR-TU Chemical Company in Salihli, Izmir.

The commercial styrene-butadiene rubber (SBR 1502) was used as a matrix component of bio-composites.

2.2 Method

The acorn cups and acorn wastes were milled to particle size of 200 µm using laboratory grinder [12, 13].

The preparation of bio-composites with different filler loadings (2, 4 and 6 wt%) was performed via compression molding.

Thermo gravimetric analysis (TGA) was performed on raw materials and composites using Perkin Elmer Diomand TG/DTA apparatus applying a heat range of 10 ^{o}C/min up to 600 ^{o}C.

Differential Scanning Calorimetry (DSC) analyses were carried out using Shimadzu-DSC 60 Plus apparatus. The samples were kept in aluminum vessels and scanned between 20 ^{o}C and 200 ^{o}C with 10 ml/min flow rate of N_2 and heating rate of 10 ^{o}C/min.

3. RESULTS AND DISCUSSION

3.1. DSC Results

The data of differential scanning calorimetry analysis of SBR, vegetable additives and composites are given in Table 1. The DSC curves of acorn cups and waste of acorns showed only

one large endothermic peak between 40-150°C with peak temperatures at 65-91°C, possibly due to the removal of free and bounded water.

The glass transition temperature of styrene-butadiene rubber was found to be at -66°C (Tg) and melting temperature at 85 °C (Tm). Besides, the reinforcements used by 2, 4, 6 % vegetable fillers effect was not found significantly on the thermal behavior of SBR. The similar Tg and Tm values were obtained from all bio-composite samples.

Table 1: *The results of DSC analysis of SBR, additives and composites*

Numune	T_g	Peak 1	Peak 2
Acorn waste	-	65.06	-
Acorn cup	-	82.05	-
SBR	-66.46	-	85.33
2% acorn waste	-67.72	-	78.62
4% acorn waste	-63.35	-	82.17
6% acorn waste	-61.12	9.86	88.31
2% acorn cup	-61.40	-	86.53
4% acorn cup	-67.10	-16.02	88.11
6% acorn cup	-70.46	-	83.51

3.2. TGA Results

The thermogravimetric curves of SBR matrix, vegetable additives (acorn cup and waste of acorn) and their composites are given in Figure 1-2.

And some data of thermal behavior of SBR, vegetable fillers and their composites are shown in Table 2.

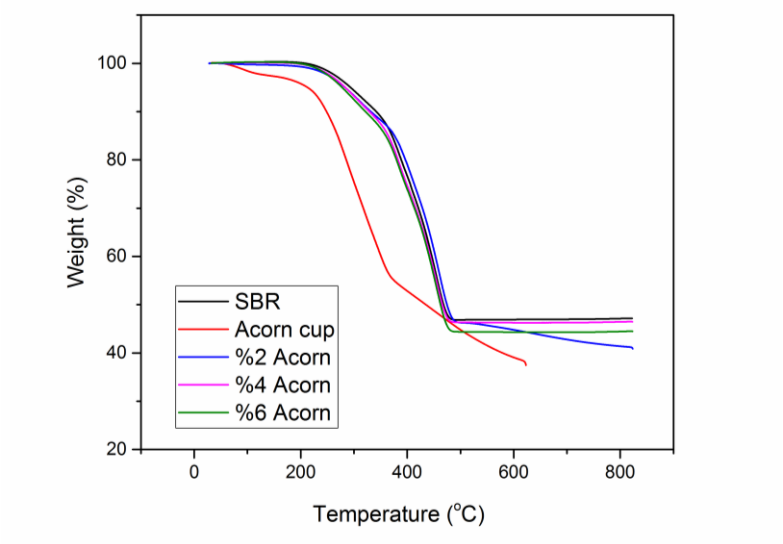

Fig.1: *TGA curves of SBR, Acorn cup and its composites*

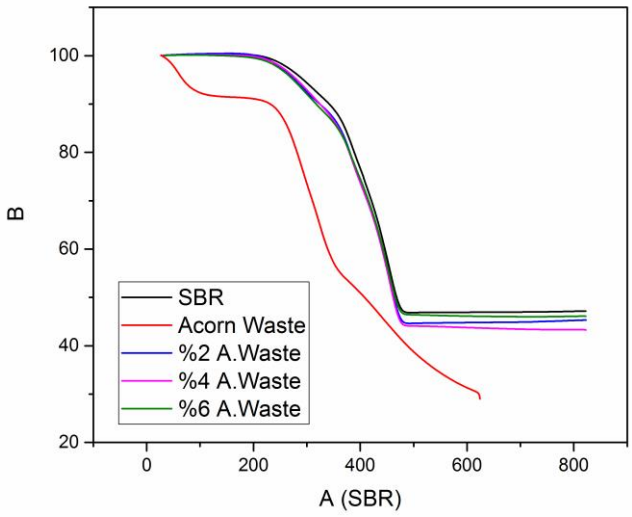

Fig. 2: TGA curves of SBR, Acorn waste and its composites

The results revealed that vegetable fillers start to decompose at lower temperatures than SBR. Considering the peak temperatures, the highest thermal values were obtained from the composites by the use of 2% vegetable fillers as reinforcement materials compared to SBR matrix. In general, the highest decomposition temperature and the lowest mass loss are provided by 2% acorn cups-SBR biocomposites. The thermal behavior of SBR matrix is affected by the addition of 2% acorn cups in a positive manner, although the other reinforcements caused a slight decrease in the thermal stability of the biocomposites. On the other hand, the results also showed the addition of bioparticles was not make significant changes in the thermal behavior of SBR so that it can be thermally processed with conventional procedures.

Table 2: *Some values about thermal behavior of SBR, and acorn based bio-composites*

MATERIAL	Temp of 10% mass loss (°C)	Temp of 50% mass loss (°C)	T_{peak} (°C)	Final mass (%)
SBR	342.11	468.43	454	47.16
Acorn waste	231,39	408,02	322,7	28,90
Acorn cup	248,54	435,20	287,3	37,41
2% acorn waste - 98% SBR composite	324.33	463.12	455	45.30
4% acorn waste - 96% SBR composite	324.73	461.69	455	43.26
6% acorn waste - 94% SBR composite	317.46	465.45	453	46.09
2% acorn cup - 98%SBR composite	331.89	474.66	459	40.82
4% acorn cup - 96% SBR composite	329.19	465.97	452	46.46
6% acorn cup - 94% SBR composite	321.87	462.57	455	44.48

4. CONCLUSION

In this study, the use of vegetable fillers as a potential reinforcement material in SBR based composites was investigated and following conclusions have been drawn;

The vegetable fillers were incorporated into the elastomer matrix successfully.

Different concentrations of vegetable fillers had no significant effect on DSC results and the highest TGA results were obtained by the use of 2% acorn cups.

Homogenous dispersion of vegetable fillers within the elastomer matrix was achieved successfully and the obtained bio-composite materials were found to be a good candidate to use as bio based footwear sole material.

ACKNOWLEDGEMENT

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE INFLUENCE OF FATLIQOURING PROCESS ON PROTECTIVE CHARACTERISTICS OF LEATHER GLOVES

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Abstract: *Appropriate protective gloves are essential for industry workers to avoid hands and wrists injuries. Leather is a common material used by professionals for technical gloves. Mechanical resistance, protection against water and high temperature has to be fulfilled by leather that is intended for using in protective gloves. In this study recipes using various fatliquoring agents with different properties such as lesitin based, lanolin based, polymeric based and water proofing fat liquor were applied to produce technical glove leather and effect of each fatliquoring product on protective performance of leathers were analyzed in terms of physical and mechanical properties including tensile (ISO 3376), stitch tear (ISO 23910), tear resistance (ISO 3377-2), static (ISO 2417) and dynamicwater absorption (ISO 5403-1) and thermal stability such as dry heat (ISO 17227) and heat stability (ISO 11645). For this purpose, chromium tanned split calf leathers were used and retanning of protective leather gloves were performed by using tara and phosphonium combination. Performance testing results obtained from four different retanning processes was compared according to the type of fatliquoring material used in the production. Post-tanning with different types of fatliquoring products have significant effect on the protective performance properties of leather gloves, in terms of mechanical and thermal properties.*

Key words: *safety equipment, protective glove, leather, faliquoring process*

1. INTRODUCTION

Hands and wrists injuries are one of the most common work associated injuries experienced by heavy industry workers. Hand protection by appropriate protective gloves is essential and workers at risk are promoted to wear these gloves to avoid such injuries. Although many fine synthetic materials have come on the market, and a number of studies regarding different types of protective gloves (synthetics, fabrics, other natural fibres etc.) [1, 2] were carried out, leather is still a common material chosen by professionals. Limited published information is available about the properties and effect of production processes on protective characteristics of leather [3-5] and the literature provides no information about the influence of fatliquoring process on leathers as a protective clothing material.

Depending on their application area, several important requirements such as mechanical resistance, protection against water and exposure to heat has to be fulfilled by leather that is intended for using in protective gloves. In this study various fatliquoring agents were applied for glove leather processing, considering the importance of the choice of the fatliquoring chemicals that affects the properties of the final leather. The effects of lesitin, lanolin, polymeric based and water proofing fatliquoring processes on protective characteristics of glove leathers were investigated by determination of strength characteristics, water absorption and thermal resistance properties.

2. MATERIALS AND METHODS

Chromium tanned split calf leathers were used for leather processing trials and retanning of protective leather gloves were performed by using tara and phosphonium combination, which provided optimum protective properties as reported in previous study [4]. To evaluate the influence of fatliquoring process on protective properties, production process was differentiated in post-tanning operations by utilizing various fatliquoring products such as lesitin based, lanolin based, polymeric based and water proofing. Conventional formulation using phosphoric ester based fat liquor was applied throughout the post-tanning processes for the production of protective leather gloves as control trial. Recipe for fatliquoring processes was given in Table 1.

Table 1. *The fatliquoring process of protective leather gloves*

Re-wetting	**%**	**Chemicals**	**°C**	**pH**	**Time**
	200	water	25		
	0.3	HCOOH			
	0.4	nonionic tenside		3-3.5	30’
Washing	200	water	35		10 x 2
Retannage					
	100	water			
	1	synthetic fatliqour			15’
	3	phosphonium			120’
	x	sodium formiate		4	
	5	phenolic replacement syntan			30’
Neutralization	2	neutral syntan		4.5-5	30’
	x	sodium formiate			3*10’
	x	sodium bicarbonate		5.5-6	45
		Drain and washing			
Retannage	100	water	35		
	2	phenolic replacement syntan			20’
	5	tara			180’
Fatliqouring	3	phosphoric ester-based oil substance			
	2	alkyl phosphates with neutral oils			60
	2	**x***			
	x	HCOOH		3.8-4	

Washing	200	water	35	10 x 2

x*; lecithin with emulsifiers; lanolin based natural fatliqour; polymeric fatliquor based on acrylic acid; Waterproofing fatliquor ing agent

Sampling and conditioning of the finished leathers were carried out according to TS EN ISO 2418 (2006) and TS EN ISO 2419 (2006) respectively [6, 7] The effect of aformentioned fatliqouring agents on thermal properties was analyzed by dry heat resistance (ISO 17227) at 200 °C for 15 min, heat stability (ISO 11645) contact at 300 °C for 1 min. Other performance properties such as tensile strength (ISO 3376), stitch tear and tear resistance (ISO 3377-2) [8] were investigated with reference to standard methods respectively. The static and dynamic water absorption behavior of the protective leather gloves was tested according to TS 4123 EN ISO 2417 and TS EN ISO 5403-1 standards respectively [9, 10]. The performance test results obtained from different fatliquoring products were comparatively evaluated with the fatliquoring products given in Table 2. The assays were performed in duplicates and results were given in mean values.

3. RESULTS AND DISCUSSION

3.1 Mechanical analysis

The mechanical properties of glove leather samples fatliquored with different fatliquoring products and comparative UNIDO standard values are reported in Table 2. The glove leather samples fatliquored with different kind of fatliqours provided satisfactory results in terms of tensile strength/tear load/stitch tear values compared to UNIDO requirements except tensile value of the leather treated with polymeric fatliqour.

Table 2: *Mechanical properties of glove leather samples*

	Thickness (mm)	**Tensile**	**Elongation at break %**	**Tear load (N/mm)**	**Stitch tear / Thickness (mm)**
Conventional fatliquoring (control)	1.1	14.93	60.44	80.55	167.96 / 1.08
Lesitin based fatliquoring	1.3	21.01	84.62	114.40	208.58 /1. 28
Lanolin based fatliquoring	1.3	16.69	56.07	91.96	167.09 / 1.23
Polymeric based fatliquoring	1.3	13.07	56.59	96.98	173.86 / 1.13
Water proof fatliquoring	1.1	22.53	65.36	111.59	171.27 / 1.13
UNIDO*	-	**15 N/mm**	-	**30 N/mm**	**50 N/mm**

***UNIDO, 1996, Acceptable quality standards in the leather and footwear industry. ISBN: 92-1-106301-9, Vienna.*

The mechanical strength properties of glove leathers fatliquored with water proof and lesitin based substances were found significantly higher than the values for the lanolin, polymeric and control trials. The leathers fatliquored with lesitin and water proof agents display the highest tensile and tear strength values when compared to all the other samples. No significant difference in strength results was observed between the leathers treated with lanolin and polymeric fatliqours. The highest increase in strength results were found by the use of lesitin fatliquoring substances.

3.2 Water absorption test

Static water absorption (Kubelka) test results of glove leather samples treated with different fatliquoring formulations are presented in Figure 1. The highest static water absorption value was obtained from control leather, whereas lesitin fatliquoring agent provided the minimum water absorption value as 147.45 ml water for 100gr leather at 24h.

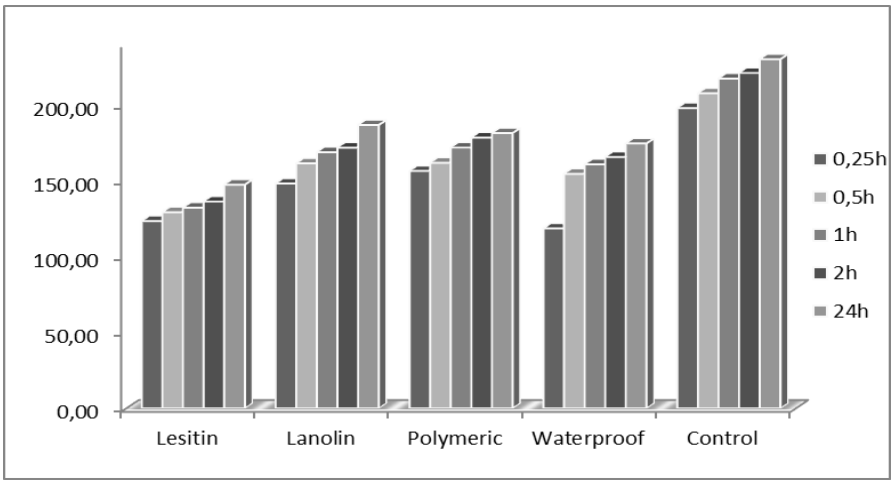


Fig.1: *Static water absorption values for glove leather samples (ml/100gr)*

Different fatliquoring agents had different effects on the dynamic water absorption values of technical glove leathers. The leathers treated with lesitin and waterproof fatliqours had minimum dynamic water absorption, although polymeric based fatliqour lead to highest water absorption. Similar results were found for the control leathers and the leathers treated with lanolin based oil fatliqour (Figure 2).

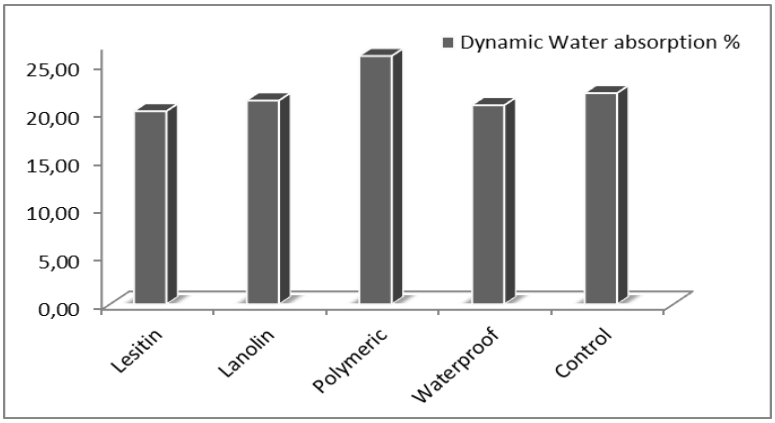


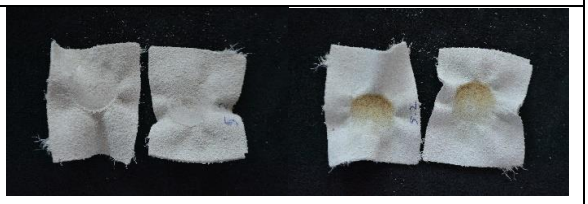
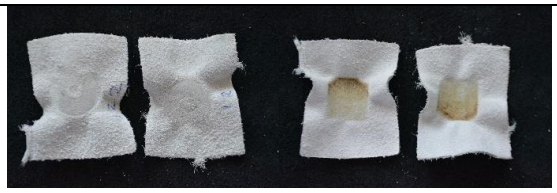
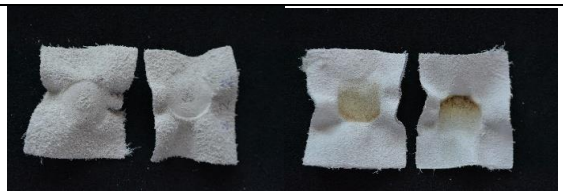
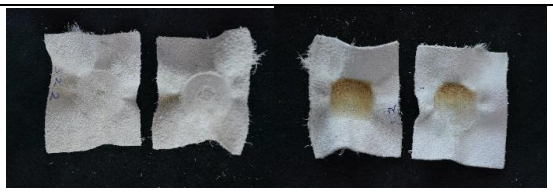
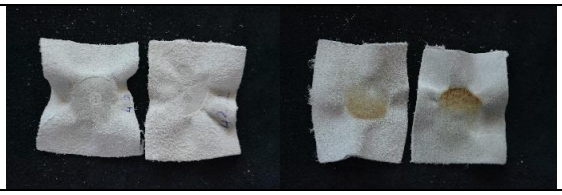
Fig.2: *Dynamic water absorption values for glove leather samples (%)*

3.3 Thermal resistance tests

The thermal resistance is an important parameter of leather meant for protective glove applications. Thermal behaviour of leather samples were evaluated in terms of surface area alteration for dry heat resistance (200°C) and appearance for heat stability test (300°C) (Table 3).

Leather specimens presented similar surface alteration values except the lesitin treated samples and the highest surface alteration value was provided by the samples fatliquored with lanolin. The minimum alteration was determined by the leathers treated with lesitin based fatliqours. All of the leather samples treated with different types of fatliquoring agent showed an acceptable thermal resistance.

Table 3. *Thermal resistance test results for aniline and pigmented finished glove leather samples*

Applications	**Dry heat resistance (200°C)**	**Heat stability test (300°C)**
	Surface area alteration (%)	**Appearance**
Conventional fatliquoring (control)	22.34	
Lesitin based fatliquoring	20.98	
Lanolin based fatliquoring	23.18	
Polymeric based fatliquoring	22.89	
Water proof fatliquoring	22.39	

The leathers treated with different kinds of fatliqours exhibited good and similar heat stability results at 300°C. In general, it was observed that lesitin type fatliqour increased the mechanical and thermal characteristics of leather glove samples as well as water absorption results.

Therefore, it can be said that treatment with lesitin based fatliqour was found more effective than the other fatliquoring products.

5. CONCLUSIONS

Preliminary trials with differentiated fatliquoring process were conducted with products available on the market, in order to determine the effect of fatliquoring process on protective performance of leathers. Protective properties of glove leathers were investigated in terms of water absorption, tensile, tear resistance and thermal resistance tests to establish how these products affect the protective properties of glove leather. The leathers treated with lesitin type fatliqours provided the lowest surface area alteration value when exposed to dry heat at 200°C. The application of lesitin and waterproofing fatliqouring agent decreased the amount of water absorbed by the leather samples. The use of lesitin fatliquor is found to show moderate decrease in thermal stability. It is revealed that all of the process variants using different types of fatliquoring agents produced satisfactory results both in terms of mechanical resistance and heat stability.

ACKNOWLEDGMENTS

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

SUSTAINABLE ENVIRONMENTAL TECHNOLOGIES INCLUDING WATER RECOVERY FOR REUSE FROM TANNERY AND INDUSTRIAL WASTEWATER – INDIAN AND ASIAN SCENARIO

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Abstract: *World leather sector generates 600million m3 of wastewater per annum. The Asian tanneries contributes more than 350 million m3 of wastewater from the process of 8 to 10 millions tons of hides and skins. Environmental challenges due to depletion of quality water resources and increase in salinity, it has become necessary to control Total Dissolved Solids (TDS) in the treated effluent with water recovery wherever feasible. Adoption of special membrane system has been engineered in many individual and Common Effluent Treatment Plants (CETPs) in India, China and other leather producing countries. The sustainability of saline reject management is one of the major challenges.*

Conventional tannery wastewater treatment systems include physiochemical and biological treatment to reduce Chromium, BOD, COD and Suspended Solids. To tackle treated effluent with TDS in the rage of 10000 to 30000mg/l, multiple stage high pressure membrane units have been designed and implemented for recovery of water. To reduce the chemical usage and sludge generation in the tertiary treatment, Membrane Bio-Reactor (MBR) has been adopted which replace secondary clarifier and sophisticated tertiary treatment units such as Reactive Clarifier, Ultra-filtration (UF), etc. Commercial scale high-tech membrane systems have been implemented in many locations for the capacities ranging from 500 to 10000m^3/day. Recent applied R&D on the environmental protection techniques with focus on water-recovery for reuse, salt recovery, marine disposal of saline reject with proper bio-control system, etc. are dealt in this novel technical paper.

Key words*: Effluent Treatment System, Environment, Sustainability, Water Recovery.*

1. INTRODUCTION

Annual leather process in Asian Countries is estimated at 8 to 10 million tons of hides and skins which is more than 50% of the estimated World leather production of about 16 million tons per year. The tanneries in Asian countries including India, China, Vietnam, etc. discharge more than 350 million m^3 of wastewater per annum [1].

Conventional physiochemical and biological treatment systems are designed and implemented only to reduce Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solids (SS), Heavy metals etc. and not TDS and salinity which are mainly contributed by chlorides, hardness and sulphates [2]. Due to inherent quality of wastewater from tanning industry, the treatment plants are unable to meet the prescribed standards in terms of TDS, chlorides in salinity in the treated effluent. The TDS limit is being enforced in India and other parts of the World depending upon the final mode of disposal. In addition to the removal of TDS in the treated effluent, it is necessary to recover water for reuse to meet the challenge of water shortage. In many states in India, the pollution control authorities insist on water recovery integrated with Zero

Liquid Discharge (ZLD) system [3]. However, the achievement of Zero Liquid Discharge concept has got many technical challenges in addition to the application of various types of membrane systems.

Recent applied R & D activities including case studies of major environmental projects implemented in India, Spain, China, etc. are covered in the novel technical paper.

2. ADVANCED TREATMENT SYSTEM FOR SLUDGE REDUCTION & TDS MANAGEMENT WITH WATER RECOVERY

Due to inherent quality of industrial wastewater such as textile dyeing units, tanneries etc., the conventional treatment plants are unable to meet the prescribed TDS level of 2100 mg/l in the treated effluent. In addition to TDS management the control of volatile solids in hazardous category sludge is also becoming a necessity.

The TDS limit is being enforced in many parts of the world depending upon the final mode of disposal. In addition to the removal of TDS in the treated effluent, it is necessary to recover water for reuse to meet the challenge of water shortage. In many states in India, pollution control authorities insist on water recovery integrated with Zero Liquid Discharge (ZLD) system.

For control of sludge and recovery of quality water from wastewater, the required treatment steps are (i) Chrome recovery and other in process control including cleaner production (ii) Conventional physiochemical and biological effluent treatment systems to reduce BOD, COD, SS etc. and (iii) Tertiary treatment systems including, micro-filter, low pressure membrane units such as ultra-filtration etc., before the application of single or multiple stage Reverse Osmosis (RO) system[4]. A special treatment process for recovery of water from waste water is given in Figure 1.

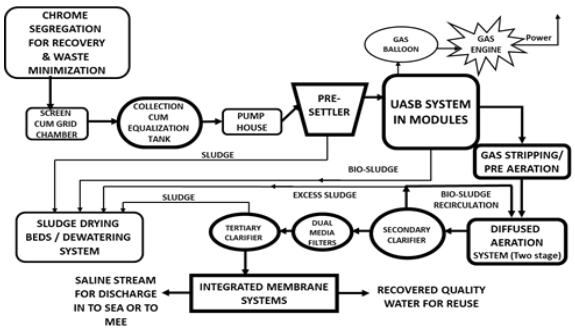

Fig. 1: *Tannery Waste Treatment & Integrated Saline Management*

After primary and secondary treatment units, Reactive Clarifier, Dual Media Filter, Micro Filter, Ultra-Filter (UF) are installed prior to RO system for recovery of water. Quality water with TDS less than 500mg/l could be achieved with rate of recovery of 70 to 90% depending upon the feed water TDS level, type and stages of membrane system etc. In addition to recovery and reuse of quality water by the industry, the additional benefits are savings in chemical usage in the tanning process and reduction in pollution load in the effluent.

3. MEMBRANE BIO-REACTOR (MBR) INTEGRATED WITH RO SYSTEM

Membrane Bio Reactor (MBR) system is adopted as tertiary treatment to remove the residual BOD, suspended solids / coliform, etc. from the effluent. A Common Effluent Treatment

Plant (CETP) in Spain with MBR and RO system for water recovery was established in 2005. After MBR / UF treatment, the suspended solids and BOD values in the effluent are below detectable level and taken for treatment with RO system for recovery of water after the removal of TDS and salinity.

In China also water is becoming a scarce commodity in many locations. Expansion of high water consuming industries is allowed only if they are provided with water recovery system in the effluent treatment plants. To recover water from the tannery wastewater, submerged MBR linked with activated biological treatment is provided in the first stage. Following MBR system an RO plant in "Christmas Tree" configuration has been installed and operated at 12–16 bars. The RO plant produces about 70% permeate and 30% concentrate. The quality of the recovered water meets the drinking water standards. The saline water concentrate stream is further treated with Fenton process before disposal[5].

A view of the submersible MBR in one of the tannery effluent treatment plants in China is shown in Figure – 2.

Fig. 2: *Submerged Membrane Bioreator*

Multiple stage evaporators using thermal and electrical power have been installed for evaporation of the reject saline stream from RO system. Further techno economical review and modified options are required on the sustainability of the multiple stage evaporator system.

4. TECHNOLOGICAL DEVELOPMENTS IN ASIAN AND MAJOR LEATHER PRODUCING COUNTRIES

The recent developments in cleaner production and waste management in Asian and other major leather producing countries are given in Table 1.

Table 1: *Technological Developments in Environmental Protection*

Country	Research & Technological Development
BANGLADESH	The main tannery cluster in Bangladesh is located in Dhaka city. Tanneries introduced cleaner technologies and chrome recovery system etc. with the support of UNIDO. The tanneries from the Dhaka city are being relocated in a newly developed industrial estate with Common Effluent Treatment Plant (CETP) of 30MLD capacity.
CHINA	There are about 800 tanneries and 13 CETPs in China. R & D activities on reduction of volume of water usage and pollution load at source through cleaner production program have been undertaken by many institutions. The tanneries are permitted to expand the capacity without increase in the water usage. One of the major tanneries has implemented the MBR and RO system for water recovery and reuse.

Country	Research & Technological Development
	As such there is no specific restriction on the Total Dissolved Solids (TDS) or salinity norms for the disposal of treated effluent. However meeting the BOD, COD norms for the saline streams from RO is one of the issues being addressed by new technological development. As a sustainability measure new licenses are given to tanneries with a processing capacity of more than 3000 tons /year of raw hides and skins.
INDIA	 **Fig. 3:** *UASB system with Bio-Energy generation from a CETP in India* Disposal of the saline stream from membrane units in land locked areas is one of the unresolved technical challenges. Treated effluent is mixed with treated domestic sewage and utilized for green development in some of the land locked areas. Decentralized secured landfill system linked with CETPs for leather sector had been implemented in many tannery clusters[6]. (First of its kind in the World). R&D activities on bio processing are under progress.
ITALY	Total aerobic biological oxidation system without the use of chemical is adopted in major CETPs for reduction of COD and sludge generation. Thermal treatment of sludge, energy generation from volatile organic matter and overall sludge management are followed. Central chrome recovery and reuse system are being adopted in many locations.  **Fig. 4** – *Extended Aerobic oxidation for sludge reduction in a CETP, Italy*
ROMANIA	R & D activities in Cleaner Production and Environmental Protection are being carried out in National Research and Development Institute for Textiles and Leather (INCDTP) / ICPI & University of Oradea, Romania. Many co-operation programmes in association with COTANCE and other institutions are under progress. Romania. Media and Conferences are effectively used to promote the importance and image of leather industry and environment protection activities[7].

Country	Research & Technological Development
RUSSIAN FEDERATION	Many institutions such as Department of Leather and Fur Technology. Water Recourses and Commodity Research, East Siberia State University of Technology and Management, Ulan-Ude, Russia and other industrial organizations promote technological development and environmental protection in leather and other industrial sector.
TURKEY	There are about 540 tanneries existing in 14 zones. Eight Common Effluent Treatment Plants (CETPs) have been established and are in operation. The biggest CETP with a capacity of 36,000m^3/day is in Tuzla near Istanbul[8]. The other major tannery cluster is in Izmir with an integrated CETP. The tanneries had resettled in industrial zones. The treated effluent is disclosed in to sea for TDS management with special bio-control.

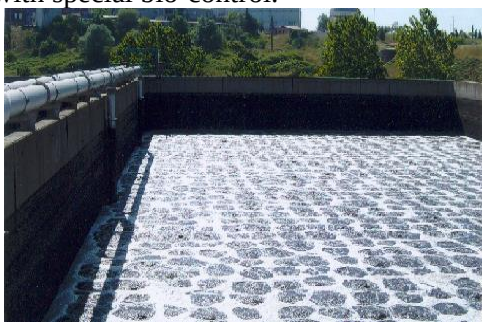

Fig.6 - *CETP in Istanbul, Turkey with Sea discharge for TDS management*

R&D activities on cleaner production and environmental protection are being continued in universities such as Ege University, Izmir etc. Sludge disposal is a major problem similar to other countries.

6. CONCLUSION

The leather production activities especially raw to semi-finishing process are being shifted from the developed nations such as United States, West European countries, etc. to Asian, North African and Latin American countries. The tanneries in major leather producing countries such as China, Italy, India, etc. have to develop and adopt new environmental protection measures such as adoption of membrane system for water recovery & TDS management due to enforcement of stringent environmental regulations. Sustainability of the small-scale units is becoming a serious issue to meet the new environmental requirements. Major investments are being made for environmental protection and resettlement of tanneries from the urban areas to the industrial parks with common effluent treatment plants. New regulations and restrictions such as REACH on the use of certain chemicals, salinity and water recovery under zero discharge concepts, disposal/ management of chrome containing sludge etc. envisage continued Research & Development activity[9]. Innovative tanning processes which will greatly reduce the water and chemical usage and minimize solid waste generation are needed together with overall environmental planning and management**.**

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ON THE THERMAL BEHAVIOR OF DIFFERENT TANNED BOVINE LEATHERS

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Abstract: *Leather is one of the most globally spread biomaterial which is obtained by the processing of different animal skins. It encompasses a wide palette of applications, from footwear and clothing to upholsteries and different types of furniture [1], [2], [3]. The main constituent of animal skins is collagen, a supramolecular fibrillar protein in the form of a triple helix. This form endows leather with elasticity, good mechanical properties and softness. A major disadvantage resides in the inapplicability of raw animal hides, due to their microbiological instability and decay through rotting. Microbiological stability is obtained through the tanning process, characterized by protein crosslinking and drying afterwards. After tanning the leather exhibits the required properties for the desired specific applications in terms of aspect, availability and sustainability [4], [5]. The study aims to elucidate the thermal decomposition process of chrome-free tanned bovine hide (wet-white) using a new product based on titanium and aluminium salts compared with the same hide tanned by chromium salts (wet-blue). The thermal behavior was studied by dynamic thermogravimetry in nitrogen atmosphere, up to 700 °C. A comparative thermal decomposition study between the different tanned bovine leathers was undertaken.*

Keywords: *Bovine leather, Thermogravimetric analysis, Thermal decomposition*

1. INTRODUCTION

Leather is one of the most widely spread biomaterial from collagen protein, which is modified for avoiding its putrefaction. One such a way may be achieved through complete stabilization with Cr III salts. Through this procedure, some properties, such as water absorption resistance, increase, together with putrefaction resistence, drying or swelling [6]. Collagen may be extracted as hydrolyzate with the Sörensen method [7]. Other improved characteristics include mechanical properties and elasticity. The tanning process consists of protein crosslinking and drying. Afterwards the tanned leather exhibits the mentioned properties for sought applications [4]. Cr III salts are still widely used as tanning material among the tanning agents. Leather manufacturing is known as one of the most polluting industry, due to the inorganic waste generated during operations. The Cr salts are heavy environmental and health pollutants. It is therefore that research in obtaining Cr free leather has expanded [1], for instance, replacing Cr III salts with waste of ultrapure titanium [5].

This study compares the thermal behavior in inert atmosphere of a Cr free 'wet–white' tanned leather (with a new product containing titanium and aluminium salts) compared with the same leather Cr III tanned ('wet–blue'), for gaining new insights and knowledge on this aspect.

2. EXPERIMENTAL

2.1. MATERIALS

The synthesis method of Ti–Al tanning agent and the obtaining of wet–white and wet–blue products were described in the literature [4], [5].

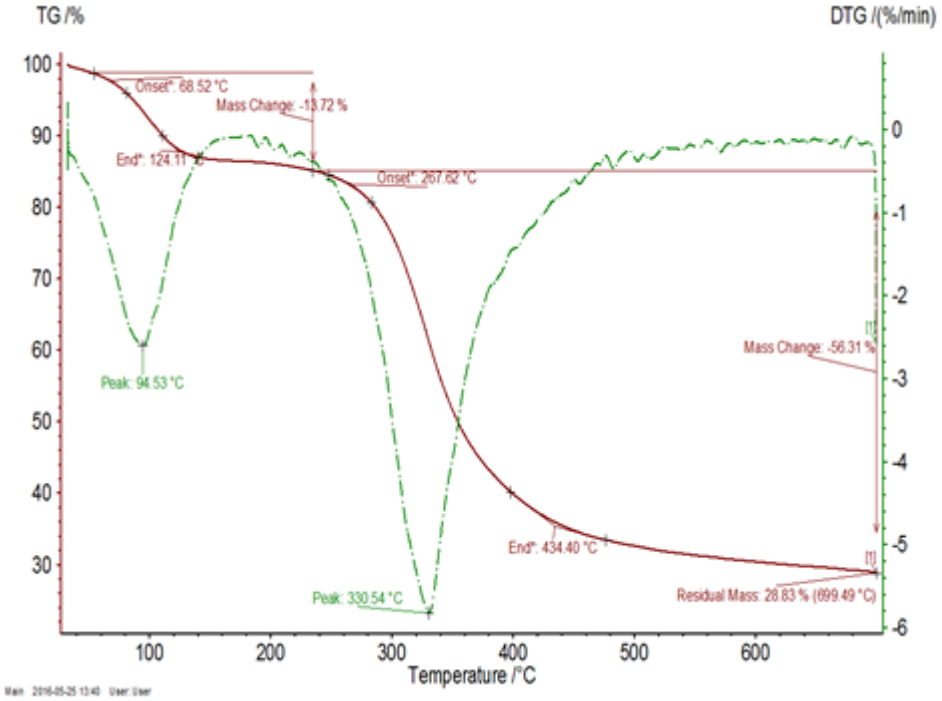
2.2. EQUIPMENT

The thermal degradation process was undertaken by means of a device of simultaneous TGA/DTG/DTA analyses STA 449F1 Jupiter model (Netzsch, Germany). 10 mg of sample was heated in the range 30–700 ^{o}C under a nitrogen atmosphere (flow rate 50 mL min^{-1}), in an open Al_2O_3 crucible and a second identical empty one was used as reference material. A heating rate of 10 ^{o}C min^{-1} was applied. The glass transition temperature domain (T_g) was determined by using the Differential scanning calorimetry (DSC) technique. The thermograms were recorded on a DSC 200F3 Maia (Netzsch, Germany) calibrated with five metals (In, Sn, Bi, Hg, Co) according to standard procedures. Samples were heated in aluminium crucibles with pierced and pressed lids for removal of any volatiles released during heating. Sapphire is used for absolute heat capacity values determination. The used DSC device covers a temperature range of –150 to 500 ^{o}C and cooling is made with liquid nitrogen. The experiments were conducted in nitrogen, as inert atmosphere, with a heating/cooling rate of 10 ^{o}C/ –10 ^{o}C and in the temperature range –50 to 300 ^{o}C.

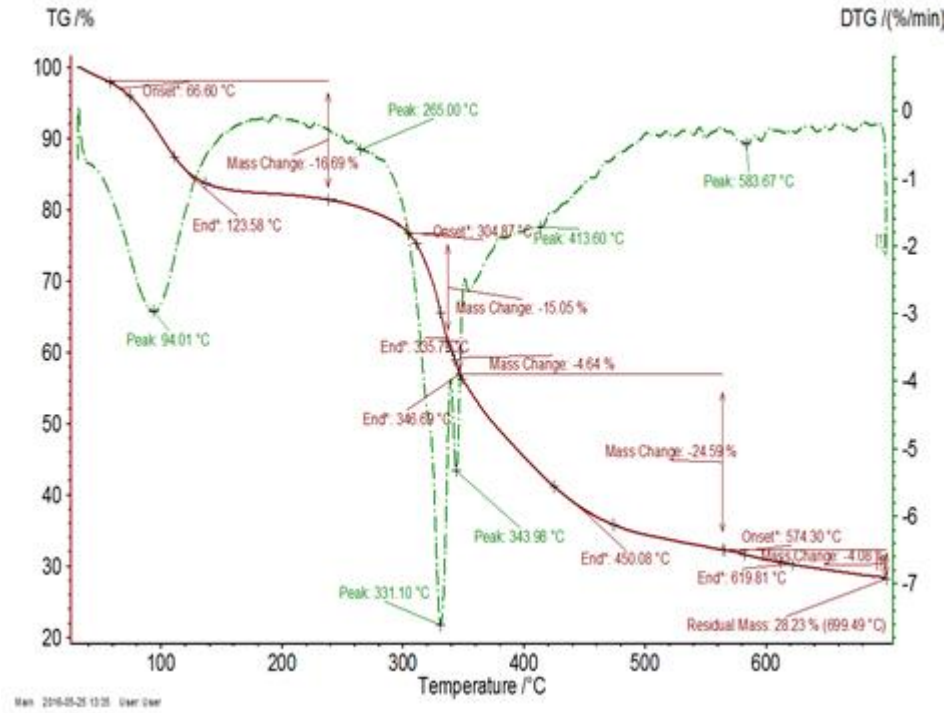
3. RESULTS AND DISCUSSIONS

In the case of both measurements, the first thermal decomposition stage is assigned to humidity loss, in the range 56–139 ^{o}C with a mass loss of up to 17 % (Fig. 1). With the aid of the first derivative (DTG) curve, one may observe that, except the 'wet-white' sample, which decomposes in two stages, the 'wet-blue' sample degrades in at least three stages. The main thermal decomposition process occurs at the initial temperature of 268 ^{o}C, for 'wet-white' leather, and 305 ^{o}C for 'wet-blue' leather, hence the presence of Cr increases thermal stability and also, generates the lowest residual mass value (28.23 %), residual mass values varying in the range 28.23, for 'wet-blue' leather, to 36.87 % for 'wet-white' leather.

The thermal decomposition studies were in a good correlation with the DSC ones (Fig. 2). The first DSC heating curves exhibited a wide endotherm profile corresponding to fibrillar collagen denaturation and water loss. This denaturation is specific to biphasic amorphous-crystalline structure specific to collagen based materials, in which the triple helix crystalline collagen structure is incorporated into an amorphous matrix. Total heat value was measured by integrating the endothermic signal and was of 370.7 J g^{-1} for 'wet-white' leather and 439.4 J g^{-1} for 'wet-blue' leather, the latter value being the highest due to Cr hardening the denaturation process and thus increasing the enthalpy of the process.



a)



b)

Fig. 1: *TG/DTG thermograms of the studied samples: (a) wet-white and (b) wet-blue leather*

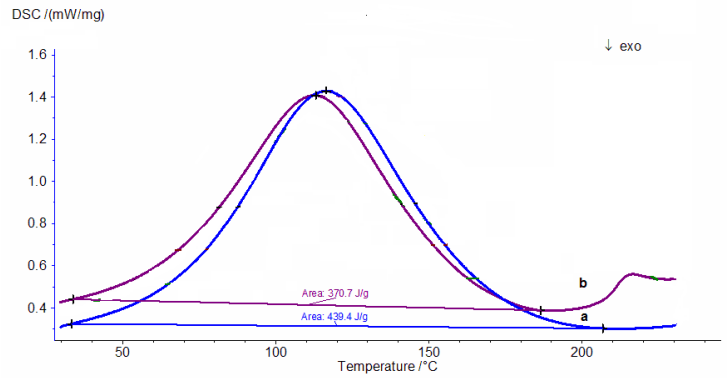


Fig. 2: *DSC curves of the first heatings of: (a) wet-blu and (b) wet-white leather*

4. CONCLUSIONS

There were undertaken comparative thermal stability studies between wet–white and wet–blue processed bovine leathers. A similar thermal behavior was observed for both samples. In the case of the wet-blue tanned leather, the presence of Cr led to an increase in thermal stability. The first DSC heating curves exhibited a wide endotherm profile due to the overlapping of collagen denaturation with water loss. Total heat value was the highest for 'wet-blue' leather, due to Cr hardening the denaturation process.

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ANNALS OF THE UNIVERSITY OF ORADEA
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COMMON APPROACH ON WASTE MANAGEMENT

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Abstract: *The world population has doubled since the 60's, now reaching 7 billion – it is estimated it will continue growing. If in more advanced economies, the population is starting to grow old and even reduce in numbers, in less developed countries, population numbers are registering a fast growth. Across the world, the ecosystems are exposed to critical levels of pollution in more and more complex combinations. Human activities, population growth and shifting patterns in consumer nature are the main factors that are at the base of thin ever-growing burden on our environment. Globalization means that the consumer and production patterns from a country or a region contribute to the pressures on the environment in totally different parts of the world. With the rise of environmental problems, the search for solutions also begun, such as methods and actions aimed to protect the environment and to lead to a better correlation between economic growth and the environment. The common goals of these endeavors from participating states was to come up with medium and long term regulations that would lead to successfully solving environmental issues. In this paper, we have analyzed the way in which countries started collaborating in the 1970's at an international level in order to come up with a common policy that would have a positive impact on the environment. The European Union has come up with its own common policy, a policy that each member state must implement. In this context, Romania has developed its National Strategy for Waste Management, a program that Romania wishes to use to reduce the quantity of waste and better dispose of it.*

Key words: *environment, regulations, waste, sustainable development, globalization.*

1. INTRODUCTION

During the UN Paris Conference in December 2015, the 21st session of Conference of Parties and the 12th session of the Reunion of Parties of the Kyoto Protocol. All participating countries assumed a common goal: to limit the increase of global temperature to less than 2 degrees and to continue their efforts of reaching their target of 1.5 degrees. The European Union took this target and put into a context, offering concrete courses of action to fulfill their engagement that until 2030, greenhouse gasses emissions will be reduced with 40% compared to the level of 1990.

2. ENVIRONMENTAL CONCERNS

2.1 Reasons that led to environmental regulations at an international level

Interest in the environment began in the 1970s' with the rise of the first ecologic policies. The United Nations Conference on the Human Environment, was first held in Stockholm, Sweden, in 1972, and marked the emergence of international environmental law. The Declaration on the Human Environment also known as the Stockholm Declaration set out the principles for various international environmental issues, including human rights, natural resource management, pollution prevention and the relationship between the environment and development. The conference also led to the creation of the United Nations Environment Programme. [1]

After the 1980s' pressures meant to increase and improve environmental standards have forced companies to synchronize their social investments with business strategies

The World Commission for Environment and Development, through the Brundland Report (1983), draws attention on the environmental problems and on how to solve them in the long term without harming the economy. The main objective of the Brundland report was to help define common perceptions of long term environmental problems and of the necessary efforts for successfully solving these issues.

After this moment, the legislation has been changed and adapted to the new environmental challenges, some of which were discussed at the Earth Summit in Rio de Janeiro (1992). The Rio Declaration was adopted then, for environment and development, the Convention for biologic diversity and the Agenda 21 were also presented. In these documents, a series of actions that governmental organizations must take to reduce the negative impact on the environment are presented. [2]

In 1997, the UN General Assembly held a special session to appraise the status of Agenda 21 (Rio +5). The Assembly recognized progress as "uneven" and identified key trends, including increasing globalization, widening inequalities in income, and continued deterioration of the global environment. A new General Assembly Resolution (S-19/2) promised further action. [3]

The United Nations Conference on Sustainable Development (UNCSD), also known as Rio 2012, (Rio+20), or Earth Summit 2012 was the third international conference on sustainable development aimed at reconciling the economic and environmental goals of the global community. The conference had three major objectives: securing renewed political commitment for sustainable development, assessing the progress and implementation gaps in meeting previous commitments and addressing new and emerging challenges. [4]

The document entitled "The future we want" is signed by the heads of states from 192 participating countries at the conference. Based on this document, the participating countries strengthen their commitments made in Agenda 21 for promoting a sustainable future. The document also contains a set of measurable targets aimed at promoting sustainable development globally. [4]

2.2 Managing waste in Uniunea Europeana

The European Union (EU), as a party to the United Nations Framework Convention on Climate Change (UNFCCC), reports annually on greenhouse gas (GHG) inventories for the year t–2 within the area covered by its Member States (domestic emissions taking place within its territory) [5]. The legal basis for compiling the EU inventory is Council Decision No 280/2004/EC concerning a mechanism for monitoring Community greenhouse gas emissions and for implementing the Kyoto Protocol. [6] The Kyoto Protocol is an international environment accord. It was negotiated in 1997 by a total of 160 countries. The accord states that for industrialized countries, a decrease of 5.2% of greenhouse gasses must be done during 2008-2012, as compared to the levels of emissions in 1990.

In the European Union, each member state has organizations in place for such things, as well as national action plans. Most of the strategies of the member states are based on a common instrument, created for reducing greenhouse gas emissions at the level of the whole Union, but also to save up resources. Environmental protection is comprised of improving its quality (the environments'), protection of public health and rational and prudent usage of natural resources.

The EU's approach in managing waste is based on four major points:

- Recycle and reuse;
- Encouraging a high level of recovery of materials from components, preferably through recycling. In this way, several waste fluxes are identified, for which recycling is very important: product wrappings, out-of-use vehicles, batteries, electric and electronic equipment.
- Trying to find how to reuse waste that is not yet recycled;
- Eliminating waste entirely – in case some waste cannot be reused, these need to be eliminated using safe methods for the environment and human health, in a program of strict surveillance. [7]

By analyzing the total waste generated in the EU according to statistics provided by EUROSTAT, we can notice an increase in waste in 2012, as compared to 2010, from 2460 mil. t of waste to 2515 mil t of waste. Although the total waste value of 2012 is higher than in 2010 and in 2008, a decrease can be noted when comparing to the year 2004. Between EU member states there are major differences in the quantity of waste that is generated, as well as between the activities that led to this waste. We consider the value of waste from 2008 and 2010 to be less, due to the economic crisis.

The activities that contributed the most to producing wastes are new construction and demolition of buildings (33%), extracting industry waste (29%), processing industries (11%), households (8%), while the rest 15% was generated by other economic activities. [8]

By analyzing the waste quantity compared to population, we find out that the average quantity of waste generated in the EU was of 4984 kg/capita. We can also note that there are great differences between member states: while in Bulgaria a total of 22.1 tons of waste were generated per capita, in Croatia there have been only 781 kg/capita. [8]

2.2 Managing waste in Romania

By Decree 870 from 2013, which entered into force in 2014, in regards to the National Strategy for Waste Management, Romania committed itself to better take care of waste disposal. With this strategy, Romania aims to prioritize its efforts in managing waste, to develop means through which to encourage waste reduction and waste recycling, increasing the rate of recycling and improving the quality of recycled materials, promoting reuse of containers, reducing the impact of carbon generated by waste, encouraging the production of energy by using non-recyclable waste, implementing the concept of cycle analysis of a product, in the waste management policy. [7]

By analyzing the situation in Romania per data provided by EUROSTAT, we can note that the total quantity of waste generated in Romania in 2010 was of about 219.309 thousand tons, while in 2012 it was about 266. 976 of the total of 2.460.330 and 2.515.110 thousand tons – representing 11.21% from the total waste produced in EU in 2010 and 10,61%of waste produced in 2012.

If we analyze the structure of waste from 2012, we can find that: mining and quaring represents 83,63% from total of waste, manufacturing 2,25%, energy 3,38%, construction and demolition 0,49%, other economic activities 8,47%, household 1,74%. [8]

3. CONCLUSIONS

Globalization and the evolution of global tendencies make the environmental conditions and policies of each country hard to manage accordingly – separated from the global dynamics. The current global megatendencies will affect consumer patterns and influence environment and climate. These megatendencies are related to the demographic evolution, economic growth, means of production and commerce, technological progress, ecosystem degradation and climate changes. Until 2050 the total population of Earth is expected to pass the 9 billion mark, according to UN projections. [9] Nowadays we are 7 billion, while in the 1950's there were less than 3 billion. From 1900 until today, the use of materials has increased tenfold [10] and it could double again until 2030. [11] Global demand of energy and water is projected to grow with 30% and 40% in the next 20 years. [12]

In these conditions, the states of the world need to unite their efforts in order to answer the new challenges. These targets can not be achieved only by engaging governments. Economic actors and civil society have an important role in this process: their role is to aplly the measures adopted at global level and implemented nationally.

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ANNALS OF THE UNIVERSITY OF ORADEA
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CAN 'UPCYCLING' GIVE ROMANIAN'S FASHION INDUSTRY AN IMPULSE?

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Abstract: *Fashion's impact on the environment includes the entire lifecycle of a garment. There are many environmental issues associated with the textile sector on the entire life cycle of production and consumption. The clothing industry needs to find imaginative solutions to produce environmental improvements. The aim of this paper is to review concepts regarding textile waste that reach the end of their first life cycle and to evaluate the potential for recyclability of those materials. Intent of this paper also tries to reduce the amount of textile waste in the landfill by exploring different methods. This was done by first assessing and analyzing the waste followed by characterizing the waste for different properties. If the properties of textile waste are not suitable enough to be manufactured in new fabrics, other alternatives could be explored. One of our proposals is to use creativity of designer in order to create new products trough upcycling. Redesigning throug a creative modification of a product out of used or upcycling in an attempt to generate a product of higher quality or value than the compositional elements can be a solution to reduce waste yet is still marginal. Starting or shifting to a business involving taxtile waste can offer an economic benefit of upcycling. However, upcycling explore to provide an interim solution to the textile waste problem, by optimising the lifetimes of discarded clothes from an inefficient system, while recycling technologies moves to develop more sustainable approaches.*

Key words: *Recycling, textile waste, fast fashion, waste management, life-cycle of clothes*

1. INTRODUCTION

In an era of fast fashion, or mass-produced, budget-priced, disposable clothing, textile waste has continued to grow. Moreover fast fashion leaves a pollution footprint, with each step of the clothing life cycle generating potential environmental hazards. Since we have enormous amounts of textile and clothing waste, redesign or upcycling has begun to be a popular fashion approach. Recycling means that the product is transformed into new material or fibres. The recycling approach needs mono materials, which means that the whole garment who is made from more materials (threads, buttons, zipper etc.) must be dismantled beforenhand.

2. THE FASHION INDUSTRY AND CLOTHING CONSUMPTION

The textile and fashion industry is one of the biggest and oldest industrial sectors in the world. Over the past decade, the fashion industry has grown at 5.5% annually[1] , to now be worth

an estimated $2.4 trillion. In fact, not only does it touch everyone, but it would be the world's seventh-largest economy if ranked alongside individual countries' GDP.

The overconsumption of fashion is stimulated by fast fashion and its cheap, constant flow of new designs and limited runs. Clothing prices fell drastic during the last 30 years; by 26.2 % in Europe and 17.1% in the US. At the same time consumption flourished with the number of pieces sold in the UK increasing by a third, leading to over 2 million tonnes of clothing being consumed every year.[2] The Environmental Protection Agency estimates that, Americans are throwing away more than 15 million tons of textiles — about 85% of their clothes — each year, accounting for 9% of total non-recycled waste. The textile waste increased from 14.33 million tons in 2012 to 15.13 million tons in 2013. In the same time, unfortunately, the percentage being recovered and recycled dropped from 15.7% to 15.2%. In terms of carbon emissions, the recycling of 2.3 million tons of clothing each year is equivalent to taking 1.3 million cars annually off the road.[3]

According to the European Commission, Europeans discard 5.8 million tonnes every year, with 75% going to landfill or incineration and only 25% being recycled [4] with the UK alone responsible for 350,000 tonnes of that [5]. That's problematic not least because nylon fabrics take around 30-40 years to decompose, rope 3-14 months, while wool emits methane as it decomposes, a key contributor to greenhouse gases [6].

Of all the old clothing, 70 % is used as second hand clothing, 6 % is waste bags and zips, 8% is used for reclaiming fibres and making recycled products, 7 % is used as wiping material and the remaining 9 % is shredded and used as stuffing. It is a surprising fact that over 70 percent of the world's population uses second hand clothing [7].

3. ENVIRONMENTAL ISSUES ON THE LIFE CYCLE OF THE CLOTHING SECTOR

There are many environmental issues associated with the clothing sector on the entire life cycle of production. In figure 1 we mention only the solid waste arising from yarn manufacturing of natural or artificial fibres, fabric and garment production, in use and disposal of products at the end of their life. Over their life-time, products can contribute to various environmental impacts. Life cycle thinking considers the range of impacts through the entire life of a product. Life cycle thinking can be used to help decision-making in the field of waste management and to identify the best environmental options. It can help policy makers understand the benefits and compromise they have to confront when making decisions on waste management strategies [8]

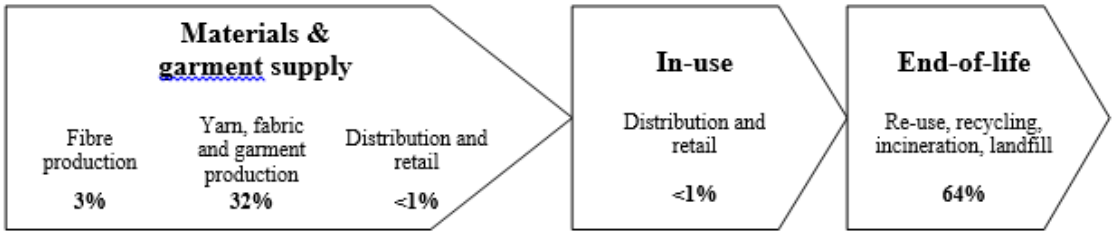

***Fig. 1**. Estimated contribution (%) of each stage of the garment life-cycle to the waste footprint (Source: adapted from WRAP,2011)*

4. RECYCLING AND UPCYCLING OF GARMETS

There are multiple environmental benefits associated with recycling clothing. It reduces the amount of pesticides used in growing cotton or to make fabrics from petroleum sources and the water needed to dye fabrics, and cuts down on the pollutants, greenhouse gases and volatile organic compounds released into the water and air from manufacturing processes.

During the last 30 years industrial development has achieved environmental improvements and has moved towards a smaller environmental impact. However, at the same time production as well as consumption has increased by the same levels, which erodes the environmental benefits of the technological advances: i.e. the rebound effect [9, 10]. The increasing amount of textile and clothing waste has led to the necessity of development of methods using the textile waste, i.e. reuse, recycling or redesign.

The waste management hierarchy, presented graphical in the form of a pyramid, indicates an order of preference for action to reduce and manage waste. The strategy to waste management must give priority in the first place the prevention, in the second place recycling, reusing and revalorization and finally dispose waste [11, 12].

The fashion industry can become environmentally active and contribute to our society more than just economically. McDonough and Braungart, creators of the cradle to cradle concept [13], have advocated radical design innovations for perpetually circular material reuse [14]. They offers a broad definition claiming that upcycling is "*optimizing the materials, ingredients, and process pathways in such a way that waste is converted to raw materials for nature or some other industry*"[15]. Many leading apparel retailers like H & M, Inditex or sportswear retailers like Adidas and Nike presents and market their products with the percentage of recycled material in the product profile. On their Annual Reports an inportant place is taken from their statistical data that disclose the quantity of clothes they have collected from their shoppers and the amount they contribute to international charity from their revenue.

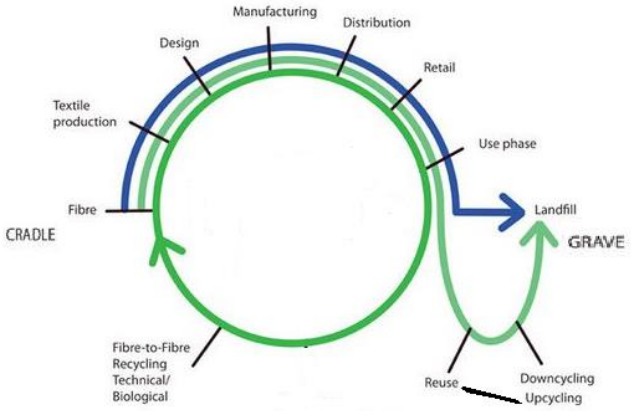

Fig. 2. *Schematic life-cycle for clothes*

4.1. Recycling of textile waste

There are in essence two types of textile recycling: fiber recycling and polymer recycling. Fiber recycling means the garment is shredded back into fibers that are typically blended with new fibers to make a new yarn for new products. Polymer recycling is typically used with polyesters that are shredded and ultimately melted down and turned into plastic pellets that are then are respun into fibers for new polyester applications[16].

The recycling of clothing process includes more steps. Clothing consisting of fabrics such as cotton, polyester, nylon and rayon. First, the unwearable garments are sorted and graded as natural, synthetic and blended fabrics. There are fundamental differences between natural and synthetic fibers but the sorting plants that recycle textiles are able to determine the future of the unwanted clothes.

In the recycling process for natural fibre (cotton, wool, silk etc) clothes, first of all, the unusable natural textiles are sorted into colours. Color sorting results in fabric that does not need to be re-dyed. The color sorting means no re-dying is required, saving energy and avoiding pollutants. The textiles are then pulled or shredded so that what is left is an amalgamation of different fibres. Depending on the end use of the yarn, other fibers may be incorporated. The yarn is then cleaned and mixed through a carding process. After that, the yarn is re-spun and ready for subsequent use in weaving or knitting. These newly produced recycled textiles are then picked up by sustainable designers and manufacturers. Woolen garments are sent to other firms that make fibre renewal to make yarn and fabric. Not all fibers are spun into yards; some of them are compressed for textile filling such as in mattresses, for fillers in car insulation, roofing felts, loudspeaker cones, furniture padding, panel linings and many other uses. Cotton clothes are recycled and used for paper manufacture, automotive, and mining industries and different other uses.

In the case of polyester-based textiles, garments are shredded and then granulated, and processed into polyester chips. Polyester is a relatively easy material to recycle. Because its oil based, it can be melted down and reformed into new fibers. The polyester chips are subsequently melted and used to create new fibers for use in new polyester fabrics.[16]

4.2. Upcycling of textile waste

Upcycling can be seen as a new environmentally conscious view in fashion design that repurposes discarded garments and textile waste and reintroduces it back into the fashion market. It's an improved form of recycling that, instead of transforming down the clothings or fabrics, uses them in their original form, giving them a new purpose and a much better quality.

Murray (2002) describes it as "*not merely conserving the resources that went into the production of particular materials, but adding to the value embodied in them by the application of knowledge in the course of their recirculation. So, if one can add value – economic, intellectual, emotional, material – to a product through the process of reuse, it can be called 'upcycled'*"[17]

The process involves a substantial amount of creativity and vision, based on a fundamental environmental consciousness. The end result is typically a product or item that is unique and sustainable. It takes courageous imagination to propose systemic solutions that bypass the mainstream of what we regard as philosophy about fashion and clothing business. The world of upcycling has exploded in the past few years, and there are a large number of inspirational designs in this facet of sustainable green fashion. At the beginning of the 21st century several designers have made use of the concept of upcycling in designing trendy products. Producing eco-friendly fashion is becoming more of a priority for brands across the board from luxury (ex. Reformation, Charlote Bias, Viktor & Rolf), to high street. Mega brands now recognise how important sustainable fashion is to their consumers. Even large companies have begun to be involved, such as the British fashion brand Marks & Spencer who launched a special suit line, which is made of recycled materials [18]. Upcycled fashion offers creativity and individuality because consumers won't see someone else wearing the same outfit. This is an ideal way for those who want to be self-expressive to find fashion that fits their style.

4.3.Textile waste and upcycling in ROMANIA

Although the amount of waste pre-consumption has steadily decreased [19] , textile waste in Romania has seen a tremendous growth lately, both due to rising imports of clothing and especially due to large imports of used clothing. Because such large volumes of second hand clothing are constantly being imported and consumed, large volumes reworn clothing held by the user are discarded. It creates a large waste stream at the end of the functional life of clothes, which are finaly disposed of in landfills but Romania has no large scale recycling [20]. From a total of 4379 companies in the garment sector, approximately 57.8% (2530 companies) have fewer than 9 employees, 26,1% (1144 companies) have between 9-49 employees, and only 0,28% from the Romanian have more than 250 employees. The sharp competition in the sector and continued decline in competitiveness of Romanian garment industry [21] may challange some companies to migrate to upcycling of textile. Integrating redesigned clothing into the fashion system could be one of many alternatives to environmentally harmful consumer behavior, such as disposing of unwanted clothes into landfills.Redesigning throug a creative modification of a product out of used or upcycling in an attempt to generate a product of higher quality or value than the compositional elements can be a solution to reduce waste yet is still marginal. Starting or shifting to a business involving taxtile waste can offer an economic benefit of upcycling.

5.CONCLUSIONS

The clothing industry needs to find imaginative solutions to produce environmental improvements. Upcycling has become lately a very popular subject in the fashion industry. It is one of the most sustainable circular solutions in the waste hierarchy, positioned between reuse and recycling, since upcycling typically requires little energy input and can eliminate the need for a new product [22]. However, upcycling explore to provide an interim solution to the textile waste problem, by optimising the lifetimes of discarded clothes from an inefficient system, while recycling technologies moves to develop more sustainable approaches.

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APPLICATION OF FUZZY LOGIC BASED APPAREL SIZE FINDER IN ONLINE MARKETING

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Abstract: *The emergence of online retailing has been one of the most significant developments in business history. Altough proportion of apparel sales in online retailing also has been shown rapid increase, there are some significant barriers to overcome for expanding this market share. It is seen in literature that there are many researchers point out that finding right size apparel is the one of the most significant problems in online retailing. There are many study to solve this problem but still there is not an exact solution yet. Creating 3D avatars for virtual try on or scanning body measurements of consumers have been used to solved this problem but any study has not come up with a reliable solution. In this study, a fuzzy logic based apparel size finder website is proposed. The benefits and working princible of this website are also explained. In this website, both of consumers and retailers can create a profile page for sharing products or following each other. Once consumers follow a profile of retailer, they can see the right size of any shared apparel. On the other hand, retailers can also directly send message to certain users for certain size apparel. This system brings advantages for both parties. Consumers can reach the correct size of apparel and retailers can reach to target customer. It is assumed that creating website alike this or application of existing online retailers will help to reduce return in apparel online retailing as well as it may help to expand online retailing.*

Key words: *Fuzzyy Logic, Online marketing, Apparel online marketing, Fuzzy relations*

1.INTRODUCTION

The emergence of online retailing has been one of the most significant developments in business history. Altough proportion of apparel sales in online retailing also has been shown rapid increase, there are some significant barriers to overcome caused by lack of physical experinece. It is noted in literature that finding right size is one the most significant obstacle for online retailing [1], [2]. Apparel size is directly related with consumer satisfaction and usage rate [3], [4]. Once consumers are not happy with the size of the apparel that bought online, they most likely to return it. On the other word, when consumers return the apparel, it means additional cost and waste of time either suppliers or consumers [5].

There are some studies to find suitable body size for apparel in online marketing. Creating 3D avatars with the body measurements of users or scanning bodies in offline store are some of

these methods [6]. However, these methods may negatively affect the shopping behavior of the people [7]. Besides, some new methods use body size that classically measured by users [8].

Fuzzy logic has been using for many textiles related problems and one of its example was application for choosing right apparel size [9]. In this study fuzzy logic based apparel size finder which is works with classically taken body measurements is applied a website and prospective benefit was evaluated either for users or retailers. In this website, both of consumers and retailers can create a profile page for sharing products or following each other. Once consumers follow a profile of retailer, they can see the right size of any shared apparel. On the other hand, retailers can also directly send message to certain users for certain size apparel. This system brings advantages for both parties. Consumers can reach the correct size of apparel and retailers can reach to target customer.

2. FUZZY LOGIC BASED APPAREL SIZE FINDER WEBSITE

2.1Finding right size for apparel via fuzzy logic

In this study, each size of a brand is considered as a separate product, and all separate products are numbered as *1, 2, …, p*. As an example, a specific brand *X* (a product) supposed to have different sizes as "Small", "Medium", "Large" and "XLarge". The measurements for these size of brand X are given in Table 1.

***Table** 1: Size Measurements for brand X*

	Small	**Medium**	**Large**	**XLarge**
Collar	35-38	39-40	41-42	43-44
Shoulder	38-42	43-44	45-46	47-48
Chest	90-98	99-104	105-110	111-114
Waist	40-46	47-52	53-54	55-56

The following rules are considered for constructing suitable fuzzy intervals;

- Measurements that smaller than client's attribute value is **not** suitable for the client's body size.
- Most suitable size for the client is the value of 96.5% of upper value of the related size (counting into account of ease).
- Loose sizes for a client also have some fitness degree, but smaller sizes are considered as NOT suitable for a client.

The fuzzy numbers constructed for sizes "Small", "Medium", "Large" and "XLarge" are in form of triangular fuzzy numbers defined as T (a, b, c), where T denotes one of the sizes of "Small", "Medium", "Large" or "XLarge", *a* is the bottom limit of the all sizes, *b* is the optimum measurement for the handled size and *c* is the upper limit of the related size (see **Fig**. 1). The following figure is an example of membership function used for collar circumference for all sizes in a brand. Functions for shoulder, chest and waist have similar shape but different lower and upper limit and core point values.

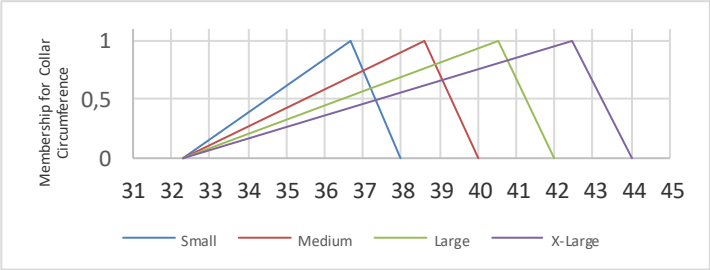


***Fig.** 1: Membership function example for collar circumference*

In the study, a web interface is constructed for the users to enter their body size measurements (weight, length, collar circumference, shoulder width, chest width, waist circumference, arm length). Also, the measurements of shirts of certain brands are kept in a database. In order to find the optimum size of product for a user, a triangular membership value is computed using the measurements of the user and the size measurements of the apparels.

The system calculates all the class membership values using measurement values of the user (collar, shoulder, chest and waist measurements in cm) comparing with all sizes. For all sizes, the minimum membership value is considered. The user is assigned to the size with the maximum membership degree among these minimum membership values.

As an example, suppose that a client *C* has measurements as *C* (collar = 38cm, shoulder = 44cm, chest = 104cm, waist = 94cm). By default, the lower limit of the size is calculated as 85% of the upper limit for convenience. This lower limit value is used as the lower limit for all sizes in related measurement. The most fitting value of the size is assumed 3.5% less than the upper limit. For example the parameters for "Small" size of "Collar" measurement is (32.3, 36.67, 38). The parameter table for "Collar" in "Small" size is shown in Table 2.

***Table** 2: Parameters for "Small" size in "Collar" attribute*

Size (Collar)	a	b	c
Small	32.3	36.67	38
Medium	32.3	38.6	40
Large	32.3	40.53	42
X-Large	32.3	42.46	44

With triangular membership for "Small" size with parameters (32.3, 36.67, 38), we get $\mu_{Small,Collar}(38)=0$.

$$\mu_{Small,Collar}(x)=\begin{cases}\frac{x-32.3}{36.67-32.3}, & 32.3<x\leq 36.67,\\ \frac{38-x}{38-36.67}, & 36.67<x\leq 38,\\ 0, & otherwise.\end{cases} \quad \textbf{(1)}$$

If the membership of this client to "Medium" size class is calculated, the parameters (32.3, 38.6, 40) is used. For medium size of client *C*, we get $\mu_{Medium,Collar}(38)=0{,}905$.

$$\mu_{Medium,Collar}(x)=\begin{cases}\frac{x-32.3}{38.6-32.3}, & 32.3<x\leq 38.6,\\ \frac{40-x}{40-38.6}, & 38.6<x\leq 40,\\ 0, & otherwise.\end{cases} \quad \textbf{(2)}$$

In the same way, values for "Large" and "XLarge" ($\mu_{Large,Collar}(38)$ and $\mu_{XLarge,Collar}(38)$) are also calculated. This operation is applied for the other attributes of the user. The degree of fitness for this client *C* to size class "Small" is computed as:

$$\mu_{C,Small} = min\{\mu_{Small,Collar}(38), \mu_{Small,Shoulder}(44), \mu_{Small,Chest}(104), \mu_{Small,Waist}(94). \quad \textbf{(3)}$$

After computing class membership values for each product (i.e. “Small”, “Medium”, “Large”, “XLarge”) for client *C*, the product (size) with the highest membership value is assigned as the most suitable product (size) for the client. In other words, size that provides

$$max\{\mu_{C,Small}, \mu_{C,Medium}, \mu_{C,Large}, \mu_{C,XLarge}\}, \quad \textbf{(4)}$$

is the best fitting size for the users within the given parameters.

Table 3 shows an example classification for a user. The user is said to be best fitted in "Large" size of this brand.

***Table** 3:Membership values for a user*

Measurement	Small	Medium	Large	X-Large
Collar (38 cm)	0,00	0,42	0,32	0,26
Shoulder (44 cm)	0,00	0,00	0,55	0,45
Chest (104 cm)	0,00	0,00	0,55	0,45
Waist (94 cm)	0,00	0,39	0,33	0,29
Member to	0,00	0,00	**0,32**	0,26

2.2 Website implementation

In website implementation of this system, each user or retailer can create a personal profile page using with basic informations of body or apparel measurements. While creating account, guiding picture also appears for measuring correctly the right size of body part (**Fig**. 2). It is a key point that, for getting size suggestion, users body measurements and given apparel measurements have to be matched.

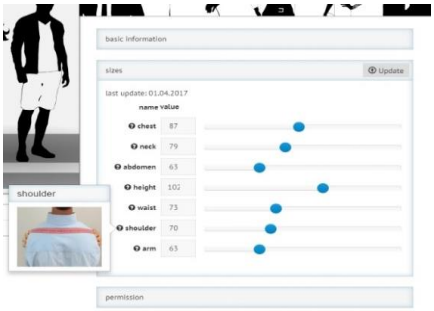


***Fig. 2:** Creating user profile*

Once users start to follow desired retailers, they are able to see best fitted size suggestion on the bottom of the any product that shared by retailers (**Fig**. 3).

***Fig. 3**: Size suggestion*

On the other hand, retailes can classified users based on their body size or degree of fitness for each product. By this way, each retailer able to reach target consumer. The amount of classified users is also reported to retailer (Fig. 4).

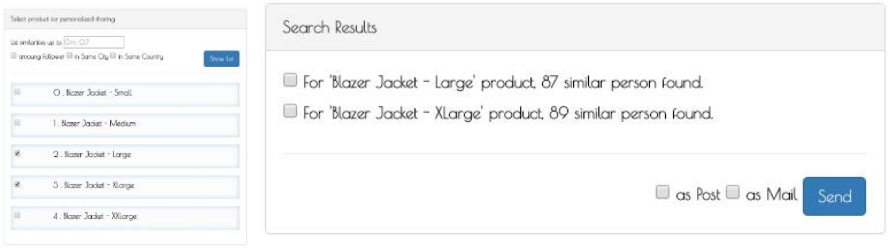
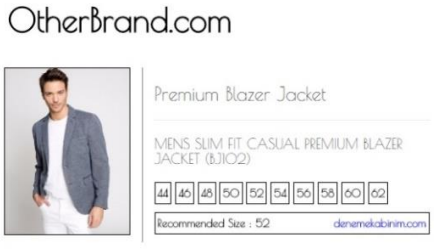


***Fig. 4:** User classiffication for retailers based on body size*

The other method of using fuzzy logic based apparel size finder system, existing online retailers can adapt this system into their website with javascript. If any online retailers share measures of apparel with designed fuzzy based system, registered users can reach right size via this system (Fig. 5).

a.

***Fig. 5: a.** Webpage screen of other retailes before fuzzy system implementation.*



b.

***Fig. 5: a. b.** Webpage screen of other retailes after fuzzy system implementation*

3. CONCLUSIONS

In the previous part of this study, working princible of fuzzy based apparel size finder was showed. In this part of study, implementation of this system in a website or adaptation of existing retailer's website were showed. There are two basic circumstances for success of this system. First, the success of this system is directly related with right body measurements. Therefore, while users

create profile with their body size, each mesuremenets illustrates with pictures that explain how and which part to measure. Second, retailers share their products with measurements of exact part. End of these two crticial steps we are able to store measurements of bodies and apparels.

There are also two important ways to use this system for either users or retailers. First, users can reach the right size of desired apparel. Second, retailers classified users based on their body measurement or degree of fitness.

The most significant benefit of this system is helping to choose right size to overcome the biggest barrier in apparel online retailing. It is assumed that this system will help to expand market share of apparel online retailing. When consumers are satisfied with the size of purchased apparels, it will help to decrease amount of return products. By this way, extra costs for users and retailers will also be prevented.

This system can also be used for strategic marketing. With this system, retailers are allowed to classified users based on their body size or the rate of fitness for any product. By this way, retailers are able to reach target consumer and it may help to increase rate of purchase.

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- All above mentioned features will be published at *www.denemekabinim.com* .

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE ANALYSIS OF THE USE OF TIME BY THE STUDENTS OF THE FACULTY OF TEXTILE AND PRINTING

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Abstract: *The main purpose of this study is to analyze how generally the students use time, how rationally they use their free time, what kinds of extracurricular activities they have and how much time they devote to individual study. The study covers the students from the Faculty of Textile and Printing of the Technical University of Moldova. The method of unassisted investigation of a sample of students consisting of 50 people was used to carry out the study. Following data processing, 31 questionnaires have been validated, based on which the results and interpretations have been analyzed and presented. Having analyzed the study results, it is observed that each person spends his/her time depending on his/her: biological rhythm; state of health; personality and skills; the number of tasks/activities he/she must fulfill etc. Since each individual is different as personality, the results on time spent for the same activity is as different in many people. For example, it has been found that in order to fulfill individual tasks a person can spend an average of about 3 hours per day, while the other one, who is at the same faculty of the same group, is spending about an hour and a half. According to the chart, a student, on average, is in class 242 minutes per day, that is 4 hours; to prepare for individual tasks he/she spends about 160 minutes per day, or 2 hours and 40 minutes. According to the data from the study we can establish that a lot of time is spent for housework, physiological needs, sleep and rest. The time used for these activities by participants in the study is about 12 hours of the 24. The other 12 hours include the remaining activities they are carrying out.*

Key words: *time management, planning, effective leadership, student, free time*.

1. INTRODUCTION

Nearly one hundred years ago, the author who laid the ground for scientific management, Frederick Taylor postulated the principle „Accurate management of working hours and standardization of job", which is a huge step towards increasing efficiency in the organization [1].

Time is an effective tool to guide the implementation of many activities. It is actually perceived and used differently from person to person. It seems that there is never enough time in the day. But, since we all get the same 24 hours, why is it that some people achieve so much more with their time than others? The answer lies in Good time management [2].

Management means effective and efficient management of an activity. From this perspective, the manager is not able to do profitable business for the company of which he/she is in charge, if he/she cannot manage resources efficiently. Time is a precious, demanding and irreversible economic resource: it is the rarest resource as it is irreplaceable, but yet „unlimited"; it is expensive but it cannot be bought, stored or multiplied; loss of time cannot be ensured even by the

largest insurance company in the world, so it cannot be „compensated"; it is highly perishable and inelastic. Nevertheless, time is not anyone's property, it is impersonal, it is not everybody's and it is cannot be stopped by physical things [1].

Paul R. Godin proposes a suggestive and succinct definition of the concept of time management: „A personal process to program, anticipate and react in a planned, predictive, efficient and effective manner" (cited by Armstrong, 1999) [2].

The main factors affecting the time management are [2]:

- the nature of the activity;
- personality/skills of the individual that carries out the activity;
- the influence of people surrounding the individual;
- the influence of the environment in which the individual works;
- culture.

So the way how to manage time depends on each person. As Dumitru Moldovan says „Ancient mystics reminded our hearts, and modern experiments demonstrated to our minds that the only force that is the strongest in the Universe is living in each of us" [3].

There are increasingly more studies conducted on this subject, as it has been realized that the time mismanagement is the main obstacle in achieving success, especially in business, but it has also been generally realized by people that proper time management can help live a more organized and balanced life. A global study was conducted by the Organization for Economic Co-operation and Development (OECD), which included people aged 15-64. In order to have relevant results, the study was conducted throughout 11 years (1998-2009) [4]; its results can be seen in the figure 1 and 2.

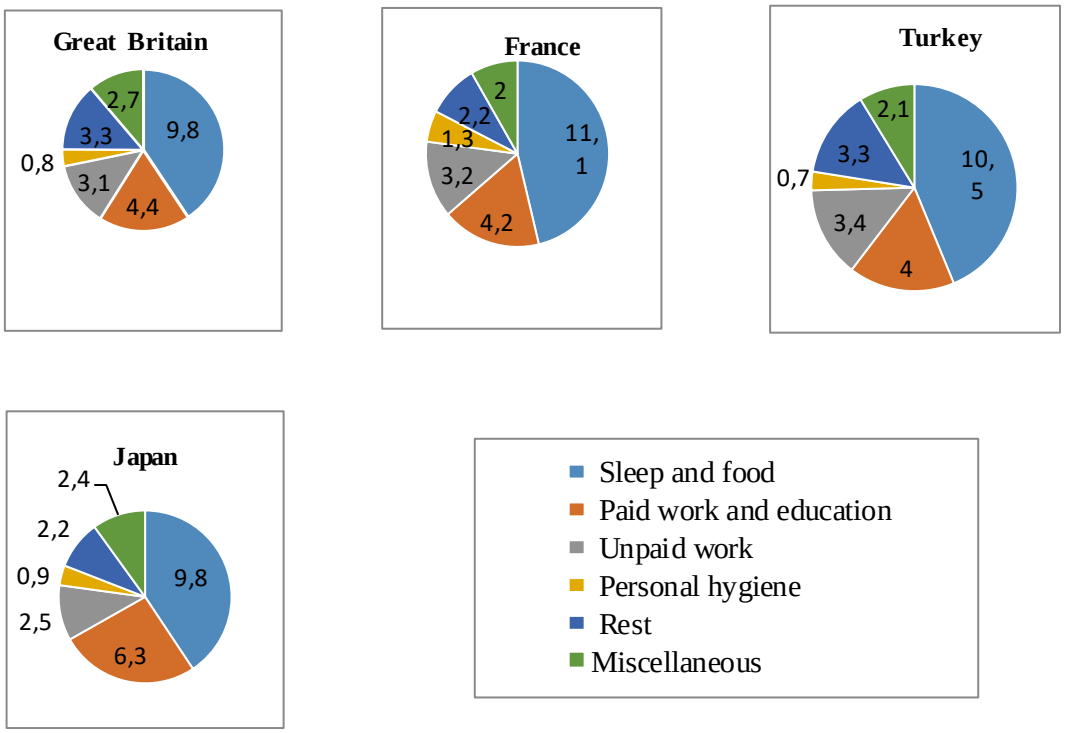

Fig. 1: *Time spent for various activities in some countries of the world*

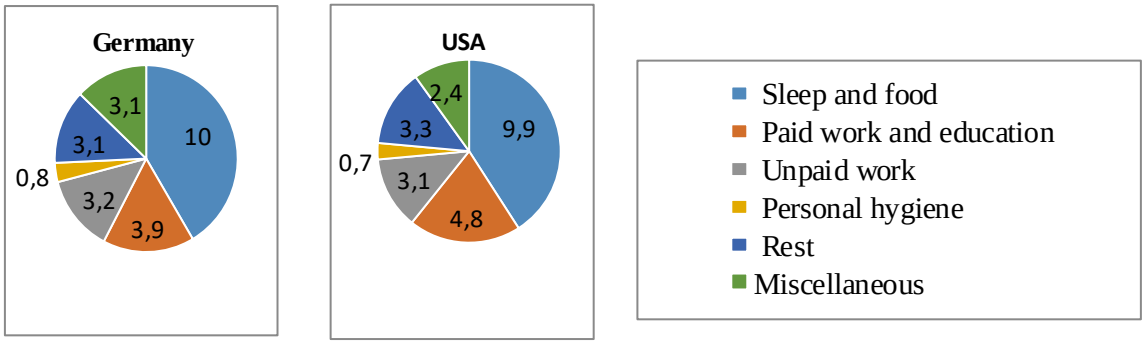

Fig. 2: *Time spent for various activities in some countries of the world*

The results of the above study show that time is spent differently in each country. This is due to the culture and customs of each nationality individually. Time management related approaches differ from author to author. In this paper we propose the time management principles put forward by Stephen Covey and Gleb Arhangheliskii, well known in the time management field, as comparative analysis, clearly outlining the priorities, table 1 [4; 5].

Table 1: *Comparative analysis of the time management approach by specialists*

Criteria	Stephen Covey	Gleb Arhanghelski
Quotes	Dealing with not urgent but important items – this is the core of efficient management.	The money lost can be won, but lost time is lost for good. Time is the material from which our lives are made.
Planning basis	Weekly planning	Daily planning
Method	Eisenhower Matrix: „Important and urgent", „Important but not urgent", „Not important but urgent", „Not important and not urgent".	Chronometry, Prioritization, Time planning by „Swiss Cheese model", etc.
Main principles	Be proactive (do not be a slave to circumstances, create your own fate).	Think of the problems in writing. Create an image of it – and you will solve it.
	Begin with the end in mind.	Highlight one thing – on what you are working and a few moments to reflect what is envisaged. Forget the rest.
	Put first things first (important things are the first to do).	Control your concentration.
	Think Win-Win. Strive for mutual benefit.	Make a decision. Do not play too much a double game.
	Seek first to understand, then to be understood.	If it is to be done – do it. If it is not to be done – do not do it.
	Synergize.	Get rid of your fear and it will disappear. Thereafter, begin to solve the problem.
	Sharpen the saw.	5-minute rest per hour. Try not to think of anything at that time.
Type of people	Linear	Parallel
Type of culture	Monoactive	Polyactive

We see obvious distinctions in the approach cited in the table. The concepts are recognized and applied for teaching purposes among large companies, which continuously intensify the problem of the efficiency of the human factor's activity. For the purpose of an activity to be responsible for a higher efficiency, with better results each time, various tools that have a recognized contribution in time management, such as questionnaires, matrices and agendas are developed [3].

2. EXPERIMENTAL RESEARCH RESULTS

The main purpose of this study is to analyze how generally the students use time, how rationally they use their free time, what kinds of extracurricular activities they have and how much time they devote to individual study. The study covers the students from the Faculty of Textile and Printing of the Technical University of Moldova. The method of unassisted investigation of a sample of students consisting of 50 people was used to carry out the study. Following data processing, 31 questionnaires have been validated, based on which the results and interpretations have been analyzed and presented. The structure of the validated sample is based on sex (female – 22 persons, male – 9 persons), years of study (first year – 11 persons, second year – 7 persons, third year – 13 persons), place of residence (dormitory – 29 persons, other - 9 persons).

In order for data processing to be possible and rational, categorization of time was performed as follows: time for attending classes; time for completing the tasks; time for housework such as: household, food preparation, etc .; time for physiological needs such as: food, bathroom, etc.; time for sleep; time for rest during the day; idle time can be: computer games, movies, online serials, social media etc.; time for recreational activities: meetings with friends; music; walks; information (news), etc.; time for sports; time for other important activities such as: shopping, visits to doctor, etc.; time for non-university activities, these can be diverse, for example: training courses, work, etc; travel time to the educational institution; other travel time.

Further, a classification of activities, recorded by the students according to previously established times, was established. This classification will show how much time people spend to carry out certain activities. The records collected from the students have been processed by the rank-ordering method. Thus, average data have been obtained on efficiency of time use by students for each category of activity. The results obtained are presented in graphical form in the figure 3.

Having analyzed the study results, it is observed that each person spends his/her time depending on his/her:

- biological rhythm;
- state of health;
- personality and skills;
- the number of tasks/activities he/she must fulfill etc.

Since each individual is different as personality, the results on time spent for the same activity is as different in many people. For example, it has been found that in order to fulfill individual tasks a person can spend an average of about 3 hours per day, while the other one, who is at the same faculty of the same group, is spending about an hour and a half. There are also other factors that influence the duration, for example:

- the importance that the individual attaches to this activity;
- a dose of subjectivity implied by selfies.

According to the chart, a student, on average, is in class 242 minutes per day, that is 4 hours; to prepare for individual tasks he/she spends about 160 minutes per day, or 2 hours and 40 minutes. According to the data from the study we can establish that a lot of time is spent for housework, physiological needs, sleep and rest. The time used for these activities by participants in the study is about 12 hours of the 24. It follows that students devote a half of their life to take a bath, to eat, to

maintain cleanliness and to sleep. The other 12 hours include the remaining activities they are carrying out.

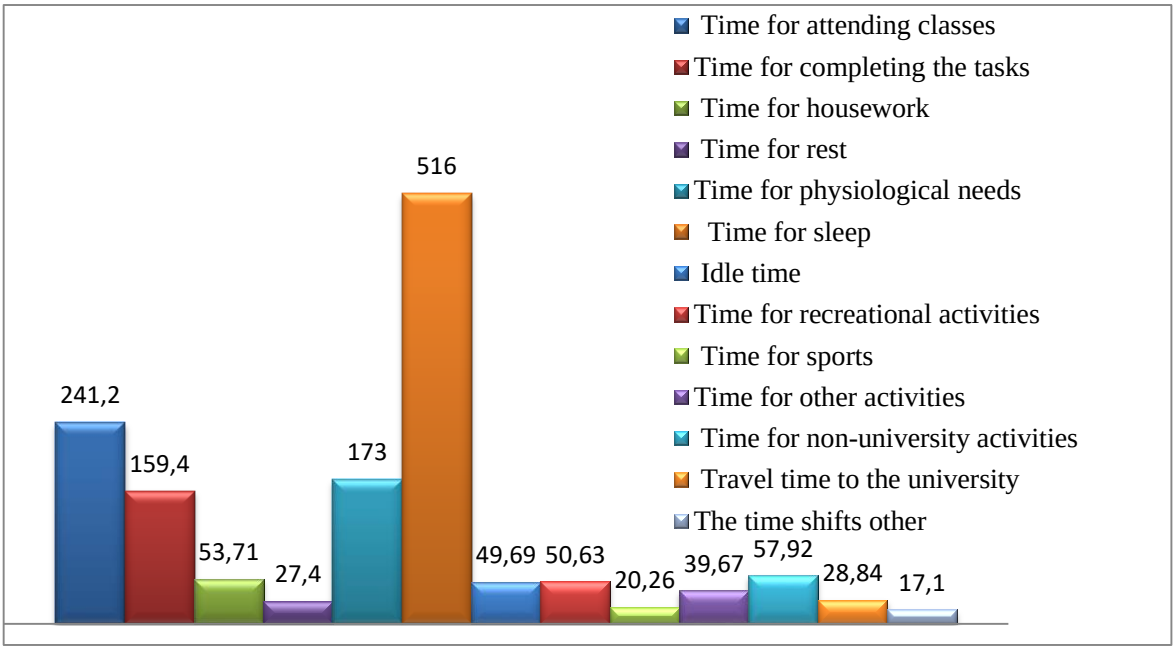

Fig. 3: *Time in minutes spent by students for daily activities*

These data are presented graphically in the figure 4.

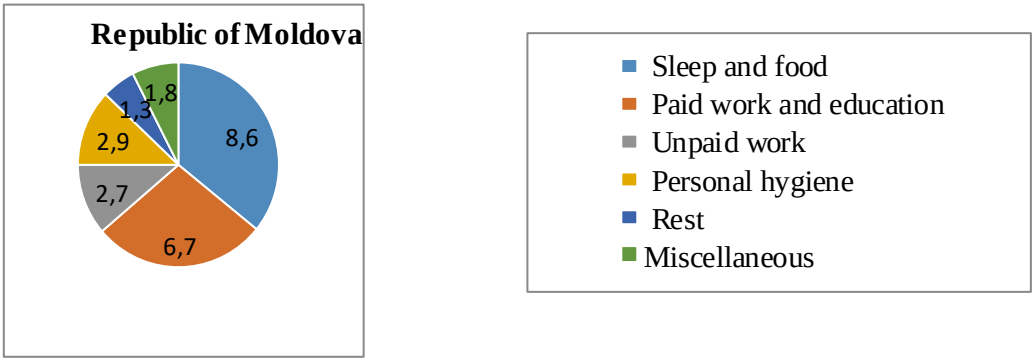

Fig. 4: *Time used by students of the Faculty Textile and Printing*

3. CONCLUSIONS AND RECOMMENDATIONS

The results of the study conducted are close to those from the Figure 1 and 2. People from these countries spend on average 10 hours for sleep and food, as the participants in the study. People from these countries spend 4.6 hours for paid work and education, while students of our study – 4.2

hours. Time spent by participants of the study for recreational activities is 27.4 min. If we focus on the principle of time management according to Gleb Arhanghelski's model from the table 1, saying it is important to rest 5 minutes every hour, we can say that this time is not enough – it should be 80 minutes. Night's sleep is especially important for students, since brain is constantly thinking during the day. The effects of sleep deprivation are well known. The analysis of the chart from the figure 3 shows that students dedicate sufficient time for sleep.

Following this study we can conclude that the results obtained are quite good. However, the students were not totally objective since it is known that they are wasting much more time to watch movies, to communicate over social media and generally to browse the Internet. A factor that greatly influenced the results obtained is that the data were collected on the eve of the session, when all the students are actively involved in individual tasks, trying to complete them to avoid academic arrears. As mentioned earlier, time management refers to the each person's personal approach, and the individual can be self-disciplined. In order to establish meetings „with oneself", thus liberating from the grip of others, to go to bed an hour earlier and to wake up an hour earlier to plan the working day, to reward when obtaining the goal or to search for a balance by practicing sports or a recreational activity are the signal of a „healthy" concern for time management. According to Patrick Forsyth, the principles of good time management are not complicated. Overall, they may be summarized as follows [6]:

- establish a list of tasks you have to fulfill;
- sort them by priority;
- fulfill the plan that you've made.

„The number one lesson" recommended by this researcher is: never and never believe in the statement „it only takes a minute".

These principles may provide support and recommendations for the participants of the study to improve the scenarios of their individual activities in relation to those planned, in order to obtain the greater efficiency.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

INCREASING THE COMPETITIVENESS OF COMPANIES IN THE TEXTILE AND CLOTHING DOMAIN AND INTEGRATION IN INNOVATIVE CLUSTERS

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Abstract: *Successful businesses require access to knowledge and highly qualified workforce, faster access in finding suppliers, customers, competitors, educational institutions and research laboratories, specialized social assistance, in a more concentrated manner. These goals can be best achieved through clustering. Cluster formation is facilitated by the following actions: dynamic analysis and continuous communication of the vision, implementation of the strategy, implementation of the action plan and meetings between stakeholders.*

The paper presents the clusters of the textile and clothing domain in Romania and the analysis of their key economic indicators. The turnover performed in 2014 by the enterprises producing textiles and clothing within the 4 Romanian clusters was about 1.09 billion lei, employing a staff of approximately 7416 people. It was seen that for 2014, Romanian Textile Concept brought together more than 2754 employees, Traditii Manufactura Viitor 2565 employees, ASTRICO 1958 employees and Transylvania Textile&Fashion with 139 employees.

Clusters have the potential to create ecosystems favorable to innovation for strengthening SMEs groups, in which their needs can be better exploited as a way to promote economic growth. As a perspective, one of the recommendations of the EU is to invest in social innovation activities. Each cluster is unique, differentiating itself by objectives, number of enterprises, composition, size, flexibility etc.

Key words: *cluster, innovative cluster, textile, clothing textiles and garments*

1. INTRODUCTION

The *cluster* is defined as a geographical concentration of competitive enterprises in an industry or service area that do business with each other [1]. Clusters represent a new way of thinking about the nation, state, local economy and give a new role to corporations, governments and other institutions for the purpose of increasing competitiveness.

Up to 20-30 years ago, the development strategy of a region was linearly (infrastructure building, investments in specific facilities, tax concessions, reduced maintenance costs), while today the successful businesses have more complex needs.

Successful businesses require access to knowledge and highly qualified workforce, faster access in finding suppliers, customers, competitors, educational institutions, research laboratories and specialized social assistance, in a more concentrated manner. These goals can be best achieved through clustering. The clusters model generated in the US was quickly adopted in the European Union, in practically all areas of activity [2]. Apparently, at the time of globalization, the importance

of clusters should decrease. An opposite development was observed, with an increased role of clusters in a complex, dynamic and knowledge-based economy [3].

The widely accepted model of cluster partnership based on innovation is one called "triple helix" [4], which brings together representatives from industry, research institutes and universities (representing providers of innovative solutions applicable to the real needs of enterprises in cluster) and representatives from local and regional government etc.

Thus, innovative clusters are a step forward as they ensure economic growth at regional and national level through cooperation of companies at a higher level as cluster components, leading them to operate in an integrated system. Thus, on a higher level, the network acquires benefits of diversity and complementarity, as well as the intense compensation between the activities involved, similarly to those of large organizations.

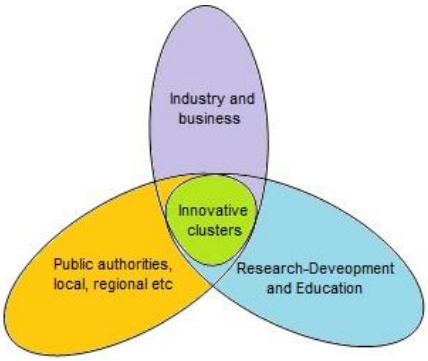

Fig. 1: *"Triple helix" model for an innovative cluster*

2. CLUSTERIZATION AT NATIONAL LEVEL

Cluster formation involves the following *steps* [5]:

a) *Analysis*, which includes: statistical analysis, interviews in companies, expert opinions, identification of opportunities;

b) *Preparation*, which includes: consulting, informative meetings, discussions, planning, debates;

c) *Strategy*, which includes: development directions, communication, consultation, branding, coordination;

d) *Organization*, which includes: training, human resources management;

e) *Action*, represented by: projects, cooperation, facilities, innovation.

Cluster formation is facilitated by the following actions: dynamic analysis and continuous communication of the vision, implementation of the strategy, implementation of the action plan and meetings between stakeholders. Cluster formation is also supported by neutral communication, good listening abilities, good interpersonal skills and the experience in multiple domains.

The textile and clothing industry has a long tradition, representing one of the traditional industrial domains of the European economy. Although global competition is fierce and the industry suffered a significant relocation of manufacturing in countries with low labor costs, textiles continue to represent one of the basic industrial domains of the European economy [6].

In order to be competitive on the world market, the European textile-clothing industry has focused its efforts on marketing (eg. design and brands) and on optimizing the supply management, in order to provide products with high added value on short term. Competitiveness depends

considerably on the ability of developing innovative products and processes, and thus, the textile industry has invested in research and implementation of new technologies.

Regarding the *cluster formation process in Romania*, within the textile-clothing domain, the following relevant issues can be mentioned:

• individual companies, especially SMEs, which usually represent the T&C industry, do not have the power to challenge the mature market, hence a solution to this problem are clusters, that can be supportive environments for cooperation in business, trade, communication, law, legislation etc.

• Romanian T&C companies have to give up their advantage of low labor cost and conquer a top position in the external market, namely the segment of medium and high priced-products, with high quality and a strong image brand, achieved through a substantial investment in design, creation, marketing and promotion.

At the moment, the database of the Ministry of Economy, Trade and Relations with Business Environment - Directorate of Industrial and Environmental Policy includes 88 clusters and competitiveness poles, of which 28 received the Bronze label and 8 received the Silver label after benchmarking studies conducted by experts of ESCA [7]. These were economic structures that could establish a partnership agreement between the various actors, representing 4 types of organizations (Romanian model): within the "Four leaf clover": industry - research - public authorities - catalyst organizations.

3. CLUSTERS IN THE TEXTILE-CLOTHING DOMAIN

Four clusters in the textile-clothing domain are operating in Romania, being members of the Romanian Cluster Association. ***The National R&D Institute for Textiles and Leather – INCDTP*** [8] is member of all the 4 clusters representing this domain.

Depending on the region, the textile clusters in Romania are:

• In the Bucharest - Ilfov Region and South - Est Region, is located the cluster ***Romanian Textile Concept - RTxC*** [9], comprising 36 representatives from the economic environment based on an association consisting of 10 manufacturing companies with old tradition in the clothing, knitwear, shoes and leather goods industry.

• In the North – East Region, is located the cluster ***ASTRICO NE*** [10]. The association of producers ASTRICO operates for a long time, being a powerful industrial group for production and marketing of knitwear, based on the company Rifil, the leading producer of yarn for knitwear in Eastern Europe. The industrial group works mostly for export to the European market and is composed of 25 companies: a spinning representative for the Romanian industry - RIFIL and 24 manufacturers of knitwear and knitted garments.

• In South - East Region, is located the cluster ***Traditii Manufactura Viitor - TMV Sud –Est*** [11]. The objective of this cluster is to focus on activities and products with focus on ~~of~~ creativity and technology, on increasing the consumer awareness and interest towards fashion, on stabilizing and improving the workforce in the area, on attracting new companies and last but not least, on the creation of a regional brand. The companies of the cluster represent the industrial domain and are both large companies and small and medium companies (SMEs), while their experience is based on more than 15 years production in clothing.

• In the Central Region is located the cluster ***Transylvania Textiles & Fashion- TT&F*** [12], which aims at strengthening relations already existing in the domain of students internships and training of specialists, but also at identifying all opportunities for performing of innovative products with increased added value, by means of technological transfer and applied research. The group is representative for the economic environment and it consists of 20 companies.

The cluster Romanian Textile Concept has the SILVER LABEL for cluster management awarded by ESCA (European Secretariat for Cluster Analysis) [13]. The other clusters in the T&C have awarded the BRONZE LABEL, too.

In 2015, the ***Competitiveness pole in the textile and clothing industry NOATEX*** was created. It brings together companies from the textile and related domains from all over Romania, research institutions, administrative units and catalyst organizations.

INCDTP is an active member in all 4 Romanian textile clusters and in the NOATEX pole. INCDTP is also member of the Romanian Cluster Association – CLUSTERO [14], through its cluster membership.

4. ANALYSIS OF ECONOMIC INDICATORS OBTAINED BY CLUSTERS OF TEXTILE-CLOTHING DOMAIN

The analysis of economic indicators obtained by the textile-clothing clusters was performed within INCDTP. Figure 2 presents the evolution of the *turnover* indicator for each of the Romanian textile clusters. The values shown in the graphs represent the cumulative value of the turnover only for manufacturing companies representing business environment. It has to be underlined that all cluster's turnover recorded an uptrend in the period 2012-2014 [15].

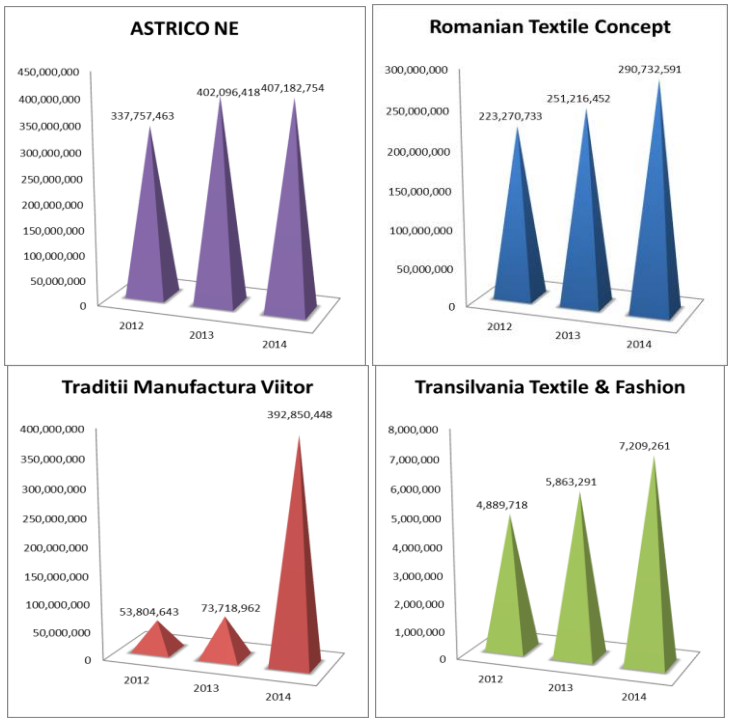

Fig. 2: *Turnover in lei, evolution for enterprises in the textile clusters in Romania*

Comparing each cluster contribution to the total of this indicator (for the year 2014), the figures were: ASTRICO 37.08% , Traditii Manufactura Viitor 35.78%, Romanian Textile Concept 26.48% and Transilvania Textile&Fashion 0.66%.

Analyzing the evolution of the percentage of the total turnover of textile clusters in the turnover achieved nationwide by the textile-clothing industry, growth was registered from 4,3% in 2012 to 6,9% in 2014 (Figure 3).

Fig.3: *Turnover for the textile clusters from the total for the Romanian textile-clothing industry*

The analysis of the graph in Figure 4 shows the *cumulative number of employees for textile clusters* and also the ranking of clusters depending on the number of employees.

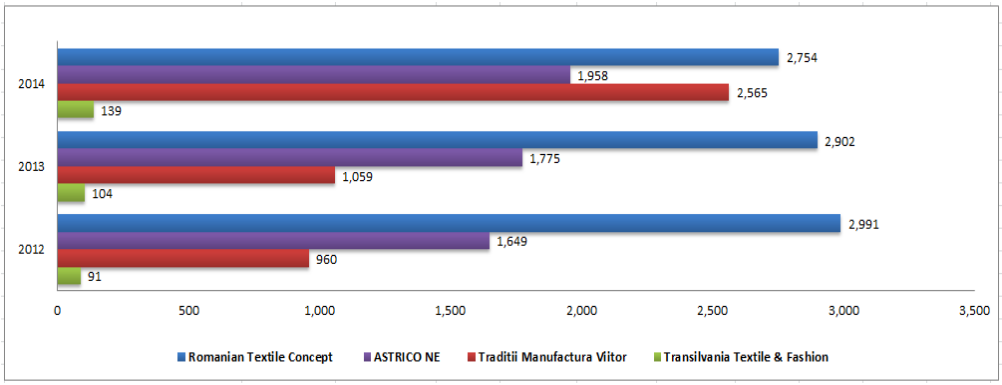

Fig. 4: *Total number of employees for the textile clusters in Romania*

It can be underlined, that in 2014, Romanian Textile Concept brought together more than 2754 employees, Traditii Manufactura Viitor 2565 employees, ASTRICO 1958 employees and the last Transylvania Textile&Fashion with 139 employees. Analyzing the evolution of the cumulative number of employees for textile clusters in the number of employees at the country level in the textile-clothing industry, it was registered a growth from 2.9% in 2012 to 3.29% in 2014 (Figure 5).

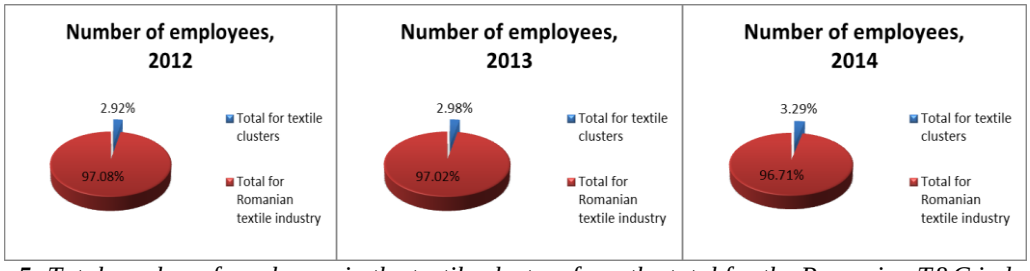

Fig. 5: *Total number of employees in the textile clusters from the total for the Romanian T&C industry*

The turnover performed in 2014 by the enterprises producing textiles and clothing within the 4 Romanian clusters was about 1.09 billion lei, while employing a staff of approximately 7416 people.

5. CONCLUSIONS

Clusters have the potential to create ecosystems favorable to innovation, for strengthening SMEs groups in which their needs can be better exploited as a way to promote economic growth. From the comparison between the results of the clusters to the overall results of the industry during the same years (sales and employment), it can be concluded, that clustering has an positive impact on the business environment.

The European Commission will facilitate matchmaking events for integrating SMEs into clusters of excellence and European value chains. Focus will not be limited to industrial domains, but will also facilitate cross-domain and cross-border collaboration and innovation.

As a perspective, in EU one of the recommendations is to invest in social innovation activities. Each cluster is unique, differentiating itself by objectives, number of enterprises, composition, size, flexibility etc. Three factors are critical to the success of the cluster: collaboration, cluster management skills and innovation capability.

ACKNOWLEDGEMENTS

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

IMPROVING THE TEXTILE'S ENTERPRISES KNOWLEDGE MATRIX

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Abstract: *The textile enterprises need adequate solutions to face the competition on the global market. Innovation leverages the enterprises competitiveness: however, improving innovation is a task of research providers in the field. The Knowledge Matrix for Innovation (KMI) represents an instrument for quantifying the intangible assets of a textile enterprise. Examples of intangible assets are: innovation strategy / culture, informational resources, training methodology, relationships portfolio, IP rights etc. By improving such factors of the KMI, the textile enterprises are going to improve their competitiveness. This main aim is tackled by the Erasmus Plus – VET Project "Matrix of knowledge for innovation and competitiveness in textile enterprises - TexMatrix" (2016-2018). The red line of the project follows the definition of the KMI, the adaptation of the Benchmarking questionnaire and its implementation on the e-learning Tool, the Benchmarking study by consulting of 50 textile enterprises at consortium level, supporting the Guide with new research and innovation management solutions for the enterprises and Blended courses for 95 young trainees, based on the Guide in e-learning format. The project also aims to counsel 100 decision-factors from textile enterprises on the new solutions comprised in the Guide, within 5 Workshops. The e-learning Tool has the URL address: www.advan2tex.eu/portal/ .*

Key words: *innovation, e-learning, questionnaire, blended courses, workshops, VET .*

1. INTRODUCTION

The intangible assets of a textile enterprise are of utmost importance for their innovation activity. Their evaluation and improvement contributes in bridging the weak points and consolidating the strong points of a textile enterprise. The concept of the Knowledge matrix for innovation (KMI) aims to create a comprehensive image of the intangible assets of an enterprise [1]. Examples of intangible assets are: innovation strategy / culture, informational resources, training methodology, relationships portfolio, IP rights etc. (Fig. 1).

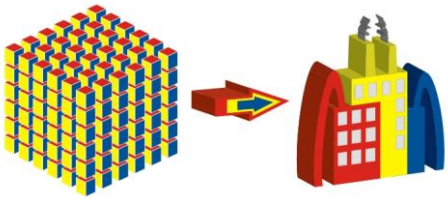

Fig. 1: *The implementation of the KMI in textile enterprises has multiple benefits*

Advantages for identifying and improving the Knowledge matrix in a textile enterprise are:

- an adequate classification of an intangible asset and their relation with other assets
- an improved of knowledge inventory
- the assets may be evaluated against their costs and overlapping assets can be eliminated
- non-productive assets may be better exploited
- all asset data of a certain criteria can be easily identified with all its relations
- certain gaps in the knowledge base can be bridged.

2. THE TEXMATRIX PROJECT

In order to tackle the implementation of the Knowledge Matrix for Innovation in textile enterprises, an Erasmus Plus project was conceived, named "Matrix of knowledge for innovation and competitiveness in textile enterprises - TexMatrix". The strategic partnership project has an implementation period of two years (Sept. 2016 – Aug. 2018) and is dedicated to Vocational Education and Training – VET – on the theme improvement of innovation. The consortium is formed of five partners with long-lasting tradition in the European textile domain: INCDTP – Bucharest (Coordinator), TecMinho – Portugal, Centrocot – Italy, University Maribor – Slovenia, Technical University "Gh. Asachi" – Iasi. The TexMatrix project 2016-1-RO01-KA202-024498 has been funded with support of the European Commission (Fig. 2).

Main Outputs of the project are:

1. The Knowledge matrix for innovation
2. The Benchmarking study
3. The Guide with new solutions for textile enterprises
4. The e-learning Tool and work-based training

The red line of the project follows the definition of the KMI, the adaptation of the Benchmarking questionnaire and its implementation on the e-learning Tool, the Benchmarking study with consulting of 50 textile enterprises at consortium level, a Guide with new research and innovation management solutions for the enterprises [2], supported by the Benchmarking study and Blended courses for 95 young trainees based on the Guide in e-learning format. The project also aims to counsel 100 decision-factors from textile enterprises on the new solutions comprised in the Guide, within 5 Workshops [3-4].

Erasmus+

TEX MATRIX
of knowledge for innovation and competitiveness in textile enterprises

Fig. 2: *Erasmus Plus and TexMatrix project's logo*

3. THE KNOWLEDGE MATRIX FOR INNOVATION

The project is after the first semester of implementation. At this moment, the Knowledge matrix for innovation was defined and the related Benchmarking matrix was established. The KMI includes 52 factors grouped in Criteria and Elements. The KMI aims to quantify the intangible assets of the textile enterprise. The Elements of the KMI represent the prerequisites a textile enterprise uses in order to fulfill its objectives: the Conditions establish the Resources, while both are conditioning the Activities and the Results. The Elements and the corresponding Criteria mutually established by the TexMatrix Partners are presented in Table 1.

Table 1: *Structure of the KMI*

No.	Element	Criteria	Factors
1.	**CONDITIONS**	Innovation culture	5
		Innovation strategy	5
		Leadership	4
		SUM =	**14**
2.	**RESOURCES**	Human resources	5
		Organizational structure	4
		Material resources	3
		External relationships	4
		Financial sources	1
		SUM =	**17**
3.	**ACTIVITIES**	Management of ideas	2
		Management of innovation projects portfolio	2
		Surveillance and knowledge management	3
		Innovation promotion	2
		IPR	3
		SUM =	**12**
4.	**RESULTS**	Evaluation and monitoring	5
		Image	3
		Learning from failures	1
		SUM =	**9**
		SUM =	**52**

4. THE BENCHMARKING QUESTIONNAIRE

The Benchmarking Questionnaire (BMQ) has a 1:1 relation with the KMI – however, the factors are meant as questions for the textile enterprises. This BMQ was implemented on the Moodle e-learning Tool as Questionnaire activity. Several types of questions were implemented, such as [5]:

- Likert scale with rating from 1 to 5
- Radio buttons – for single answer questions
- Check boxes – for multiple answer questions
- Numeric fields – for numbers

Examples of Factors conceived in Likert scale are:

- The company promotes innovation initiatives on a regular basis; with a scale from 1 to 5.

Radio buttons and check boxes were used for more detailed answers such as:

What methods and sources for innovation does the enterprise apply?

a) Innovation ideas from own staff
b) Scientific magazines
c) Business fairs
d) Marketing Dept.
e) Internal R&D Dept.

This online questionnaire is hosted on the project's e-learning Tool at the URL address: www.advan2tex.eu/portal . It is meant for completion by 50 textile enterprises at consortium level, under authentication (Fig. 3).

Fig. 3: *Screenshot of the e-learning Tool – benchmarking questionnaire in Italian*

5. CONCLUSIONS

The Erasmus Plus VET project TexMatrix aims to improve the textile enterprise's competitiveness based on the instrument of the Knowledge matrix for innovation. The project has achieved for the first semester of implementation a unitary Matrix for all partners and the related questionnaire. This questionnaire is going to be completed online by 50 textile enterprises on the e-learning Tool of the project. The project's website is www.texmatrix.eu .

For the subsequent semesters of the project, the research providers of the project's partnership will assess the benchmarking study and will identify certain gaps for each textile enterprise to be bridged. They will contribute with new solutions based on research results, new technologies and innovation management. Moreover, they will identify the needs of the textile enterprises in order to be able to conceive new research projects, for strengthening their innovation capability and to fostering their competitiveness on the global market. Innovation is one of the top priorities of the European Technology Platform for Fibres-Textiles-Clothing [6].

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE CURRENT STATE OF CLOTHING TRADE IN THE BALKAN COUNTRIES

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Abstract: *The study presented here is aimed at analysing the current state of clothing trade in the Balkan states. The dynamics of change over a 15-year period following economic reforms are revealed. The clothing industries play a significant role and continue to contribute to the economic prosperity of countries with an inexpensive labour force. For most Balkan States clothing's export plays an important role in promoting economic growth and development – for example, exports of garments Albania was in 2015, 16.81% of its exports, Republic of Macedonia 11.75% of its exports, in Turkey10.51% etc. The main factors which influence the level of competitiveness of clothing products from the Balkans are the gross value added per employee and wages. When the producers of the Balkan countries will create products with higher added value in garment industry the competitiveness of these countries will decrease. Also rising wages in this industry, as a result of trade union pressure or government policy, will lead to decreasing competitiveness of these products on the EU market and implicitly to the decrease of exports of garments from these countries. The main challenges that must face the Balkan States are related to restructuring of economic system, changing trade markets and patterns, declining of domestic demand of most merchandise, reduction of competitive ability, narrow export base, and lower economies of scale. The main opportunities that most of these countries can exploit are related to their geographical position, membership of the EU market, infrastructure in garment sector, and highly skilled workforce.*

Key words: *clothing, trade, economic prosperity, gross value added per employee, wages*

1. INTRODUCTION

Globalization affects the economies of most of the world's countries, as capital is free flowing over the world, seeking a host country where the costs are as low as possible.

International competitiveness is influenced by numerous and interrelated factors. In the Community legal order the artificial notion of "consumer citizen", a reduced functional concept of the individual, a holder of economic freedoms, a quality that gives him the judicial power to play a role in the community market, has become a beginning.[1]

Our study is based on the microeconomic concepts and indicators of competitiveness who have a more consolidated theoretical base because they focus on the essential characteristics of producers in competition for market share and profits or the capability to export. The Balkans [2],

along with the East European countries, is economically the least developed region of Europe, and is significantly differentiated within itself by level of economic development. For all Balkan countries export plays an important role in promoting economic growth and development. They have been confronted with problems such as restructuring of economic system, changing trade markets and patterns, reduction of competitive ability, narrow export base, and lower economies of scale. In presented context, we considered opportune to analyses the current situation from Balkan countries (Albania, Bulgaria, Bosnia and Herzegovina, Croatia, Greece, Montenegro, Serbia, Slovenia, Republic of Macedonia and Turkey) in the clothing's European market.

Scope and objective of the research

The main aim of this paper is to examine and analyse the current state of clothing trade in the Balkan countries. In this sense, we presented the level of imports and exports of clothing in the Balkan countries, for the year 2015. The level of competitiveness of clothing products is tightly correlated to the gross value added per employee. Therefore, we present the Gross Value Added per employee, in manufacture of wearing apparel, in 2014 and the wages and salaries per employee in full-time equivalents, per hour (EURO), in manufacture of wearing apparel, in 2014 for each studied country.

The results of this research will help clarify trends in the structural change of the Balkan countries' clothing trade and the quality level of exports achieved in each of the observed countries.

Methodology and methods

Methods of the scientific research that have been employed in the paper are scientific analysis and summarizing of literature, and comparative analysis of statistic indexes.

In this paper, we use the structure of exports and imports by SITC (Standard International Trade Classification) to a two- (a three-) digit level for Turkey, Bulgaria, Greece, Slovenia, Romania, Croatia, Serbia, Bosnia-Herzegovina, Montenegro, extra EU28.

The paper is organized as follows: the first part presents the current state of clothing trade in the Balkan countries. The second part presents the main factors which influence the level of competitiveness of clothing products and the final part draws some conclusions based on the findings.

2. THE CURRENT STATE OF CLOTHING TRADE IN THE BALKAN COUNTRIES

The clothing industry has a venerable history and tradition of supplying good quality products and despite increasingly ferocious global competition and significant relocation of manufacturing to low-wage countries. [3] This chapter analyses the evolution of the Balkan clothing trade and shows the position held by the total trade products of these industries. For this purpose, the annual data has been taken from the website of WTO for the variables such as clothing sector export of each country, world total clothing exports, total exports of each country of all commodities, total world exports of all commodities. Data is taken in US $.

The level of imports and exports of clothing in the Balkans, for the year 2015, is revealed in Figures 1 and 2.

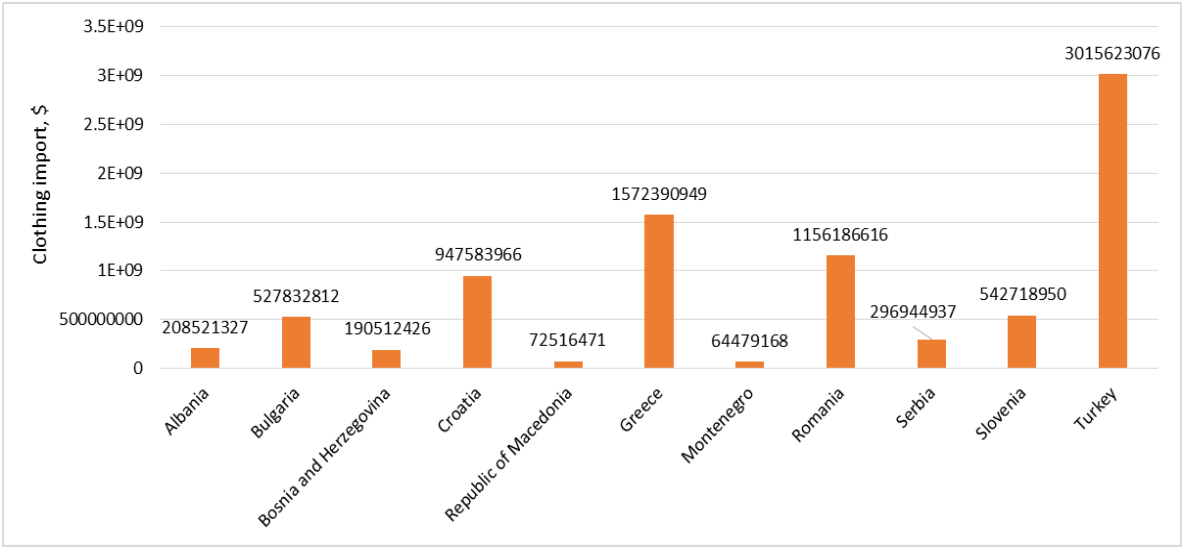

Fig.1: *The level of imports of clothing in the Balkan countries, for the year 2015 [4]*

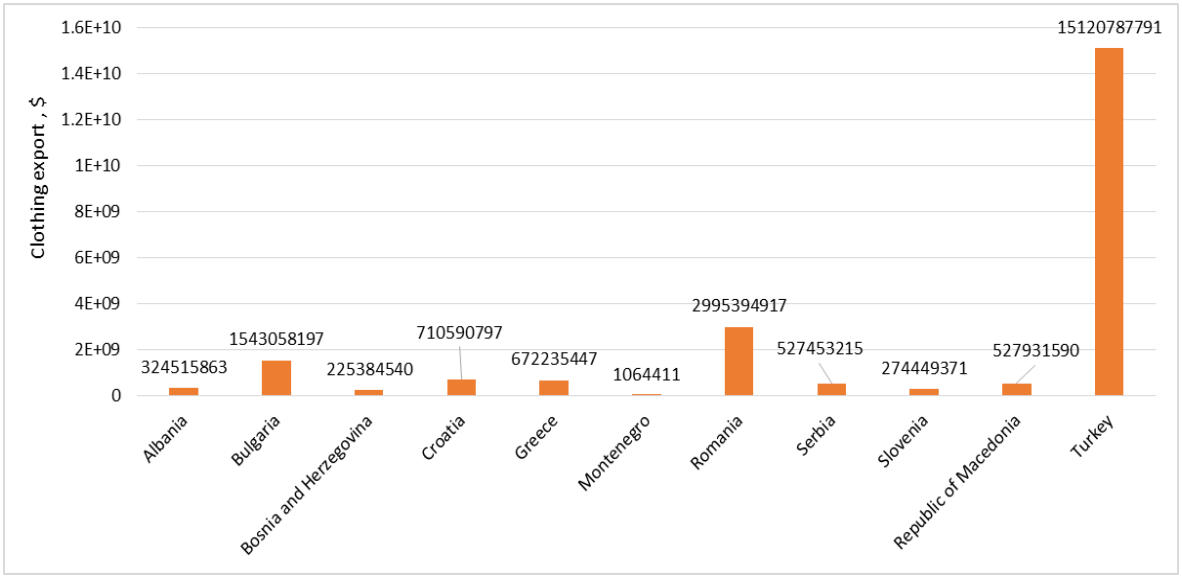

Fig. 2: *The level of exports of clothing in the Balkan countries, for the year 2015 [4]*

As can be seen first position, both in terms of exports and imports clothing's is held by Turkey followed by far from Romania and Bulgaria regarding exports and by Greece and Romanian in terms of imports.

Important is not only the quantity actually exported but also share held by these exports in total exports of garments at countries analysed. As can be seen from table no 1, garment exports from countries such as Albania and Republic of Macedonia, although not large in terms of value, they represent the highest percentage of exports of those countries.

***Table 1**: Share of clothing export in total exports, in the Balkan States*

	Bulgaria	Croatia	Greece	Romania	Slovenia	Albania	Bosnia Herzegovina	Montenegro	Serbia	Republic of Macedonia	Turkey
% garments exports	6,00	5,50	2,34	4,94	0,85	16,81	4,41	0,30	3,94	11,75	10,51

Source: Calculated by the authors according to the WTO dates.

The largest part of exports of garments of EU member countries is carried on the Community market. For some countries the proportion of these exports is over 90%, as 95.08% for Romania, Croatia 94.49% and Bulgaria 94.41% (see table 2)

***Table 2**: Percentage share of EU member Balkan countries' clothing export in the EU-28 market*

	Bulgaria	Croatia	Greece	Romania	Slovenia
%	94.25	95.23	73.72	95.37	82.75

Source: Calculated by the authors according to the EUROSTAT dates.

***Table. 3**: The export value (EURO) from EU member countries - the subgroups of clothing products (according classification SITC) - on the Extra and Intra EU market, in 2015*

PRODUCT	**84**	**841**	**842**	**843**	**844**	**845**	**846**	**848**
PARTNER	EU28_EXTRA							
BULGARIA	79,857,972	25,638,188	11,667,614	1,704,566	8,597,234	22,114,195	8,878,744	1,257,431
GREECE	159,207,461	7,927,976	14,578,721	1,386,725	12,816,796	14,445,575	1,229,097	106,822,571
CROATIA	30,519,969	2,803,165	1,753,106	958,553	1,083,503	13,469,020	2,045,339	8,407,283
ROMANIA	125,321,945	32,048,073	54,024,977	3,497,990	5,766,039	15,980,581	10,515,624	3,488,661
SLOVENIA	42,667,216	4,310,068	4,792,191	1,220,155	2,353,763	12,883,800	14,246,855	2,860,384
PARTNER	EU28_INTRA							
BULGARIA	1,310,911,020	349,508,937	353,029,308	67,768,124	229,335,763	256,389,842	42,929,247	11,949,799
GREECE	446,682,982	31,905,994	60,445,280	14,406,358	192,031,683	101,452,094	19,011,358	27,430,215
CROATIA	609,940,416	51,707,452	41,033,698	12,426,747	99,650,831	205,072,390	189,822,014	10,227,284
ROMANIA	2,584,308,894	771,852,279	1,016,690,550	76,395,869	219,584,028	351,599,250	88,339,420	59,847,498
SLOVENIA	204,695,894	21,036,361	28,536,253	9,452,622	11,170,537	75,498,636	47,082,519	11,918,966
Total	**5,594,113,769**	**1,298,738,493**	**1,586,551,698**	**189,217,709**	**782,390,177**	**1,068,905,383**	**424,100,217**	**244,210,092**

Source: Eurostat - EU trade since 1988 by SITC [DS-018995] [5]

The classification SITC refers to: **Division: 84 - Articles of apparel and clothing accessories -** is divided into the following Groups: **841** - Men's or boys' coats, capes, jackets, suits, blazers, trousers, shorts, shirts, underwear, nightwear and similar articles of textile fabrics, not knitted or crocheted; **842** - Women's or girls' coats, capes, jackets, suits, trousers, shorts, shirts, dresses and skirts, underwear, nightwear and similar articles of textile fabrics, not knitted or crocheted; **843** - Men's or boys' coats, capes, jackets, suits, blazers, trousers, shorts, shirts, underwear, nightwear and similar articles of textile fabrics, knitted or crocheted; **844** - Women's or girls' coats, capes, jackets, suits, trousers, shorts, shirts, dresses and skirts, underwear, nightwear and similar articles of textile fabrics, knitted or crocheted; **845** - Articles of apparel, of textile fabrics, whether or not knitted or crocheted, n.e.s.; **846** - Clothing accessories, of textile fabrics, whether or not knitted or crocheted; **848** - Articles of apparel and clothing accessories of other than textile fabrics; headgear of all materials

Among the most important clothing products made in the Balkan countries member EU and exported in the EU 28, could be ranked: women's or girls' coats, capes, jackets, suits, trousers, shorts, shirts, dresses and skirts, underwear, nightwear and similar articles of textile fabrics, not

knitted or crocheted (group 842), amounting 1,586,551,698 Euro, men's or boys' coats, capes, jackets, suits, blazers, trousers, shorts, shirts, underwear, nightwear and similar articles of textile fabrics, not knitted or crocheted (group 841) amounting 1,298,738,493 EURO si articles of apparel, of textile fabrics, whether or not knitted or crocheted, n.e.s..(group 845) amounting 1,068,905,383 EURO.

In 2015, Turkey exported clothing of USD 10,94 billion to the EU, which was equivalent to73,74% of Turkey's total clothing exports. "T-shirts, singlets and other vests" and "Women's/girls' suits, dresses, skirt etc & shorts" are the most important export products in woven clothing sector. In 2015 exports of "T-shirts, singlets and other vests" and "Women's/girls' suits, dresses, skirt etc & shorts" were USD 2.98 billion and US$ 1.27 billion, respectively.

In 2015, the total value of clothing exports was US$ 15 billion. The sector exports about 65% of its production. Approximately 80% of the clothing exported is cotton clothing. Knitted clothing and accessories, with an export value of US$ 8.9 billion, had a share of 60,14% in total clothing exports, and woven clothing had a share of 39,86% with a value of US$ 5.9 billion in 2015. T-shirts and pullovers are the most important export products in knitted clothing sector. Exports of t-shirts and pullovers were US$ 2.9 billion and US$ 1.6 billion respectively in 2015. In addition, as the second largest manufacturer in the world, Turkey's hosiery exports amounted to US$ 1.02 billion in 2015.[6]

3. THE MAIN FACTORS WHICH INFLUENCE THE LEVEL OF COMPETITIVENESS OF CLOTHING PRODUCTS

The main factors which influence the level of competitiveness of clothing products from the Balkans are the gross value added per employee and wages. When the producers of the Balkan countries will create products with higher added value in garment industry the competitiveness of these countries will decrease. Also rising wages in this industry, as a result of trade union pressure or government policy, will lead to decreasing competitiveness of these products on the EU market and implicitly to the decrease of exports of garments from these countries.

The level of competitiveness of clothing products is tightly correlated to the gross value added per employee. As can be seen from figure 3, it has the lowest values, respectively 4.3; 5.1 and 6.3 in the countries with the highest value of competitiveness index RC (Republic of Macedonia, Bulgaria and Romania)

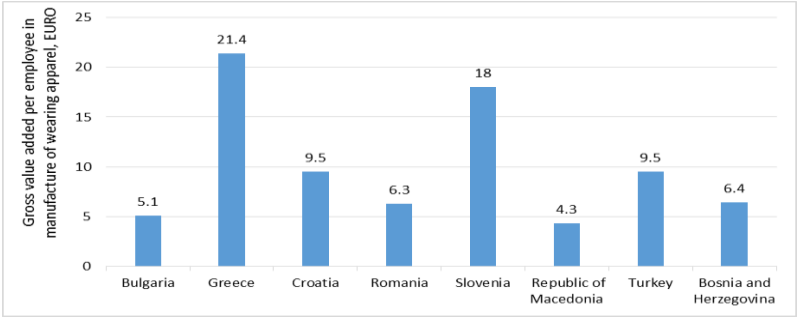

Fig. 3: *Gross value added per employee, in manufacture of wearing apparel, in 2014 (source EUROSTAT)*

High competitiveness of clothing industry in the EU candidate countries could be due to the low level of wages on this sector. Small salaries have the employees of garment firms from Bulgaria

and Romania, where RCA have the highest values for EU member countries (except Croatia). In Slovenia and Greece where the wages are highest, 10.02 EURO / hour respective 8.51 EURO / hour, is recorded the lowest values of RCA - 0.45 in Slovenia and 1.27 in Greece.

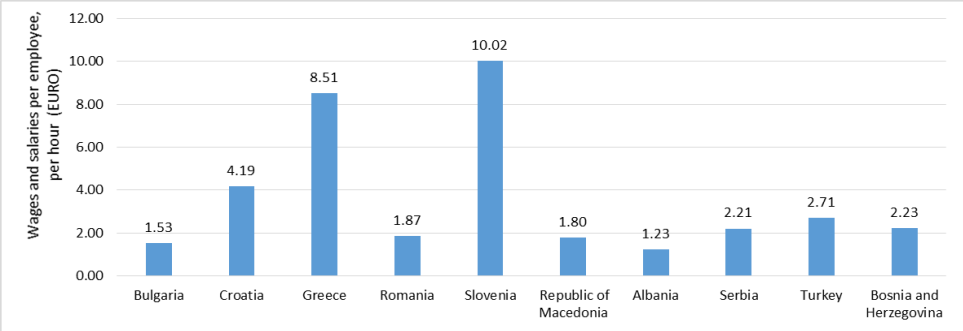

***Fig.4**: Wages and salaries per employee in full-time equivalents, per hour (EURO), in manufacture of wearing apparel, in 2014 (source EUROSTAT)*

4. CONCLUSIONS

The study presented here is aimed at analysing the current state of clothing trade in the Balkan countries. The dynamics of change over a 15-year period following economic reforms are revealed. The clothing industries play a significant role and continue to contribute to the economic prosperity of countries with an inexpensive labour force.

Based on the present analysis several conclusions can be drawn with respect to the clothing export competitiveness of Balkans.

For most Balkan Countries, clothing's export plays an important role in promoting economic growth and development – for example, exports of garments ALBANIA was in 2015, 16.81% of its exports, Republic of Macedonia 11.75% of its exports, in Turkey10.51% etc.

The main challenges that must face the Balkan Countries are related to restructuring of economic system, changing trade markets and patterns, declining of domestic demand of most merchandise, reduction of competitive ability, narrow export base, and lower economies of scale. The main opportunities that most of these countries can exploit are related to their geographical position, membership of the EU market, infrastructure in garment sector, and highly skilled workforce.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ABC ANALYSIS in a CLOTHING COMPANY

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Abstract: *In today's conditions, clothing companies should cope with the rivalry in order to survive in the sector. Shortening the process times, decreasing the costs, improving the quality are some of the ways of overcoming the competition.*
ABC analysis, which is also named pareto method or 80/20 rule, is a method that can be used for solving many problems in the factory. It helps to rank the data according to their importance degree. It prevents the company to concentrate on less important causes instead of doing something for vital ones. Thus, by focusing the main important issues, labor can be used for more efficient works and it is possible to save money and time.
In this study, ABC analysis was used for the data of fabric defects in quality control department of an apparel company. The apparel company procures the needed knitted fabric from different fabric suppliers. Working with different suppliers increases the diversity of problems. Monthly fabric quality control data were examined. All fabric defects were listed and then were ranked according to their quantity. By the help of this ranking, the primary fabric problems were detected and besides, the suppliers were evaluated predicating on these defects. Finally, precautions that are have to be taken were discussed.

Key words: *Pareto, ABC analysis, fabric defects, 80/20 rule, apparel*

1. INTRODUCTION

Apparel industry is essential with its effect on export income, employment and added value in manufacturing for most of developing countries.

The companies should improve their manufacturing processes as one of the things to do in order to get competitive advantage, to preserve their market share and to survive.

ABC analysis is one the methods that will help the companies to make some betterments in their processes. ABC analysis is also named pareto method or 80/20 rule in literature. The method sorts the data by their importance and is used in a variety of fields. In clothing companies, it is used in stock control, time management, process control and many others. Thus, it contributes to the improvement of works and it helps the companies to understand and to cater for the customer demands, to improve relationship with suppliers and sometimes to discover some investment opportunities.

In this study, ABC analysis is used to understand the main fabric defects in incoming quality control in an apparel company which has been sewing knitted garments. It was aimed to make some improvements in product quality and to take some precautions in fabric supplying process.

2. ABC ANALYSIS

Pareto analysis which is also called as the 80/20 rule and as ABC analysis classifies items according to their relative precedence values. It helps to distinguish vital causes from other less important causes and thus, labor can be used for more efficient works [1]. Juran named this principle as “vital few and trivial many”. It states that for many events, roughly 80% of the effects come from 20% of the causes. [2,3]

ABC analysis means to classify subprojects into three classes A, B, and C [4,5,6]:

"A items" are very important and with very tight control and accurate records.

"B items" are media-important and with less tightly controlled and good records.

"C items" are less important with the simplest controls possible and minimal records.

The steps of ABC analysis are below [2]:

1. Collecting data on the most common problems or errors
2. Determining the frequency of repetition of problems during the implementation of projects;
3. Determining the percentage share of each problem;
4. Determining the cumulative percentage of each problem;
5. Forming the Pareto diagram;
6. Analysis of diagrams and proposing measures of improvement.

3. MATERIAL AND METHOD

This study was carried out in quality control department of a clothing company which is producing knitting garments. The monthly data of fabric incoming quality control were examined. The company worked with eight fabric suppliers in this time interval. Kilogram was used as the units for the defects of fabrics. The similar fabric defect types which were detected in the orders of different suppliers were sum up to define the total defect quantities in terms of types. Then, calculated total quantities were sorted in descending form. The percentage shares and then the cumulative percentage shares of the defects were calculated. Considering these cumulative percentage values, the defect types were classified as A, B and C.

4. RESULTS

During incoming quality control of fabric, the company confronted twenty-six defect types. However, only first four defect types which were classified as A, constituted the 76.2% of all as seen in Table 1 and Figure 1.

Table 1: *Classification of Fabric Defects*

Fabric Defects	Quantity(kg)	Percentage (%)	Cumulative %	Class
Color	2874.33	28.72	28.72	A
Fabric weight	2058.77	20.57	49.29	A
Hand	1569.16	15.68	64.97	A
Spirality	1123.7	11.23	76.2	A
Abrage	714.7	7.15	83.35	B
Point mark	580.8	5.80	89.15	B
Turning yellow	356	3.56	92.71	B
Raising	326	3.26	95.97	B
Shrinkage	217.49	2.17	98.14	C
Report size	136.1	1.36	99.5	C
Pilling	30.12	0.3	99.8	C
Smear	20.56	0.2	100	C

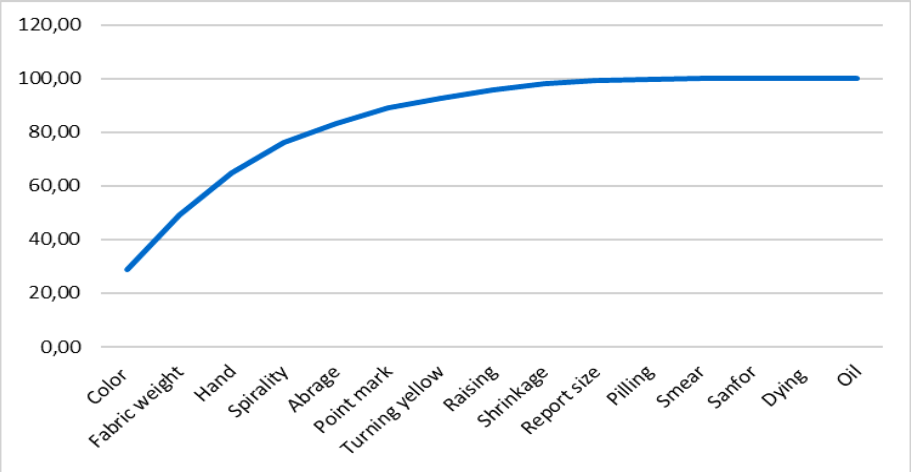

Fig 1: *Fabric Defects ABC Analysis Graph*

B and C class defects constituted 23,8% and 4,03% respectively. The company should concentrade on A class. For a further analysis, the data of A class were examined with the aim of seeing the distribution of these defects according to the suppliers (Table 2).

Table 2: *Distribution of A class Defects according to the Suppliers*

Fabric Defects	FABRIC SUPPLIERS							
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**
Color	2,9%	60,41%	27,7%	6,6%				3,2%
Fabric weight	5,2%	29,19%	69,47%	1,2%				
Hand		19,85%	64,28%		15,5%			0,3%
Spirality		58,9%					41,1%	

In Table 2, some the suppliers show big problem about some defects. The company can follow the performances of the suppliers and may eliminate bad performers and work intensely with the good performers.

5. CONCLUSION

Time and money are fundamental competition arguments for most of companies in a competitive environment. They should use their resources efficiently. ABC analysis is one of useful tools that will help to achieve this.

At the end of our study, it was seen that there were just four main type of fabric quality problems and the company should use their limited resources to minimise them. These results also showed the performances of suppliers and gave an idea about which precautions should be taken.

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