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ANALYSIS OF FOOTWEAR BUSINESS DEVELOPMENT STRATEGY USING QSPM AND SWOT ANALYSIS

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ANALYSIS OF FOOTWEAR BUSINESS DEVELOPMENT STRATEGY USING QSPM AND SWOT ANALYSIS

ABSTRACT. The main objective of this research is to analyze the strategy of developing the footwear business. Case studies were carried out at CV Hikmah Shoes Bogor. The initial analysis was carried out by identifying the business of the ongoing CV Hikmah shoe model and analyzing the external and internal scope to identify problems that occurred in the company. The descriptive method used to identify CV Hikmah Shoes Bogor using, Internal Factor Matrix (IFE) and External Factor Evaluation (EFE) used to analyze internal and external factors at CV Hikmah Shoes Bogor. SWOT matrix selected to determine the strategy to be implemented and Quantitative Strategy Planning Matrix (QSPM) is used as a process to determine strategic priorities for the company. The results of the SWOT Matrix in this study produced six alternative strategies which were chosen as development strategies at CV Hikmah Shoes Bogor. The best strategy is taken in developing the footwear business strategy, maximizing promotion and marketing using social media or e-commerce and continuing with the improvement business

KEY WORDS: IFE, EFE, QSPM, SWOT Matrix

ANALIZA STRATEGIEI DE DEZVOLTARE A AFACERILOR ÎN DOMENIUL ÎNCĂLŢĂMINTEI FOLOSIND ANALIZA QSPM ŞI SWOT

REZUMAT. Obiectivul principal al acestei cercetări este de a analiza strategia de dezvoltare a afacerilor în domeniul încălţămintei. S-au efectuat studii de caz asupra companiei CV Hikmah Shoes Bogor. Analiza iniţială a fost efectuată prin identificarea strategiei de afaceri actuale asupra modelelor de încălţăminte CV Hikmah şi prin analizarea cadrului intern şi extern pentru a identifica problemele apărute în cadrul companiei. Pentru a identifica strategia companiei CV Hikmah Shoes Bogor s-a utilizat metoda descriptivă prin evaluarea factorilor interni (IFE) şi evaluarea factorilor externi (EFE) în vederea analizării acestor factori în cadrul companiei. S-a selectat analiza SWOT pentru a determina strategia care urmează să fie pusă în aplicare şi s-a utilizat matricea planificării strategice cantitative (QSPM) ca proces de determinare a priorităţilor strategice pentru companie. Rezultatele analizei SWOT din acest studiu au generat şase strategii alternative selectate ca strategii de dezvoltare a companiei CV Hikmah Shoes Bogor. S-a ales cea mai bună metodă pentru elaborarea strategiei de afaceri în domeniul încălţămintei, maximizarea promovării şi marketingului prin utilizarea reţelelor sociale sau a comerţului electronic şi continuarea îmbunătăţirii afacerii.

CUVINTE CHEIE: IFE, EFE, QSPM, analiza SWOT

ANALYSE DE LA STRATEGIE DE DEVELOPPEMENT DES AFFAIRES DANS LE SECTEUR DE LA CHAUSSURE UTILISANT L'ANALYSE QSPM ET SWOT

RÉSUMÉ. L'objectif principal de cette recherche est d'analyser la stratégie de développement des affaires dans le secteur de la chaussure. Des études de cas ont été réalisées chez l'entreprise CV Hikmah Shoes Bogor. L'analyse initiale a été réalisée en identifiant la stratégie d'affaires en cours pour les modèles chaussure de CV Hikmah et en analysant la portée externe et interne pour identifier les problèmes survenus dans l'entreprise. Pour identifier la stratégie de l'entreprise CV Hikmah Shoes Bogor on a utilisé la méthode descriptive en évaluant les facteurs internes (IFE) et les facteurs externes (EFE) afin d'analyser ces facteurs au sein de l'entreprise. L'analyse SWOT a été choisie pour déterminer la stratégie à mettre en œuvre, tandis que la matrice de planification stratégique quantitative (QSPM) a été utilisée comme processus de détermination des priorités stratégiques de l'entreprise. Les résultats de l'analyse SWOT de cette étude ont généré six stratégies alternatives retenues comme stratégies de développement de l'entreprise CV Hikmah Shoes Bogor. La meilleure méthode a été choisie pour développer la stratégie commerciale de la chaussure, maximiser la promotion et le marketing grâce à l'utilisation de réseaux sociaux ou de commerce électronique et continuer à améliorer l'entreprise.

MOTS CLÉS : IFE, EFE, QSPM, analyse SWOT

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INTRODUCTION

Manufacturing industries that focus on labour or non-oil and gas densities from 2011-2015 experienced an average growth of 6.1% per year and almost 60% of the output of this industrial sector was dominated by labour-intensive industries which included the footwear industry, TPT industry (Textiles and Textile Products) and metal processing machines [1]. The manufacturing industry for processing genuine and imitation leather into footwear is an industry that is usually done both on a small scale industry or household and industry on a large scale. The existence of these small footwear industries plays an important role in the acquisition of foreign exchange and strengthens the national industrial structure [2], especially through the utilization and development of natural resource potential (SDA) owned by Indonesia and is one of the mainstay of sources of income and foreign exchange revenues originating from the non-oil and gas sector. Indonesian footwear exports in 2015 reached $ 4.7 billion in footwear and have experienced significant development [3].

The Indonesian footwear industry has fulfilled 3% of the world's footwear needs. Indonesia has a high quality supply of Javanese cowhide which increases the attractiveness of the Indonesian footwear industry. The main markets for Indonesian exports are America, Europe and Japan. There are two types of manufacture of various footwear or shoes in Indonesia, the first through factories or industries, second through small and medium industries. The most dominant commodity of Indonesian or domestic original shoe making is through the Small and Medium Industries [4].

The small and medium industry sector is believed to be a sector that can lead other sectors in an economy towards progress because it has a high absorption capacity of labor to 57.9 million people in various regions in Indonesia. The small and medium industry sector according to its type there are two forms, manufacturing industry and service industry. The manufacturing industry which includes the processing industry, in its journey this industry has demonstrated its ability to absorb high labor reaching 15.73 million people in 2013, or approximately 13.87% of Indonesia's workforce and ranked the 4th largest after agriculture, trade, and services [5].

Bogor Regency is one of the regencies in West Java Province which has a small and medium industry. One of the most prominent is the footwear processing industry compared to other processing industries with a total gross domestic income of Rp 100.528 billion in 2016 and an average growth of around 9 to 10% from 2011-2016 [1]. Ranked first in its contribution to GDP with a footwear processing business, one of the main businesses in Bogor Regency. The business in the field of footwear is one business that has a high level of competition. This requires producers to increase creativity which will produce their own ideas and uniqueness so that it can be an attraction to customers. A company that can produce a creative business needs the right strategy to produce excellence and be able to face the current and future business challenges. One of the business actors who tried to capture this opportunity was CV Hikmah Shoes, which is a company engaged in the field of footwear located in the city of Bogor, West Java.

The management of CV Hikmah Shoes plans to increase the company's revenue, but the company realizes that to support the current business growth, the right steps and strategies are needed in order to increase revenue well. Increasing the company's revenue source becomes a promising business prospect and becomes a consideration for prospective investors in CV Hikmah Shoes.

The plan desired by the management of CV Hikmah Shoes is also not easy to implement, management realizes that it still has some obstacles in business development, not finding the right solution in opening new markets

for its business products which have been dependent on supplying certain brands, as well as competitive conditions companies in the business environment, not only in the products produced, variations in creative and innovative value added from each competitor must also be balanced in order to win the market [6].

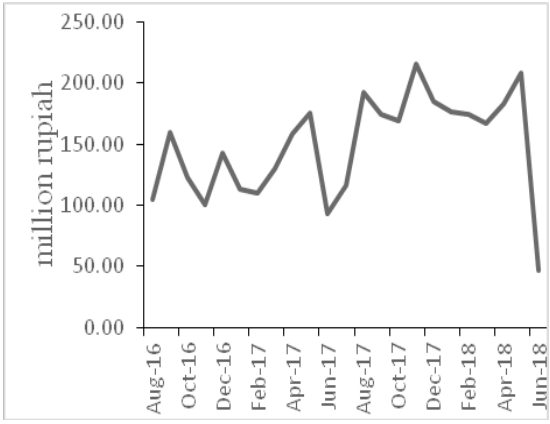

Figure 1. CV Hikmah Shoes total income for 2016-2018 (in millions of rupiah)

This can be seen from Figure 1 which shows the revenue of sales (revenue) of CV Hikmah Shoes for two years, from 2016 to 2018, during which period the company's income fluctuated which has not produced optimal performance. The company strives to achieve a monthly sales target of two hundred and fifty million a month but based on the revenue obtained from that period does not reach the expected target, there is even a decrease in income and a sharp decline in income after May 2018 directly affect the company's income. Business development CV Hikmah aims to get an overview and identification of current business, formulate strategies for product business development to achieve the company's revenue targets at CV Hikmah Shoes.

Giesen et al. [7] explain that business innovation is very important in achieving success in the present and future. When environmental conditions change rapidly and are so complex, company leaders need to understand when to adapt to business models and how to implement changes. Amit and Zott [8] emphasize that business innovation can provide significant opportunities both during the period of rapid economic growth and during times of turmoil.

METHODS

This research was conducted at CV Hikmah Shoes which began in October 2018-January 2019 in the village of Ciomas Harapan RT 01 RW 02 No 5 City of Bogor, West Java. This study used two types of data, primary data and secondary data. Primary data is obtained from in-depth interviews and filling in expert questionnaires by internal parties, the Manager, Production Section, Controlling Section, Management Section, External Reseller Design Section (PT Lastibani), Reseller (PT Bangjoan), Expert. Secondary data is obtained from documents owned by the company and literature studies.

Data Analysis and Processing Method

Data processing and analysis of this study uses the Environmental analysis aiming to identify strategic factors that will determine the company's future. Environmental analysis monitors, evaluates and disseminates information from the internal and external environment to the main person in the company [9]. Environmental analysis is divided into two, external and internal. Based on the level of influence on the company, the business environment or company environment can be divided into two categories, Internal Environment and External Environment [10]. By conducting environmental analysis companies or organizations will simultaneously be able to identify each critical threat, as well as its opportunities in a competitive environment [11]. The environmental analysis for the company can be used to measure how far competition in the environment has developed and its implications from evolution for opportunities and threats.

Through this mapping technique an overall description of the business processes

carried out by the company will be obtained. The process of knowing the strategies that can be done to find out strategies for the company, used the SWOT Analysis method. According to David [12] SWOT Matrix (Strengths Weakness Opportunities Threats) is the right tool to help managers build four types of strategies, SO (Strengths Opportunities), WO (Weakness Opportunities), ST strategies (Threats Strengths) and WT strategies (Weakness Threats) [13]. Furthermore, quantitative data from and SWOT Analysis are processed to compile and map strategies. At the stage of decision making the tool used is QSPM.

Quantitative Strategic Planning Matrix

Quantitative Strategic Planning Matrix (QSPM) is analytical tool used to decide on strategies to be used based on the attractiveness of alternative strategies that exist and to help assess alternative strategies objectively. QSPM is a tool used in the stages of decision making strategy and factors used in QSPM using factors that have been determined in the input stage, determining external factors and internal factors. Calculation of QSPM is based on input from the weight of the IFE and EFE matrix, as well as the alternative strategy at the matching stage [12]. The literature review provides a rationale for compiling a research framework on the influence of organizational justice in performance appraisal on satisfaction assessment and performance.

RESULTS AND DISCUSSIONS

Internal Factor Analysis

Internal factor analysis aims to identify the strengths and weaknesses in company. Strength is something that is owned by a company that is different from other companies and can support the company's activities. Weakness is the limitations or deficiencies in resources, skills and capabilities that seriously hinder the company's effective performance in the internal organization. As a result, organizational activities have not been carried out optimally [12]. The strengths and weaknesses in CV Hikmah shoes are shown in Table 1 IFE.

Table 1: IFE

NO	Internal Factor	Weight	Rating	Score Weight
	Power			
1.	Variable footwear model and design	0,09	4	0,36
2.	Experienced producing quality shoes	0,11	4	0,44
3.	Product images that are already known	0,10	4	0,40
4.	Availability of raw materials	0,09	3	0,27
5.	CV Hikmah Shoes has a skilled and experienced workforce	0,08	4	0,32
Sub total				1,79
	Weakness			
1.	The marketing and promotion system that has not been maximal	0,12	1	0,12
2.	Employee skill quality is still low in using technology	0,11	2	0,22
3.	The production system is still based on orders	0,09	2	0,18
4.	The selling price is still determined based on the wholesale price	0,10	2	0,20
5.	The financial condition of the CV Hikmah shoes is limited	0,11	1	0,11
Sub total				0,83
Total		1		2,62

The results of table 1 provide information about the strengths and weaknesses in CV Hikmah Shoes, sub-total strength has a weighting score of (1.79) with experienced variables producing quality shoes having the highest score (0.44). The highest weakness factor for weighting scores, the selling price is still determined based on the wholesale price (0.20) and sub-total (0.83). Scores of weights are obtained after multiplying the weights and ratings with the total weighted score with total accumulation of the variable strength and weakness of (2.62).

External Factor Analysis

The analysis of the external environment seeks to sort out the global problems facing the company in the form, function and interrelationship between the sections. For strategic development, this analysis is needed not only limited to the detailed analysis of opportunities and threats, but also to determine where and for what results of the analysis are used [12].

Opportunities are an important profitable situation in a corporate environment, which needs to be utilized by companies in developing business.

Table 2: EFE

NO	External Factor	Weight	Rating	Score Weight
	Opportunity			
1.	Increasing footwear export market in the world changes in style and lifestyle konsumen	0,11 0,08	4 3	0,44 0,24
2.	Progress in online business technology market in Indonesia	0,11	4	0,44
3.	The large population in Indonesia is ranked Fourth in the world	0,11	4	0,44
Sub total				1,56
	Threat			
1.	Increasing imports of similar footwear products	0,13	1	0,13
2.	High level of competition in footwear production	0,11	1	0,11
3.	Fluctuations in raw material prices	0,12	2	0,24
4.	Unstable economic conditions Indonesia and world	0,12	2	0,24
5.	The Indonesian government policy less supportive of the development of the footwear industry	0,11	2	0,22
Sub total				0,97
Total		1		2,53

Threat is a danger that usually occurs due to unfavorable developments, which will have impacts such as reduced profits and sales if no action is taken to survive. External factor aims to identify opportunities and threats that must be faced by the company (Table 2 EFE).

Based on the results of table 2 EFE, sub total opportunities is (1.56). The progress of online business technology gets the highest score with weight (0.44). Fluctuations in raw material prices and less stable economic conditions have the highest weighting score (0.24) and total weighted scoring opportunities and external factor threats are (2.53).

SWOT Diagram

Based on the calculation of Internal and External Factor analysis on CV Hikmah shoes, it can be illustrated in the SWOT diagram of Table 3.

Table 3: Matrix SWOT

IFAS		EFAS	
CATEGORY	TOTAL	CATEGORY T	TOTAL
STRENGTH (S)	1,79	OPPORTUNITY (O)	1,56
WEAKNESS (W)	0,83	THREAT (T)	0,97
TOTAL (S-W)	0,96	TOTAL (S-T)	0,59

The results of the IFAS and EFAS matrix found that IFAS's final score was 0,96 and the total EFAS final score was 0,59. These results are then shown through the SWOT matrix.

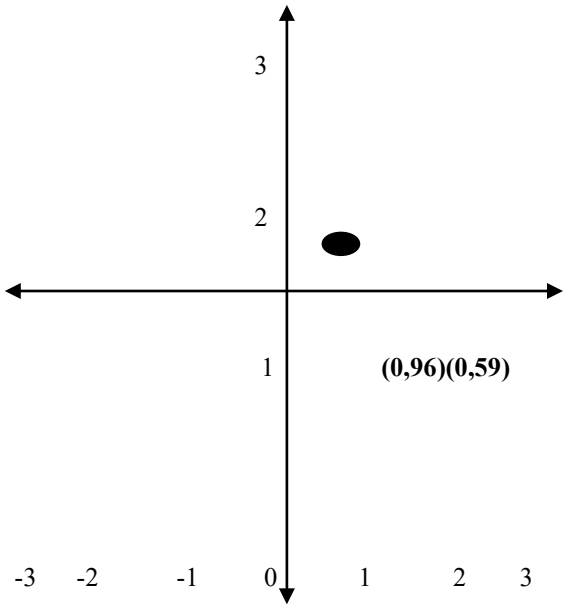

Figure 2. SWOT Diagram

Based on the SWOT diagram analysis, the position of CV Hikmah Shoes, in quadrant I, where in this position it is a condition that is very profitable for the company. The company can take advantage of existing opportunities [14]. CV Hikmah shoes must take advantage of opportunities as much as possible, using an aggressive strategy to gain new market share. The strategies are presented in the Table 4 SWOT Matrix.

Table 4: SWOT Matrix

Internal	Strengths	Weaknesses
External	1 Variable footwear model and design 2 Experienced producing quality shoes 3 Product images that are already known 4 Availability of raw materials 5 CV Hikmah Shoes has a skilled and experienced workforce	1 The marketing and promotion system that has not been maximal 2 Employee skill quality is still low in using technology 3 The production system is still based on orders 4 The selling price is still determined based on the wholesale price 5 The financial condition of the CV Hikmah shoes is limited
Opportunities	**Strategy S-O**	**Strategy W-O**
1. Increasing footwear export market in the world 2. Changes in style and lifestyle konsumen 3. Progress in online business technology market in Indonesia 4. The large population in Indonesia is ranked Fourth in the world	1. Promotion and marketing strategies using social media or e-commerce to support activities to expand the marketing area of footwear products (S1, S2, S3, O1, O2, O3, O4) 2. Innovation and variety of footwear products using information technology (S1, S2, O2, O3, O4)	1. Cooperating with partner institutions and banks in developing businesses (W1, W5, O1, O2) 2. Maintain product quality and feature distinctive brand products (W1, W3, W4, O1, O2)

Threats	Strategy S-T	Strategy W-T
1. Increasing imports of similar footwear products 2. High level of competition in footwear production 3. Fluctuations in raw material prices 4. Unstable economic conditions Indonesia and world 5. Government policies are less supportive footwear production	1. Increase productivity capacity to increase the quantity of footwear production (S1, S3, S4, S5, T1, T2)	1. Collaboration with the government regarding HR training, licensing, and pathways for marketing processes outside the region (W1, W2, T1, T3, T4, T5)

Stages of Strategy Decision Formation in CV Hikma Shoes

Making a decision on strategy priorities that are run by the company is the final stage of strategy formulation. The method used in the priority assessment is based on the attractiveness of alternative strategies, so that it can affect the company's internal and external environment. The results of the SWOT matrix analysis produced four alternatives, the SO strategy, the ST strategy, the WO strategy, and the WT strategy. The strategy will be entered into the QSPM matrix which will be estimated by weight and Attractive Score (AS) [15]. SWOT Analysis and Quantitative Strategic Planning Matrix (QSPM) are advanced analyses commonly used in determining managerial strategies [16, 17].

Strategic priority assessment is done by using the QSPM matrix method by multiplying the weights in the IFE and EFE matrices, multiplying them by the attractive score to produce the Total Attractive Score (TAS). The total number of TAS of each of these strategies determines the priority of the strategy, Determination of Attractive Score (AS) on QSPM and Processing of Total Attractive Score (TAS) QSPM. The results of the Quantitative Strategic Planning Matrix (QSPM) for CV Hikmah Shoes assessment can be seen in Table 5.

Table 5: Alternative strategy

NO	Alternative strategy	TAS
1	Promotion and marketing strategies using social media or e-commerce to support policies to expand the marketing area of footwear products Maintain product quality and highlight the distinctive brand characteristics of the product.	6,34
2	Cooperate with partners, banking institutions and communities in developing businesses	6,24
3	Innovation and variety of footwear products by utilizing information technology	6,18
4	Cooperate with the government regarding HR training, tax incentives, and pathways for marketing processes outside the region	5,96
5	Increasing labour productivity to increase the quantity of footwear production.	5,87
6		5,67

Based on the results of the QSPM assessment, the order of the highest to lowest TAS (total Attractiveness Score) is obtained. This sequence can be generated by priority strategies that can be implemented at CV Hikmah shoes.

Managerial Implications

Managerial implications are the company's activities in developing the company's business development strategies that are tailored to the current conditions and capabilities of the company [18]. Based on the results of research on CV Hikmah Shoes, the steps and strategies carried out by making these repairs are carried out as part of the company's sustainability efforts and in an effort to increase the company's revenue. Adjustments from time to time and evaluation of the development of business

models is very important in implementing a successful business [19].

The implement a prototype business that can be used as a technical description of the strategy obtained from the results of QSPM to support the main business conducted by policies of CV Hikmah Shoes. The company is encouraged to move forward in the business of market penetration in an effort to increase revenue streams. Market penetration will help companies to be independent from reseller dependence. Steps and efforts to do this by using an online business strategy that is an alternative strategy for the company. The strategy based on the results of the QSPM is at the highest value and is in accordance with the results of the IE on quadrant 1 matrix which focuses on market penetration efforts in marketing the product. Online business strategies can also help companies avoid collision marketing with permanent resellers of companies in conventional markets [20].

Another strategy that can be applied by the company is maintaining product quality and highlighting the characteristics of products with its own brand. Companies in marketing can try to create their own brand that represents the identity of CV Hikmah Shoes. Companies can form their own divisions that will carry out promotional programs and market penetration so that existing organizational structures are not disrupted by new programs and strategies that the company will run.

The results of the preparation of the company's business development strategy are logical decisions and consequences that must be prepared by CV Hikmah Shoes in implementing the strategies that have been produced from developing a business improvement but the decision is left entirely to the internal management decisions of CV Hikmah Shoes to be able to measure the company's ability and resource allocation in implementing business development strategies.

CONCLUSION

The results of calculations on internal and external factors indicate that the current position of CV Hikmah Shoes is in quadrant I which supports aggressive growth policies (Growth oriented strategy). It is very possible to continue to expand, increase growth and achieve maximum progress with a value of (1.04; 0.61).

SWOT analysis that produces six alternative strategies with priority strategies with QSPM is a promotion and marketing strategy using social media or e-commerce to support the policy of expanding the area of marketing of footwear products with 6.34 in overcoming the problem of decreasing income and in achieving the desired income target.

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EXPERIMENTS TO OBTAIN NEW BIOPRODUCTS BASED ON PROTEIN EXTRACTS FROM WET-WHITE LEATHER WASTE INTENDED FOR THE TOTAL OR PARTIAL REPLACEMENT OF PHENOL FORMALDEHYDE RESINS IN WET FINISHING OF LEATHER

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EXPERIMENTS TO OBTAIN NEW BIOPRODUCTS BASED ON PROTEIN EXTRACTS FROM WET-WHITE LEATHER WASTE INTENDED FOR THE TOTAL OR PARTIAL REPLACEMENT OF PHENOL FORMALDEHYDE RESINS IN WET FINISHING OF LEATHER

ABSTRACT. Leather retanning is a key operation in the wet finishing stage, playing a very important role in diversification of assortments, but at the same time using complex chemicals can induce important eco-toxic effects especially in the liquid effluents (residual float). This paper presents some of the achievements related to the expansion of eco-friendly auxiliary product range for wet finishing of leather (filling-retanning) with predominantly natural (protein) components, combined with metal oxides other than Cr2O3 and without phenolic compounds, concomitantly with the leather industry's advance towards circular economy and increasing eco-efficiency. An experimental model was developed for functionalization of collagenic materials obtained by acid hydrolysis of pre-tanned wet-white bovine hide waste in order to obtain new bioproducts intended for the replacement of phenolic compounds for wet finishing of leather (filling-retanning).

KEY WORDS: leather waste, circular economy, retanning products

EXPERIMENTĂRI DE OBŢINERE DE NOI BIOPRODUSE PE BAZĂ DE EXTRACTE PROTEICE DIN DEŞEURI DE PIELE TĂBĂCITĂ ÎN SISTEM WET-WHITE DESTINATE ÎNLOCUIRII TOTALE SAU PARŢIALE A RĂŞINILOR FENOLFORMALDEHIDICE LA FINISAREA UMEDĂ A PIEILOR

REZUMAT. Retăbăcirea pielii este o operaţie cheie în etapa de finisare umedă, jucând un rol foarte important în diversificarea sortimentelor, dar în acelaşi timp utilizarea substanţelor chimice complexe poate induce efecte eco-toxice semnificative, mai ales în efluenţii lichizi (flota reziduală). Această lucrare prezintă unele realizări legate de lărgirea gamei de produse auxiliare eco-prietenoase pentru finisarea umedă a pieilor (umplere-retanare) cu componente preponderent naturale (proteice) în combinaţie cu oxizi metalici alţii decât Cr2O3 şi fără compuşi fenolici, concomitent cu apropierea industriei de pielărie de economia circulară şi creşterea eco-eficienţei. S-a dezvoltat un model experimental pentru funcţionalizarea materialelor colagenice obţinute prin hidroliză acidă a deşeurilor de piele bovină wet-white pretăbăcită pentru a obţine noi bioproduse destinate înlocuirii compuşilor fenolici la finisarea umedă a pielii (umplere-retanare).

CUVINTE CHEIE: deşeuri piele, economie circulară, produse retanare

EXPÉRIENCES POUR OBTENIR DE NOUVEAUX BIOPRODUITS À PARTIR D'EXTRAITS PROTEIQUES DE DÉCHETS DE CUIR WET WHITE POUR LE REMPLACEMENT TOTAL OU PARTIEL DES RÉSINES PHÉNOL-FORMALDÉHYDE DANS LA FINITION DU CUIR

RÉSUMÉ. Le retannage du cuir est une opération clé dans l'étape de finition humide, jouant un rôle très important dans la diversification des assortiments, mais en même temps, l'utilisation de produits chimiques complexes peut induire des effets écotoxiques importants, en particulier dans les effluents liquides (bain résiduel). Cet article présente quelques réalisations relatives à l'élargissement de la gamme de produits auxiliaires écologiques pour le finissage humide du cuir (remplissage-retannage) avec des composants principalement naturels (protéines), en combinaison avec des oxydes métalliques autres que Cr2O3 et sans composés phénoliques, concomitamment avec le progrès de l'industrie du cuir vers l'économie circulaire et l'amélioration de l'efficacité écologique. Un modèle expérimental pour la fonctionnalisation de matériaux collagéniques obtenus par hydrolyse acide de déchets de cuir de bovins wet white a été développé afin d›obtenir de nouveaux bioproduits pour le remplacement des composés phénoliques dans l'étape de finition humide (remplissage-retannage).

MOTS-CLÉS : déchets de cuir, économie circulaire, produits pour le retannage

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INTRODUCTION

Leather tanned up to the wet-blue/wet-white phase is processed according to typical technologies, diversification of assortments being carried out subsequently through wet finishing operations [1, 2].

If we study individually the factors that determine the diversification of assortments starting from the same type of substrate, we first find the existence of factors related to a series of constructive and functional characteristics of the machines used for wet and surface finishing.

Although the worldwide production of semi-finished leather is dependent both on the fluctuations of fashion (which from one season to another may evolve in the most unexpected directions) and on the ecological requirements of the consumers (for example, "free of chrome"/ FOC leather), the selected technologies must invariably take into account the favourable influences of each technological operation on:

- surface yield (economic aspect);
- improvement of the aesthetic characteristics, resistance, special characteristics etc. (qualitative aspect);
- environmental protection and safety of individuals, from tannery workers to users of leather products (ecological aspect).

Leather retanning is a key operation in the wet finishing stage, playing a very important role in diversification of assortments, but at the same time using complex chemicals can induce important eco-toxic effects especially in the liquid effluents (residual float).

Generally, for the correct management of the retanning operation, the properties and effects of auxiliary materials used must be taken into account, depending on the desired characteristics to be obtained for each assortment of semi-processed leather:

- the actual tanning effect;
- the filling effect;
- the influence of softness;
- the dispersion effect of natural tannins;
- the effect on the colour (dark/light);
- natural colour;
- the influence of the dyeing capacity;
- the influence of mechanical resistance;
- ecological implications.

This paper presents some of the achievements related to the expansion of eco-friendly auxiliary product range for wet finishing of leather (filling-retanning) with predominantly natural (protein) components, combined with metal oxides other than Cr_2O_3 and without phenolic compounds, concomitantly with the leather industry's advance towards circular economy and increasing eco-efficiency.

MATERIALS AND METHODS

Materials

The following materials were used in experiments:

- bovine leather tanned in wet-white system (INCDTP - Division ICPI), split and shaved;
- commercial auxiliary products for wet finishing of leather (neutralizing, fixing, acidifying, fatliquoring, washing, degreasing agents);
- pre-tanned bovine leather waste with titanium-zirconium based tanning agents (shavings) (INCDTP - Division ICPI);
- industrial water;
- acids for technical use (formic, lactic);
- commercial acrylic resin;
- aluminium triacetate (commercial product).

Machines/Devices Used

- CALORIS reactor (Romania) for hydrolysis of wet-white leather waste;

- VALLERO rotating drum (Italy) for wet finishing of bovine leather;

- GIULLIANI device (Italy) for the determination of hydrothermal resistance (shrinkage temperature).

Methods Used

- laboratory analytical determinations for physical-chemical characterization of waste, collagen materials, new bioproducts, retanned leather in accordance with the regulations (standards) in force;

- physical-mechanical tests for the characterization of crust semi-finished leather obtained in accordance with the regulations in force.

EXPERIMENTAL

Experimental Model for Obtaining Collagen Hydrolysates Extracted from Tanned Wet-white Leather Waste

The use of protein materials (collagen) to obtain new auxiliaries for leather processing is an important component of research in the field [3-13]. Figure 1 schematically shows the experimental model for obtaining collagen hydrolysates from chrome-free tanned (wet-white) leather waste.

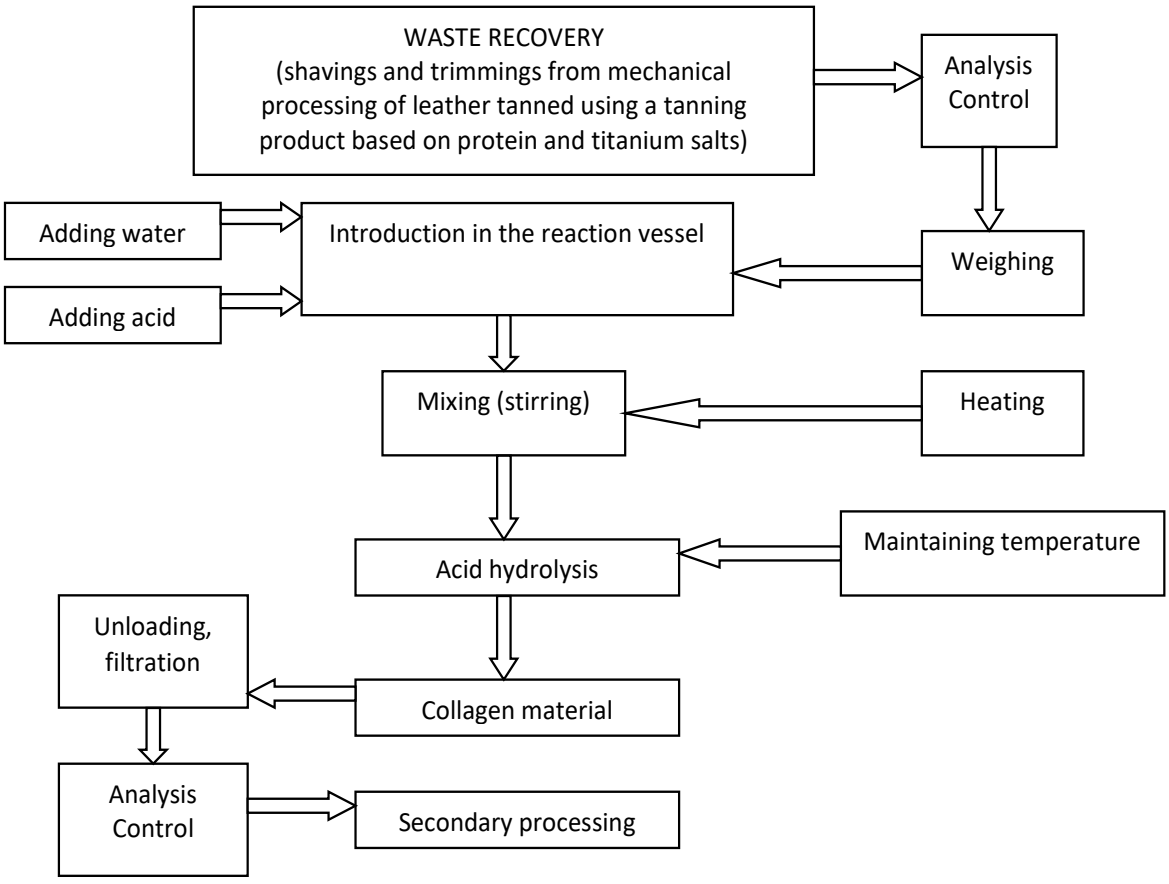

Figure 1. Diagram of the experimental model for obtaining collagen hydrolysates from chrome-free tanned (wet-white) leather waste

Table 1 presents the technological algorithm (according to the proposed experimental model) for obtaining (hydrolysed) collagen intended for the formulation of new filling-retanning agents.

Table 1: The technological algorithm for obtaining (hydrolysed) collagen for the formulation of new filling-retanning agents

No.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Waste recovery		Shavings as well as trimmings are collected as a result of the shaving and trimming operation performed on wet-white leather pretanned with the HCT product (based on titanium oxides and proteins, both recovered from unrecyclable untanned hide waste)	
2.	Analysis/control		Physical-chemical characterisation (see Table 4)	
3.	Grinding		Only large pieces of trimming are ground	
4.	Weighing		Waste is weighed to determine the net weight considered as reference for dosing the other materials	
5.	Filling the reaction vessel	30-35% waste 60-70% water 2-5% formic acid	The reactor is filled in the specified order, under continuous stirring	
6.	Hydrolysis		Stirring is continued at the temperature of 85-95°C for 12-24 h	Control pH=4-5 hydrolysate homogeneity
7.	Filtration (release from the reactor)		Once released from the reactor, the obtained hydrolysate is filtered (Nuce filter, porous/textile material)	
8.	Analysis/control		Physical-chemical characteristics of the collagen material (hydrolysate containing metal oxides) are determined (see Table 2)	
9.	Weighing		Collagen material is weighed to determine net weight	

The physical-chemical characteristics of the obtained collagen material (marked R_0) are presented in Table 2.

Table 2: Physical-chemical characteristics of the collagen material obtained (R_0)

No.	Characteristic	UM	Resulting values	Standard
1.	Dry substance	%	30-35	SR EN ISO 4684-2006
2.	Ash	%	25-30	SR EN ISO 4047-2002
3.	Total nitrogen	%	10.5-11.5	SR ISO 5397-96
4.	Protein substance	%	60-65	SR ISO 5397-96
5.	pH 10% solution	%	4-5	STAS 8619/3-1990
6.	Metal oxides	%	20-22	

Experimental Model of Formulation/ Functionalization of Protein Materials

Figure 2 schematically presents the experimental model of formulation/ functionalization of protein materials in order to obtain new bioproducts for leather retanning.

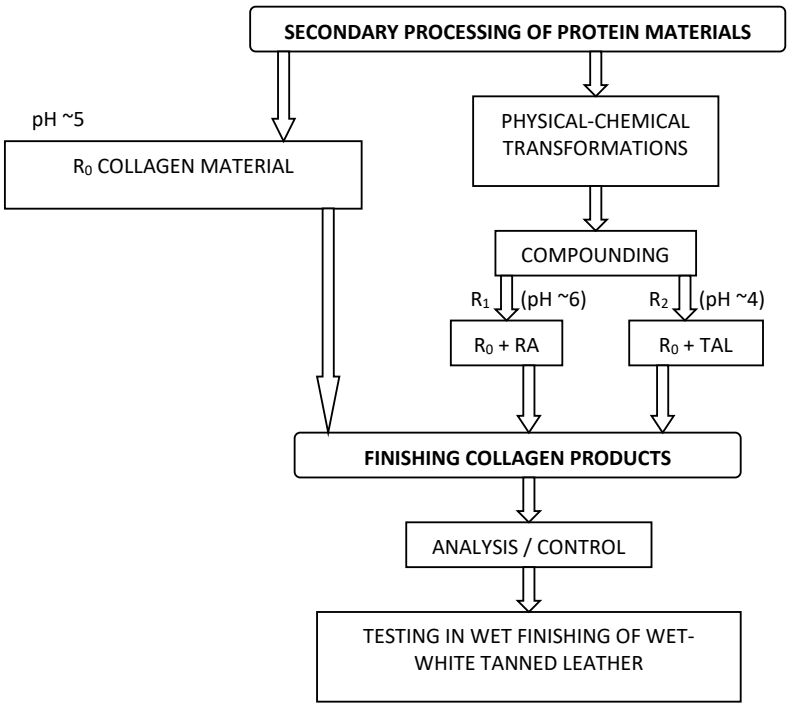

Figure 2. The experimental model of formulation/functionalization of protein materials in order to obtain new bioproducts for leather retanning (R_0: - collagen hydrolysate obtained by acid hydrolysis of leather waste tanned with titanium-zirconium-based products, R_1: R_0 + acrylic resin, R_2: R_0 + alumnium triacetate)

Experimental Model for Obtaining New Bioproducts for Leather Retanning

Table 3 presents the experimental model for obtaining new bioproducts for leather retanning.

Table 3: Experimental model for obtaining new bioproducts for leather retanning

No.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Physical-chemical transformation by compounding	**R1** 75-80% R0 20-25 acrylic resin **R2** 70-80% R0 20-30 Al triacetate	After adding acrylic resin and the aluminium triacetate compound, the mixture is stirred for 15-20' in a mixer-type reaction vessel, the compounding components being solid and/or paste, without exceeding the temperature of 30-35°C	Control: Homogeneity of resulting pastes is controlled
2.	Finishing collagen products			
3.	Analysis/control		Physical-chemical characteristics of the new retanning bioproducts are determined (see Table 4)	
4.	Unloading device			

Characterisation of New Bioproducts for Wet Finishing of Leather

Table 4 presents the physical-chemical characteristics of the new bioproducts intended for leather retanning.

Table 4: Physical-chemical characteristics of new bioproducts intended for leather retanning

No.	Characteristic	UM	Resulting values		Standard
			R_1	R_2	
1.	Dry substance	%	33-36	40-45	SRENISO 4684-2006
2.	Ash	%	25-30	28-31	SRENISO 4047-2002
3.	Total nitrogen	%	9-10	7.0-7.5	SRISO 5397-96
4.	Protein substance	%	50-55	36-41	SRISO 5397-96
5.	pH 10% solution	%	5.0-6.5	4.0-4.5	STAS 8619/3-1990
6.	Metal oxides	%	9-11	25-27	SRENISO 4684-2006

Figure 3 shows the new biomaterials for wet finishing (retanning) of leather.

Figure 3. New biomaterials for wet finishing (retanning) of leather

Testing New Bioproducts for Retanning Wet-white Bovine Leather

Obtaining wet-white leather that will be used to test the new wet finishing materials

Table 5 presents the framework technology for obtaining wet-white leather.

Table 5: The framework technology for obtaining wet-white leather

No.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Pre/tanning	-30-70% pickling float 20-25°C -3-5% tanning agent based on polyaldehyde and/or glutaraldehyde -2-3% pre-fatliquoring agent resistant to electrolytes	After adding the pre/tanning agent the drum rotates for 30' then the pre-fatliquoring agent is added and stirring is continued for another 80-90'	Control: pH=2,8-2,9
2.	Basification	+0,5-1,5% self-basification agent	After adding the self-basification agent, the drum rotates for 240-360'	Control: pH=3,9-4,2 T_s = 70-75°C
3.	Unloading drum			
4.	Rest		Leather left on the pallet for 24-48 h	
5.	Sammying	Sammying machine with cylinders and felt		
6.	Splitting	Splitting machine with belt tape knife	Leather is split at a thickness as close to that of shaving (+0,1-0,2 mm)	
7.	Shaving	Shaving machine with sharp knives	Shaving at the required thickness for the desired assortment	
8.	Trimming	Manually, using a knife/special scissors	Adhesions, areas with varying thickness or unusable areas are removed	
9.	Weighing	Calibrated industrial scales	The net weight of shaved leather is determined, as reference for dosing floats and wet finishing materials	

Wet Finishing of Wet-white Bovine Leather Using the New Bioproducts

Table 6 presents the technological algorithm for wet finishing of wet-white leather using the new bioproducts.

Table 6: Technological algorithm for wet finishing of wet-white leather using the new bioproducts

NO.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Washing, degreasing	200% float at 30°C 0,5% surfactant	Leather is drummed for 10-15'	
2.	Draining			
3.	Neutralization	150% float at 30°C 2-3% neutraliztion agent	Leather is completely deacidified in cross section. The drum rotates for 60'. If the section is not fully neutralized, neutralisation is continued until reaching the desired effect (even over night with intermittent stirring)	Control: pH=4,2-5,8 Ø=100%VBC

4.	Draining			
5.	Washing	200% float at 20-25°C	Leather is washed for 20-30'	
6.	Draining			
7.	Fatliquoring	100% float at 50-55°C 6-10% oil mixture	Drum rotates for 40-60'	Organoleptic control
8.	Fixing (acidification)	+0,5% formic acid (diluted 1:10)	Leather is drummed for 15-20'	White base leather (**NR**)
9.	Draining			
10.	Retanning	100% float at 30-35°C 3-8% **R_0 / R_1 / R_2**		Leather and float control
11.	Fixing (acidification)	+0,5% formic acid	Drum rotates for 15-20'	pH=4-4,5
12.	Draining			
13.	Rinsing	200% float at 20°C		
14.	Unloading drum			
15.	Rest	Minimum 12h		

Figure 4 shows the crust leather obtained using the new materials (after drying and staking).

Figure 4. Crust leather obtained using the new materials (after drying and staking)

RESULTS AND DISCUSSION

The crust leather obtained using the new materials have organoleptic, physical-chemical and mechanical characteristics at least comparable to those of leather processed using classical technology.

Characterization of Crust Wet-white Leather Using the New Bioproducts

Visual and Organoleptic Characterization

Table 7 presents the visual-organoleptic characteristics of the crust leather wet finished using the new bioproducts.

Table 7: The visual-organoleptic characteristics of the crust leather wet finished using the new bioproducts

No.	Characteristics	Nr	R_0	R_1	R_2
1.	Thickness (mm)	0,8-0,9	1,0-1,1	1,1-1,2	1,2-1,3
2.	Colour (visual)	white-slightly yellow	white-cream	white-cream	white-cream
3.	Fullness (organoleptic, marks 1-5)	1 (poor)	2-3 (moderate)	4-5 (good, very good)	5 (very good)
4.	Softness (organoleptic, marks 1-5)	2-3 (moderate)	3-4 (good)	2-3 (moderate)	5 (very good)
5.	Grain appearance (visual, organoleptic)	smooth, slight loosening	smooth, fine	smooth, full, firm	smooth, full, firm

Figure 5 shows the increase in thickness (volume) of the leather retanned with (R_0, R_1, R_2) compared to non-retanned leather (only fatliquored / white base).

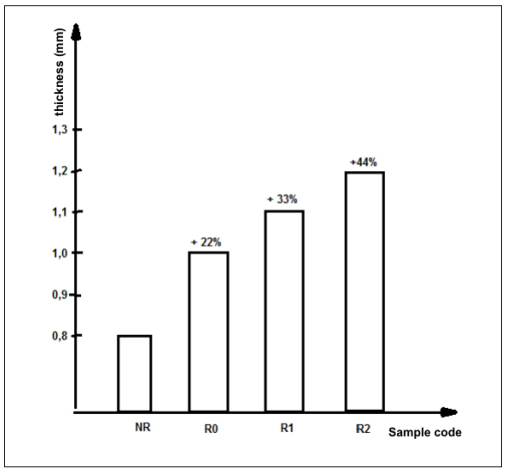

Figure 5. Thickness (volume) of the leather retanned with (R_0, R_1, R_2) compared to non-retanned leather (only fatliquored / white base)

As seen from Table 7 and Figure 5, all the new bioproducts have very good filling ability, highlighted by the obvious increase in volume (thickness).

Characterization of crust (wet-white) leather retanned using the new bioproducts in terms of hydrothermal resistance

Table 8 shows the shrinkage temperature values of the crust leather retanned using the new bioproducts in terms of hydrothermal resistance.

Table 8: Shrinkage temperature values of crust leather retanned using the new bioproducts

No.	Characteristic	UM	Sample code					Standard
			WW	NR	R_0	R_1	R_2	
1.	Shrinkage temperature	°C	70-72	75-76	76-78	78-80	81-82	SR EN ISO 3380:2003

Figure 6 shows an increase in hydrothermal resistance (shrinkage temperature) of the retanned leather (with R_0, R_1, R_2) compared to the non-retanned leather (only neutralized and fatliquored / white base) and the pre-tanned (wet-white) leather.

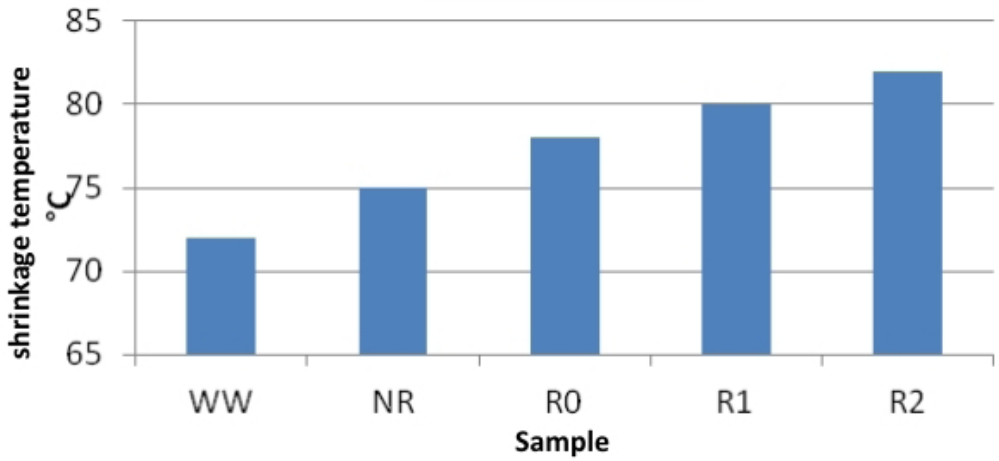

Figure 6. Shrinkage temperature of retanned leather (with R_0, R_1, R_2) compared to non-retanned leather (NR) (only neutralized and fatliquored / white base) and pre-tanned (wet-white) leather (WW)

The new bioproducts for filling-retanning also have tanning ability, increasing hydrothermal resistance of leather (shrinkage temperature) by 4-12°C.

Physical-chemical Characteristics of Crust (Wet-white) Leather Wet Finished (Retanned) Using the New Bioproducts

Table 9 presents the physical-chemical characteristics of the crust (wet-white) leather wet finished (retanned) using the new bioproducts.

Table 9: Physical-chemical characteristics of crust (wet-white) leather wet finished (retanned) using the new bioproducts

No.	Characteristics	UM	Sample code								Standard
			NR		R_0		R_1		R_2		
1.	Tensile strength and percent elongation										SR EN ISO 3376-2012
	Elongation:										
	-at 10N/mm	%	45	66	32	54	32	85	52	82	
	-at break	%	75	104	68	54	74	128	91	120	
	-tensile strength	N/MM	9.6	20	10.3	10.0	27	17	21	16	
2.	Tear strength	N/MM	67	78	32	28	59	55	52	49	

Physical-mechanical characteristics of crust leather obtained from wet white retanned with the new bioproducts are comparable to those of similar assortments obtained internationally, and even with those of leather tanned using Cr salts and retanned with commercial products commonly used in the industry.

Characterization of the Residual Float

Table 10 shows the residual residual float in terms of phenol content when using the new retanning bioproducts (R_0, R_1, R_2) compared to those used industrially (M).

Table 10: Characterization of residual float in terms of phenol content when using new retanning bioproducts (R_0, R_1, R_2), compared with those used industrially (M)

No.	Characteristic	UM	Sample code / resulting values				Standard
			M	R_0	R_1	R_2	
1.	Phenol content	mg/l	20-80	0.4-0.5	0.5-0.6	0,5-0.7	SRISO 6439:2001

CONCLUSIONS

An experimental model was developed for functionalization of collagenic materials obtained by acid hydrolysis of pre-tanned wet-white bovine hide waste in order to obtain new bioproducts intended for the replacement of phenolic compounds for wet finishing of leather (filling-retanning).

The use of new bioproducts in the wet finishing of bovine leather (retanning-filling) has led to:

- semi-processed wet-white crust bovine leather with physical-mechanical and aesthetic characteristics at least comparable to those produced internationally but also to those produced industrially with classical recipes (tanned with chrome salts and using phenolic compounds for retanning-filling);
- non-modification of existing industrial technologies;

- an obvious retanning effect characterized by an increase in shrinkage temperature by 8-12°C, a 10-30% increase in volume, which gives leather fullness and superior strength.

In addition to technical advantages presented above, production and use of new bioproducts based on collagen hydrolysate extracted from waste resulting from leather processing intended to replace the materials currently used for filling-retanning of leather (phenolic compounds) also induce multiple advantages, such as:

- environmental:
  - reduction/elimination of phenolic compounds from liquid effluents from wet finishing (from 20-80mg/l to 0.5-0.7mg/l phenol);
- social:
  - protection of tannery workers by eliminating some compounds with eco-toxic potential (phenolic compounds);
  - the possibility of creating new jobs through the creation of chemization stations in the tanneries;
- economic:
  - the reduction of depollution, storage and/or waste elimination expenses;
  - obtaining high value products relatively simply;
  - reduction of expenses for the purchase of auxiliary materials.

In conclusion, it can be stated that this work contributes to the expansion of the range of eco-friendly auxiliary products for wet finishing of leather (filling-retanning) with predominantly natural (protein) components concomitant with the leather industry's advance towards circular economy and increasing eco-efficiency.

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THE QUALITY OF RABBIT HIDE TANNED BY MANGROVE (*Rhizopora mucronata*)

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THE QUALITY OF RABBIT HIDE TANNED BY MANGROVE (*Rhizopora mucronata*)

ABSTRACT. Mangrove stem (*Rhizopora mucronata*) contains a tannin compound which has potential as tanning material as well as tanner leather coloring. Meanwhile, the public uses more tannin from mimosa tannin and has not optimized the use of mangrove tannins. This study aimed to determine the quality of rabbit hide tanned from mangrove tannin and mimosa tannin. The material used was Rex rabbit hide of 1-year age cut. The research method used a completely random design (CRD) experiment. The treatment ratio of mangrove stem tannin and tannin mimosa concentration were 0:30%, 10:20%, 20:10% and 30%:0. The parameters measured by chemical properties consist of: degree of tanning, moisture, ash and tannin bound to the skin. Physical properties consisted of: tensile strength, elongation and sewing strength. The results showed that the use of mangrove tannin and mimosa tannin for tanning ratios had no significant effect (P> 0.05) on the level of tanning, moisture, ash, and tannin that were bound to tanned skin, tensile strength, elongation and sewing strength. The results showed that the quality of tanned hide had a tanning degree of 62.31%, 13.32% moisture content, 1.57% ash content, and 25.14% tannin content. The physical quality of tensile strength was 356.35 N/cm, elongation was 29.80% and sewing strength is 84.41 Kg/cm. The results of the quality of this tanned hide had fulfilled SNI 06-6121-1999 of leather goods. The conclusion was that tannin extract from mangroves can be used as vegetable tanning agent, with the same quality as mimosa tanning agent.

KEY WORDS: mangrove tannin, mimosa tannin, rabbit hide, quality of hide

CALITATEA PIELII DE IEPURE TĂBĂCITĂ CU MANGROVE (*Rhizopora mucronata*)

REZUMAT. Tulpina de mangrove (*Rhizopora mucronata*) conţine un tanin care are potenţial ca material de tăbăcire, precum şi de colorare a pielii tăbăcite. Pe de altă parte, se foloseşte mai mult tanin din mimosa, iar utilizarea taninului din mangrove nu este optimizată. Acest studiu are scopul de a determina calitatea pielii de iepure tăbăcite cu tanin din mangrove şi tanin din mimosa. S-a utilizat ca material o piele de iepure Rex, la vârsta de 1 an. Metoda de cercetare a presupus desfăşurarea unui experiment cu design complet aleatoriu (CRD). Rapoartele de concentraţii de tanin din tulpină de mangrove şi tanin din mimosa au fost de 0:30%, 10:20%, 20:10% şi 30%:0. Parametrii măsuraţi prin proprietăţile chimice au reprezentat: gradul de tăbăcire, umiditate, cenuşă şi taninul legat de piele. Proprietăţile fizice au constat în: rezistenţă la tracţiune, alungire şi rezistenţă la coasere. Rezultatele au arătat că utilizarea taninului din mangrove şi a taninului din mimosa în raporturile de concentraţii menţionate nu a avut niciun efect semnificativ (P> 0,05) asupra valorilor gradului de tăbăcire, umidităţii, cenuşii şi taninului legat de pielea tăbăcită, rezistenţei la tracţiune, alungirii şi rezistenţei la coasere. Rezultatele au arătat că pielea tăbăcită a avut un grad de tăbăcire de 62,31%, umiditate 13,32%, conţinut de cenuşă 1,57% şi conţinut de tanin 25,14%. În ceea ce priveşte proprietăţile fizice, rezistenţa la tracţiune a fost de 356,35 N/cm, alungirea de 29,80% şi rezistenţa la coasere de 84,41 Kg/cm. Rezultatele au arătat că nivelul de calitate a pielii tăbăcite a îndeplinit standardele indicate în SNI 06-6121-1999 referitor la articolele din piele. Concluzia a fost că extractul de tanin din mangrove poate fi folosit ca agent de tăbăcire vegetal, obţinând aceeaşi calitate ca în cazul utilizării agentului de tăbăcire din mimosa.

CUVINTE CHEIE: tanin din mangrove, tanin din mimosa, piele de iepure, calitatea pielii

LA QUALITÉ DE LA PEAU DE LAPIN TANNÉE PAR MANGROVE (*Rhizopora mucronata*)

RÉSUMÉ. La tige de la mangrove (*Rhizopora mucronata*) contient un tanin au potentiel tannant, ainsi qu'une coloration de la peau tannée. D'autre part, on utilise davantage de tanin de mimosa, tandis que l'utilisation de tanin de mangrove n'est pas optimisée. Cette étude vise à déterminer la qualité de la peau de lapin tannée au tanin de mangrove et au tanin de mimosa. Une peau de lapin Rex, âgée de 1 an, a été utilisée comme matériau. Un essai totalement randomisé (CRD) a été utilisé comme méthode de recherche. Les rapports des concentrations de tanin de mangrove et de tanin de mimosa ont été : 0 : 30%, 10 : 20%, 20 : 10% et 30% : 0. Les paramètres mesurés par les propriétés chimiques ont représenté : le degré de tannage, l'humidité, les cendres et le tanin lié à la peau. Les propriétés physiques sont les suivantes: la résistance à la traction, l'allongement et la résistance à la couture. Les résultats ont montré que l'utilisation du tanin de mangrove et du tanin de mimosa dans les rapports de concentration mentionnés n'avait pas d'effet significatif (P> 0,05) sur les valeurs de tannage, d'humidité, de cendres et de tanins liées au cuir tanné, de résistance à la traction, d'allongement et de résistance à la couture. Les résultats ont montré que le cuir tanné avait un niveau de tannage de 62,31%, une humidité de 13,32%, une teneur en cendres de 1,57% et une teneur en tanin de 25,14%. En ce qui concerne les propriétés physiques, la résistance à la traction était de 356,35 N/cm, l'allongement de 29,80% et la résistance à la couture de 84,41 kg/cm. Les résultats ont montré que le niveau de qualité du cuir tanné était conforme aux normes indiquées dans le document SNI 06-6121-1999 concernant les articles en cuir. La conclusion a été que l'extrait de tanin de mangrove peut être utilisé comme agent de tannage végétal, à la même qualité que lors de l›utilisation de l›agent de tannage mimosa.

MOTS CLÉS : tanin de mangrove, tanin de mimosa, peau de lapin, qualité de la peau

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INTRODUCTION

Natural tanning material is more environmentally friendly than synthetic tanning material. Currently the natural tanning material which is widely used is mimosa tannin. Excess use of mimosa tannin can reduce Cr (VI) when used as a re-tanning [1]. In addition, mimosa tannin as tanning material can increase tensile strength, tensile strength and elongation of the resulting leather [2]. Tanning with mimosa tannin has several properties including tightening and preserving the skin from microbial invasion and can give color to tanning skin as a secondary effect of tanneries [3].

However, one of the weaknesses of the tanning leather with mimosa tannin include low heat stability because the cross-linking between the tanning material and collagen tissue is not strong enough [4]. Besides, tanning with mimosa tannin takes longer and is expensive. For this reason, it is necessary to look for alternative natural ingredients, one of which is tannin taken from mangrove stems (*Rhizophora mucronata*).

Mangrove (*Rhizophora mucronata*) in addition to having ecological value also has economic value, the use of its parts such as leaves, fruit, bark, mangrove stems have been widely developed including drugs for hematuria (bleeding in urine), syrups and chips from mangrove fruit, essential oils from leaves as an antidote to malaria mosquitoes [5] and extracts of mangrove plant parts can be used as natural coloring material [6]. However, the use as a tanning material has not been widely studied, even though tannin compounds contained in mangroves have the potential as natural tanning material on leather [7].

According to Rusila *et al*. [8], mangrove bark (*Rhizophora mucronata*) is a potential source of tannin as a vegetable tanning which is classified as condensing tannins [9]. Tannin from mangrove bark can be used as an alternative to vegetable tanning because the FTIR spectrum data of mangrove tannin is similar to FTIR spectrum of mimosa [10]. Furthermore, according to Paridah and Musgrave [11], the tannin content in mangrove bark reaches 26%. It was also said that tannin from mangrove stem extracts can be used as vegetable tanning. Unfortunately, the problem is the tannin content in mangroves is not as much as the amount of tannin content from mimosa that is equal to 45% [12].

This study examined the physical and chemical quality of rabbit hide tanned by mangrove bark compared with mimosa tannin.

EXPERIMENTAL

Materials and Methods

Instrument

The equipment used was tanning drum, manual scale, litmus paper, analytical scale, stainless steel knives, basin, nails, hammer, measuring cups, pencil, scissors, plywood, thermometers, buckets, spatula and foundation boards to dispose meat and fur.

Material

The material of this study used 12 pieces of rabbit hide 20 cm x 20 cm obtained from a breeder of rabbits in Malang, while the mangrove tannin extract (*Rhizophora* Sp.) was extracted by the researcher. Other chemicals used were: Mimosa acacia, lime (4%), sodium sulfide (2%), Za (3%), sulfuric acid (0.75%), gasoline (5%), teepol (2%), orophone (1%), syntan (10%), TRO oil (5%), and formic acid (1%).

Research Method

The study was conducted through experiment with a Completely Random Design (CRD). The parameters measured were the quality of rabbit hide consisting of chemical quality and physical quality. Chemical quality consisted of water content, ash content, tanning degree, tannin content. Physical quality consisted of the leather tensile strength, the elongation, the sewing strength of the leather. The research treatments were the different ratio of mangrove tannins (*Rhizophora* Sp) and tannin mimosa: (0%:30%), (10%:20%), (20%:10%), (30%:0%).

Observation of Chemical and Physical Quality

The tanned hide was chemically observed, based on Indonesian National Standard (SNI) 06-0463-1989 which included measurement of water, ash, degree of tanning, and tannin contents. Physical testing which included the

strength of tearing leather, elongation of leather and sewing strength of leather on leather using Indonesian National Standard (SNI) 06-1117-1989.

Tanning Process

The tanning process for rabbit using tannins and mimosa tannin is shown in Table 1 below. The process started with washing and finished with retanning.

Table 1: The process of tanning leather using mangrove and mimosa tannin

Processing Stage	Chemical Material	Concentration (%)	Time (minute)	pH
Washing	Running water		15-minute spin	7
Liming	Na_2S (± 1° Be)	2	30-minute spin	9-10
	Ca (OH)2	5	30-minute spin	
	Water	50	Soaked overnight	
Fleshing and unhairing	-	-		
Deliming	Water	200	30-minute spin	7-8
	H_2SO_4	1	30-minute spin 60-minute spin	
Degreasing	Water	100	30-minute spin	7-8
	Teepol	2	45-minute spin	
Bating	Water below 40° C	100	120-minute spin	7-8
	Orophon / bating Agent	1		
Tanning	Water below 40° C Tannin	100	30-minute spin	7-8
	Mimosa mangrove	1). 0% : 30%	120-minute spin	
		2). 10% : 20%	120-minute spin	
		3). 20% :10%	120-minute spin	
		4). 30% :0 %	120-minute spin	
Re-tanning	Water	100		7-8
	Syntan	10	30-minute spin	
Drying				

Mangrove Stem Tannin Extract Process

The process to do mangrove stem tannin extract was done by the Counter current process, which was done by the fresh mangrove stems were given high concentrated juice, while mangrove stems that were almost out of juice were confronted with fresh water. Tannins contained in mangrove stems are condensed tannins. Condensed tannins for tanning processes are more preferable than the hydrolyzed tannins because they have higher affinity to collagen as the main structural protein of connective tissue. That is because of their high molecular weight and the number of phenolic groups giving many points to the bonds that occur with the carbonyl group of peptides [14].

RESULT AND DISCUSSION

The analysis of the quality of rabbit hide tanned by mangrove tannin extract and mimosa tannin with various ratio are presented in Table 2.

Table 2: Analysis result between chemical and physical quality of tanned rabbit hide

No	Variable	Unit	Ratio mangrove tannin: mimosa tannin				
			0% : 30%	10% : 20%	20% : 10%	30% : 0%	SNI 06-6121-1999
1.	Degree of tanning	%	62.31 [a]	54.39 [a]	53.81 [a]	58.69 [a]	Minimum at 25
2.	Water content	%	13.32 [a]	12.99 [a]	12.66 [a]	13.00 [a]	Maximum at 20
3.	Ash content	%	1.47 [a]	1.13 [a]	1.57 [a]	1.43 [a]	Maximum at 2
4.	Tannin content	%	25.14 [a]	21.9 [a] 9	23.24 [a]	23.95 [a]	-
5.	Tensile strength	N/cm	354,13[a]	350.25 [a]	351.39 [a]	356.35[a]	Minimum at 300
6.	Elongation	%	28.67 [a]	27.74 [a]	25.28 [a]	29.80 [a]	Maximum at 40
7.	Sewing strength	Kg/cm	70.19 [a]	69.81 [a]	84.41 [a]	81.19 [a]	Minimum at 50

Note: Different superscript in the same row indicated significant differences (P <0.05)

The quality of tanned rabbit hide from mangrove tannin extract and mimosa tannin from various ratios was explained as follows:

Chemical Properties (Tanning Degree, Moisture Content, Ash Content and Tannin Content)

The degree of tanning is the processing level of tanned hide. If tanning degree percentage is high, it is indicated that the hide was perfectly processed and the physical properties were also good. In contrast, the low tanning degree indicated if the hide was not well-processed yet. Table 2 showed that the use of tanned materials with 30% mimosa tannins or 30% mangrove tannins gave the same degree of tanning at a significance level of 5%. This indicated that mimosa tannin and mangrove tannin can bind to skin collagen, because the skin contains C, H, and O. Hydrogen bonds between collagen and tannin also covalent bonds between collagen and tannin make the tanned skin well and evenly processed. Increasing the degree of tanning the hide depends on the amount of tannin that is bound by skin collagen. Thus, the temperature used for tanning rabbit hide from mimosa tannin and mangrove tannin meets SNI 06-6121-1999 by minimum of 25. It means that the use of mangrove tannin is as good as mimosa tannin, which is probably because the tannin levels from mangroves and from mimosa able to bind perfectly with skin collagen.

Table 2 showed that the water content of tanned hide with mangrove tannin and mimosa tannin produced tanned hide with a lower water content by 13.32% from the regulation of the SNI 06-6121-1999 standard with maximum water content of 20%. Low water content can also be affected by free water and bound water that comes out because of the olation process. In the tanning process, the olation process occurred, which was a binding between the same two molecules into larger molecules by removing water. The release of free water and water bound to the tanning process can cause the water content in the skin to decrease, so that its amount becomes relatively the same.

The results of ash content in Table 2 showed the highest ash content value was 1.57%, which was still low compared to SNI 06-6121-1999, which is a maximum of 2.00%. Ash content on tanned hide shows the amount of minerals found in the tanned hide itself. Some mineral elements contained in the tanned hide include potassium, calcium, iron, phosphorus, chloride, sulfate, and carbonate [13]. The low ash content in the tanned skin results showed that the tanning process runs perfectly, so that many minerals dissolved in water. In addition, the deliming process that run well was able to release mineral elements attached to the skin such as Ca.

Bound tannin level is influenced by the amount of tannin that can diffuse into the skin tissue. From Table 2, bound tannin level was ranging from 21.9%-25.14%. The highest bound tannin content was obtained by mimosa tannin 30%. From Table 2, it can be seen that the lower the concentration of mimosa tannin material used, the less amount of tannin that could enter the skin tissue, so that the amount of tannin bound by skin collagen was lower. However, the tannin level was high again when using tannin material from mangrove tannin. It indicated that mangroves and mimosa are condensing tannin groups. Condensed tannins are preferred for tanning processes compared to hydrolyzed tannin because they have a higher affinity to collagen tissue because of their high molecular weight and the number of phenolic groups which give many points to the bonds that occur with carbonyl groups from peptides [14].

Physical Properties (Tensile Strength Elongation and Sewing Strength)

The highest tensile strength was obtained in tanning with mangrove tannin 30% at 356.35 N/cm and the lowest was in the mangrove: mimosa 10%:20% = 350.25 N/cm ratio. However, all treatments of the research results were stated to meet SNI 06 -6121-1999 concerning leather goods which required a minimum tear strength of 300 N/cm. This shows that the tensile strength values in all treatments met the consumer acceptance standards. The results of tanned rabbit hide with mimosa tannin and mangrove tannin showed that it could be used as accessories in the leather goods manufacture. Tanned rabbit hide which meet the consumer acceptance standard of tensile strength according will be more durable, so that when it is used to make leather shoe product, it can provide consumer comfort in its use.

The elongation percentage of the hide tested showed the elasticity of the hide. The high elongated leather allows the leather to not be easily torn or damaged during its use [13]. In Table 2, it can be seen that the highest elongation was 29.80% in tanned skin with 30% mangrove tannin. While the lowest elongation was 27.74% in tanned skin with a mangrove tannin ratio of 10%: mimosa 20%. Extensions for all treatments met the requirements of SNI 06-6121-1999, which require a maximum of 55%. It means that the elongation value of rabbit hide in all treatments met the consumer acceptance standard (maximum 40%). The higher the value of the stretched skin (close to and or higher than the standard value), it will produce an unstable product (changes in shape and size) so it is not comfortable to wear. Skin elongation has a major influence on the product, for example if elongation value is very low, then when the product (shoes) are woven with a machine then the skin will break or crack. On the contrary, too high elongation results in shoes getting bigger and changing shape during use because the skin has increased length. In general, limp leather has a high tensile strength, so that when receiving maximum traction force until breaking, it will be more elastic and provide greater length increase.

Sewing strength is one of the physical strength parameters of the tanned hide. The sewing strength will be different if the thickness of the hide is different. It is because the thickness of the hide is a numerator in the calculation of the sewing strength test. The thicker the hide, the smaller the value of the sewing strength. Conversely, the thinner the hide, the greater the value of the sewing strength. In Table 2, it can be seen that the highest sewing strength was 84.41 kg/cm by using a ratio between mangrove and mimosa tannin by 20%:10%. While the lowest sewing strength was 69.81 kg/cm by using a ratio between mangrove and mimosa tannin by 10%:20%. However, the tensile strength for all treatments fulfilled the requirements of SNI 06-6121-1999, which requires a minimum of 50 kg/cm. Tannin which is bound by the leather in the tanning process will coat the collagen fibers that are exposed during the calcification process, so that the fibers will become stronger. It is the cause of the good sewing strength in this study.

CONCLUSION

The conclusion of this research is the tannin extract from mangrove stems can be used as a tanned material (vegetable) for rabbit skin because its quality is as good as the rabbit skin tanned with mimosa tannin extract.

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APPLICATION OF OXAZOLIDINE IN WET-WHITE TANNING

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APPLICATION OF OXAZOLIDINE IN WET-WHITE TANNING

ABSTRACT. The commitment to sustainable development has been one of the main concerns of the world. In this sense, this work aims to develop a process for the application of oxazolidine in wet-white tanning and its viability for increasing the thermal stability of leather, reducing in this way the environmental impact of the tanning process. In order to achieve the higher shrinkage temperature, different parameters have been tested, such as time of reaction of the gluteraldehyde; the time of reaction and concentration of oxazolidine; the effect of synthetic and vegetable tannins at different conditions. Important conclusions were achieved, such as the direct relation between thermal stability and oxazolidine concentration, and the direct relation with the application time of tannins. The main result, a shrinkage temperature of 84.2°C, was obtained with a concentration of 6% w/w of oxazolidine and a contact time of 8 hours. Although the shrinkage temperature is high, there are still many improvements that must be done to achieve higher stability and then be exported to a pilot scale.
KEY WORDS: oxazolidine, shrinkage temperature, glutaraldehyde, leather

APLICAREA OXAZOLIDINEI LA TĂBĂCIREA PIELII WET-WHITE

REZUMAT. Angajamentul faţă de dezvoltarea durabilă este una dintre principalele preocupări ale lumii. În acest sens, această lucrare îşi propune să dezvolte un proces pentru aplicarea oxazolidinei la tăbăcirea wet-white şi viabilitatea acesteia pentru creşterea stabilităţii termice a pielii, reducând astfel impactul procesului de tăbăcire asupra mediului. Pentru a obţine o temperatură de contracţie mai mare, s-au testat diferiţi parametri, cum ar fi reacţia gluteraldehidei în timp, timpul de reacţie şi concentraţia oxazolidinei, efectul taninurilor sintetice şi vegetale în diferite condiţii. S-au obţinut concluzii importante, cum ar fi relaţia directă între stabilitatea termică şi concentraţia de oxazolidină şi relaţia directă cu timpul de aplicare a taninurilor. Rezultatul principal, o temperatură de contracţie de 84,2°C, a fost obţinut cu o concentraţie de 6% oxazolidină în greutate şi un timp de contact de 8 ore. Deşi temperatura de contracţie este ridicată, se pot face multe îmbunătăţiri pentru a obţine o stabilitate mai mare, având posibilitatea apoi să se aducă procesul la scară pilot.
CUVINTE CHEIE: oxazolidină, temperatura de contracţie, glutaraldehidă, piele

L'APPLICATION D'OXAZOLIDINE DANS LE TANNAGE WET-WHITE

RÉSUMÉ. L'engagement en faveur du développement durable a été l'une des principales préoccupations du monde. En ce sens, ce travail vise à développer un procédé d'application de l'oxazolidine dans le tannage wet-white et sa viabilité pour augmenter la stabilité thermique du cuir, réduisant ainsi l'impact environnemental du processus de tannage. Afin d'atteindre la température de rétraction supérieure, différents paramètres ont été testés, tels que le temps de réaction du glutaraldéhyde, le temps de réaction et la concentration d'oxazolidine, l'effet de tanins synthétiques et végétaux dans différentes conditions. Des conclusions importantes ont été tirées, telles que la relation directe entre la stabilité thermique et la concentration en oxazolidine et la relation directe avec le temps d'application des tanins. Le résultat principal, une température de rétraction de 84,2°C, a été obtenu avec une concentration de 6% en poids d'oxazolidine et un temps de contact de 8 heures. Bien que la température de rétraction ait été élevée, de nombreuses améliorations doivent encore être apportées pour atteindre une plus grande stabilité et pour ensuite porter le processus à une échelle pilote.
MOTS CLÉS: oxazolidine, température de rétraction, glutaraldéhyde, cuir

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INTRODUCTION

Over the last few years, the commitment to sustainable development has been the main concern of the world, in order to reduce the environmental impact on ecosystems and human health. One of the industries that has been directly affected by these measures is the tanning industry.

Characterized as one of the most polluting industries due to the high quantities of waste generated, this industry has been highly studied by researchers looking for new and less harmful strategies to transform the hide into leather.

Traditionally, the tanning process applies chromium salts as a tanning agent [1], where "85% of all leathers are produced with a chrome based process technology" [2]. With higher stability to thermal exposure (above 100 degrees), enzymatic attack and thermo-mechanical stress [3] and excellent flexibility [4], the chrome-tanned leather is the base process for "almost all types of leathers" [5].

However, the use of chromium salts results in low chromium exhaustion in the tanning bath and a significant presence in the solid waste [6]. This fact requires new research for tanning agents, with the same capacity for producing stable leather. There are several types and combinations of tanning agents that can be considered including mineral agents (aluminium, zirconium), vegetable agents and aldehydes [7].

New studies suggest the use of oxazolidine as an example of an aldehydic tanning agent, which results from the reaction of aldehydes with amino-hydroxy compounds [8, 9]. This product is considered a good substitute due to its versatility when reacting with condensed tannins (phenols) and proteins (collagen), providing the possibility to introduce it at different phases in the tanning process [10]. The crosslinking reaction starts with the opening of the monocyclic or bicyclic oxazolidine ring to form the N-methylol intermediate [11]. In the presence of a tannin molecule, this compound reacts with the polyphenol ring at the 6 and 8-position through covalent bonds [10, 12]. In the case of collagen, the reaction occurs with the active groups (amino) from its triple-helical structure [10].

There are two types of oxazolidine which are usually used as tanning agents, type A (4,4-dimethyl-1,3-oxazolidine) and type E (1-aza-3,7-dioxabicyclo-5-ethyl (3,3,0) octane). Comparing both oxazolidines, type E has a high dependence on pH and a lower reaction rate than oxazolidine A [10]. The need to work at a pH around 8 for better reactivity of oxazolidine minimizes the positive charge of the collagen amino groups. In addition, it reduces the repulsion between same charges and prevents the swelling that usually weakens the collagen structure [13].

In this context, this work aims to evaluate the viability of oxazolidine in the stability of wet-white leather, taking into account environmental concerns by avoiding the pickling stage in the tanning process.

EXPERIMENTAL

Materials and Methods

The raw material used in this work was a bovine hide obtained from a lot of limed hides, from a Tannery Industry of Portugal, split to a 3.5mm of thickness.

All the chemicals used in tanning process were obtained from Indinor, a chemical industry located in Portugal and from Angus Chemicals of the Dow Chemical Company.

The trials were carried out using laboratory drums (LFA-9293, Mathis), with temperature and speed control and all the products quantities were based on the weight of bovine hide.

Tanning Process

Bovine hides were firstly washed and then delimed with 2.5wt% of ammonium sulphate, 0.5wt% of Sodium bisulphide, 2wt% of acetic acid (1:10) and 100wt% of water at 33°C, for 30min (pH≈8) and then bated with a protease, for the same time and temperature.

The delimed and bated skins were washed and pretanned with the mixture of oxazolidine, water (200wt %) and fungicide (0.3wt%) at 35°C. The pH was decreased until a pH of 4.5, then the skins were tanned with a mixture of 4wt% of glutaraldehyde (Fortan 2GL) an 0.5wt% of a fatliquor (Corilene HLG), at 35°C. After completing this phase, the mixture of 1wt% of dispersant (Inditan RS), 0.5wt% of fatliquor, 6% of vegetable extract (Tara and Mimosa (1:1)) was added, then the skins were left overnight. Finally,

the next day, the drums were running for another hour and the pH was decreased to between 3.5 and 4.0 with 5wt% formic acid (1:10).

Effect of Oxazolidine Concentration

The effect on shrinkage temperature of oxazolidine concentration was tested: 2%, 4%, 6% and 8% w/w, at 35°C and pH of 8.

Effect of Synthetic and Vegetable Tannins at Different Conditions

The use of synthetic tannin was tested rather than vegetable extracts, and its stage of addition was tested in two ways: trial A was carried out by initially applying 4% of glutaraldehyde and 0.5% of fatliquor for 1 hour. Following this 6% of synthetic tannin and 0.5% of fatliquor were added and the hides were left running overnight; trial B was carried out by applying the products in reverse order: 6% of synthetic tannin and 0.5% of fatliquor for 1 hour and then 4% of glutaraldehyde and 0.5% of fatliquor were added and the hides were left running overnight.

The influence of synthetic tannins was evaluated against vegetable tannins and their application time: synthetic tannin for trial C, and vegetable tannin (3% w/w of mimosa and 3% w/w of tara) for trial D. Another trial, trial E, was made with the application of a mixture of synthetic tannin (10% w/w) and tara extract (10% w/w).

The study of tannin application time (trials C, D, F and G) was also performed, changing the time from 5 hours and 30 minutes (trials C and D) to a contact time of 21 hours (trials F and G).

For all the trials, the hydrothermal stability of leather was evaluated by the determination of the shrinkage temperature.

Experimental Design for Oxazolidine and Glutaraldehyde Reaction Time Evaluation

Through a two-level experimental design, different contact times of oxazolidine and glutaraldehyde were tested in order to evaluate their effect on the hydrothermal stability of leather. The tanning process was performed at different contact times, from 1 to 7 hours for glutaraldehyde, and from 4 to 8 hours with oxazolidine. The evaluation of the design took into account the analysis of hydrothermal stability by the determination of the shrinkage temperature.

Table 1: Study of technical conditions in the 2^2 factorial design, with duplicated trials

	Oxazolidine time (t_z)	Glutaraldehyde time (t_G)
Level -1	4h	1h
Level 0	6h	4h
Level +1	8h	7h

Hydrothermal Stability of Leather

The hydrothermal stability of leather was evaluated by the determination of the shrinkage temperature, measured in a small strip of leather with an area of 10cm^2. The samples were immersed in a water bath, at a controlled temperature for 3 minutes. The rate of heating was maintained at 2°C after 3 minutes of immersion.

The temperature at which the strip of leather shrunk more than 5% of its area was taken as the shrinkage temperature.

RESULTS AND DISCUSSIONS

The effect of oxazolidine offer by the shrinkage temperature obtained for 2, 4, 6 experiments and 8%w/w is shown in Figure 1.

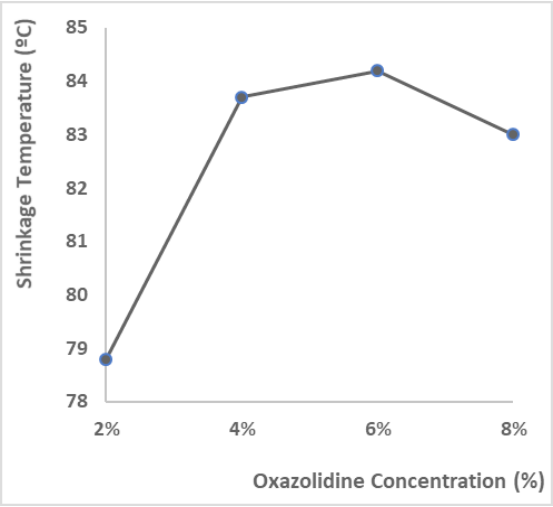

Figure 1. Effect of oxazolidine offer on shrinkage temperature

From the figure it can be seen that a shrinkage temperature of 84.2°C, for 6% w/w of oxazolidine, is the highest result.

It is also observed that there is a direct relationship between the concentration and the

thermal stability of leather. However, when the concentration is over 6%, oxazolidine reactivity decreases with a corresponding decrease in the shrinkage temperature.

Comparing the present results with those found in the literature [13], only the use of 2% and 4% of oxazolidine were reported with shrinkage temperature values of 78.8°C and 83.7°C, respectively, which approximate those obtained in this work.

Nevertheless, the concentration of 6% w/w of oxazolidine is the obvious choice for further tests.

For the second phase of the work, the effect of synthetic tannins and vegetable tannins at different conditions, both trials A and B shrunk at the same temperature, 80.2°C, showing that there is no difference when using either the synthetic tannin or the glutaraldehyde first.

Figure 2 shows the result for comparison of synthetic tannins and vegetables extracts.

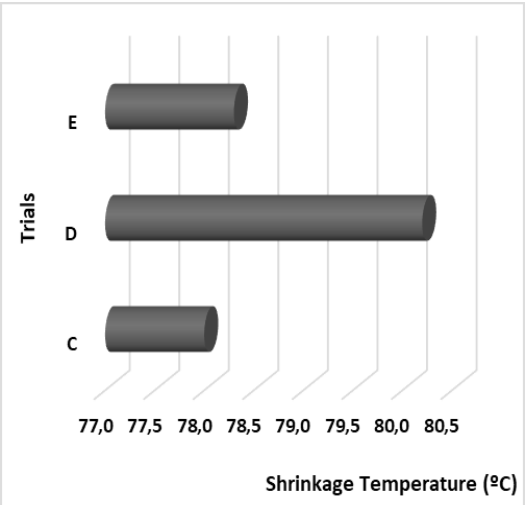

Figure 2. Effect of tannins on shrinkage temperature

It can be seen that the trial with vegetable tannins (trial D) led to the best result, a shrinkage temperature of 80.2°C, while trial C, using synthetic tannin, had the lowest shrinkage temperature, 78.0°C. This result is similar to the one of trial C (mixture of tannins), for which the leather shrank at 78.3°C.

For the study of tannin application time, Figure 3 shows the shrinkage temperature results, where it is possible to evaluate if the time has some effect on the leather stability.

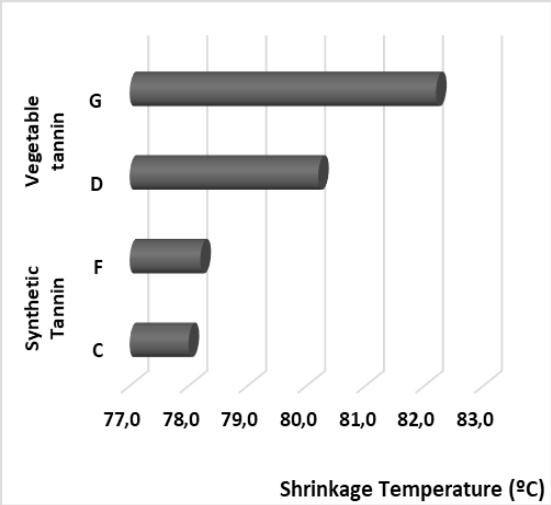

Figure 3. Effect of tannin application time on shrinkage temperature

Comparing the results shown in Figure 3, it is possible to observe that the highest contact time (trial F and trial G) led to the highest shrinkage temperature and both trials, with vegetable extracts, present the best results for thermal stability when compared with synthetic tannin. Therefore, the thermal stability of leather is greater after applying the tannins for longer periods.

Experimental Design for Oxazolidine and Glutaraldehyde Reaction Time Evaluation

To evaluate the effect of the contact time on the hydrothermal stability of leather, different conditions were evaluated in a total of ten experiments. All possible combinations of factors were used, and a matrix was established according to their low and high levels, represented by -1 and +1, respectively (Table 2).

Table 2: Factorial design

	Test1	Test2	Test3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
Oxazolidine time (t_Z)	1	-1	1	-1	1	-1	1	-1	0	0
Glutaraldehyde time (t_G)	-1	-1	1	1	-1	-1	1	1	0	0
$t_Z.t_G$	-1	1	1	-1	-1	1	1	-1	0	0

The average results of the shrinkage temperature for the factorial design experiments are shown in Figure 4.

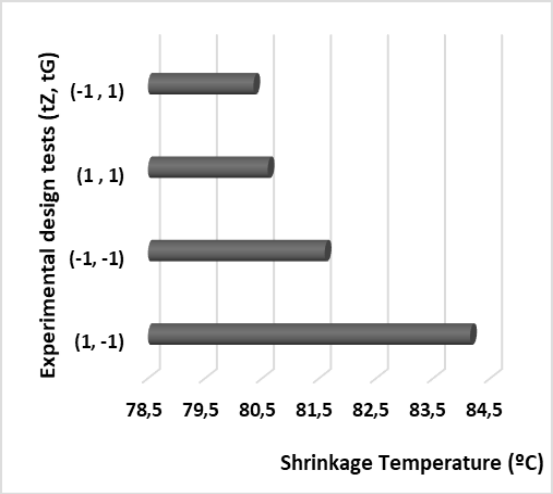

Figure 4. Average results for the experimental design tests

Comparing the results obtained, it can be seen that for the higher shrinkage temperature, 84.2°C, the relevant factor is the combination of a higher oxazolidine contact time and a lower glutaraldehyde contact time, as shown in Table 3.

Table 3: Statistical parameters for the 2^2 factorial design

	Oxazolidine time (t_z)	Glutaraldehyde time (t_G)	t_z. t_G
Effect	5.6	-9.6	-4.6
Coefficient	0.7	-1.2	0.575

Considering the two-level factorial design, the defining Equation 1 takes the form:

$$R = 81{,}38 + 0{,}7t_Z - 1{,}2t_G - 0{,}575t_Zt_G \quad (1)$$

Due to the lower positive effect of the oxazolidine application time, a change in the values from low to high levels results in an almost insignificant increase in the leather stability. In addition, the glutaraldehyde application time is important because of its negative effect, assuming the main role in this case. At its highest level this factor promotes a decrease of 11,2% in the shrinkage temperature.

By evaluating the importance of combining the two factors it is possible to observe that the 8 hours of oxazolidine and 7 hours of glutaraldehyde leads to a lower leather stability, when compared with the times of 4 and 1 hours, respectively. This change in time value, from low to high level, results in a reduction of 3% in the shrinkage temperature.

Thus, by factorial design, the conditions that lead to an optimal result are an oxazolidine time greater than 8 hours and a glutaraldehyde time less than 1 hour.

CONCLUSIONS

This work studied the application of oxazolidine in wet-white tanning and its suitability for increasing the thermal stability of leather without applying the pickling step in the tanning process. Different conditions were tested, which resulted in a shrinkage temperature of 84.2°C for a concentration of 6% w/w of oxazolidine and a contact time of 8 hours, and for 4% w/w of glutaraldehyde with a contact time of 1 hour.

Other important conclusions were achieved, such as the direct relation between thermal stability and oxazolidine concentration, the direct relation with the tannin application time and the best result of vegetable extracts when compared with synthetic tannin.

Nevertheless, there are still many improvements to be made in the process to achieve higher stability. Pilot-scale experiments need to be performed with the best result obtained.

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ANTIFUNGAL AND ANTIBACTERIAL TREATMENTS BASED ON NATURAL COMPOUNDS FOR LINING LEATHER AND FOOTWEAR ARTICLES

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ANTIFUNGAL AND ANTIBACTERIAL TREATMENTS BASED ON NATURAL COMPOUNDS FOR LINING LEATHER AND FOOTWEAR ARTICLES

ABSTRACT. The purpose of this research is to obtain antifungal and antibacterial treatments based on natural compounds of essential oils of geranium, pine, and rosemary for cotton and leather linings to make leather, fur articles, and footwear. The main characteristic absorption bands for the functional groups of geranium, pine and rosemary essential oils were investigated by Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR). Microbiological antifungal test was performed in the presence of *Candida albicans* ATCC 10231 fungus and antibacterial activity was determined in the presence of *Staphylococcus aureus* ATCC 25923 (Gram-positive bacteria), and *Escherichia coli* ATCC 25922 (Gram-negative bacteria). The absorption method involved the inoculation of the bacteriological test inoculum directly on the treated samples. Microbiological tests have revealed a high antifungal and antibacterial activity of the essential oils of *Aetheroleum pini sylvestris*, *Aetheroleum geranii*, *Rosmarinus officinalis* on cotton and leather linings and the possibility to be used in various compositions for the treatment of different lining materials for gloves, caps, shoes or other articles with essential bioactive properties for health and environmental protection.

KEY WORDS: natural compounds, antifungal and antibacterial treatments, cotton cloth lining, leather lining, health and environmental protection

TRATAMENTE ANTIFUNGICE ŞI ANTIBACTERIENE PE BAZĂ DE COMPUŞI NATURALI PENTRU CĂPTUŞELI ARTICOLE DIN PIELE ŞI ÎNCĂLŢĂMINTE

REZUMAT. Scopul acestei cercetări este de a obţine tratamente antifungice şi antibacteriene bazate pe compuşi naturali ai uleiurilor esenţiale de geraniu, pin şi rozmarin pentru căptuşelile din bumbac şi meşină utilizate la confecţionarea articolelor din piele, blană şi încălţăminte. Principalele benzi de absorbţie caracteristice grupărilor funcţionale ale uleiurilor esenţiale de geraniu, pin şi rozmarin au fost determinate prin spectroscopie în infraroşu cu transformată Fourier - reflexie totală atenuată (FTIR-ATR). Testul antifungic microbiologic a fost efectuat în prezenţa *Candida albicans* ATCC 10231, iar activitatea antibacteriană a fost determinată în prezenţa *Staphylococcus aureus* ATCC 25923 (bacterie Gram-pozitivă) şi *Escherichia coli* ATCC 25922 (bacterie Gram-negativă). Metoda de absorbţie a implicat inocularea directă a inoculului de test bacteriologic pe eşantioanele tratate. Testele microbiologice au relevat o activitate antifungică şi antibacteriană ridicată a uleiurilor esenţiale de *Aetheroleum pini sylvestris*, *Aetheroleum geranii*, *Rosmarinus officinalis* pe căptuşelile din bumbac şi meşină, precum şi posibilitatea de a fi utilizate în diverse compoziţii pentru tratarea diferitelor materiale de căptuşeală pentru mănuşi, şepci, pantofi sau alte articole cu proprietăţi bioactive esenţiale pentru protecţia sănătăţii şi a mediului.

CUVINTE CHEIE: compuşi naturali, tratamente antifungice şi antibacteriene, căptuşeală din pânză de bumbac, căptuşeală din meşină, protecţia sănătăţii şi a mediului

TRAITEMENTS ANTIFONGIQUES ET ANTIBACTÉRIENS À BASE DE COMPOSÉS NATURELS POUR LA DOUBLURE D'ARTICLES EN CUIR ET CHAUSSURES

RÉSUMÉ. Le but de cette recherche est d'obtenir des traitements antifongiques et antibactériens à base de composés naturels d'huiles essentielles de géranium, de pin et de romarin pour les doublures en coton et leathere destinés à la confection du cuir, des articles en fourrure et des chaussures. Les principales bandes d'absorption caractéristiques des groupes fonctionnels des huiles essentielles de géranium, de pin et de romarin ont été étudiées par spectroscopie infrarouge à transformée de Fourier-réflectance totale atténuée (FTIR-ATR). Un test antifongique microbiologique a été réalisé en présence du champignon *Candida albicans* ATCC 10231 et l'activité antibactérienne a été déterminée en présence de *Staphylococcus aureus* ATCC 25923 (bactérie à Gram positif) et *Escherichia coli* ATCC 25922 (bactérie à Gram négatif). La méthode d'absorption a impliqué l'inoculation de l'inoculum de test bactériologique directement sur les échantillons traités. Des tests microbiologiques ont révélé une activité antifongique et antibactérienne élevée des huiles essentielles d'*Aetheroleum pini sylvestris*, d'*Aetheroleum geranii* et de *Rosmarinus officinalis* sur les doublures en coton et leathere et la possibilité d'être utilisées dans diverses compositions pour le traitement de différents matériaux de doublure pour gants, bonnets, chaussures ou autres articles dotés de propriétés bioactives essentielles à la protection de la santé et de l'environnement.

MOTS CLÉS: composés naturels, traitements antifongiques et antibactériens, doublure en tissu de coton, doublure en leathere, protection de la santé et de l'environnement

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INTRODUCTION

The interest in using of essential oils extracted from plants with bioactive properties to prevent and stop the development of fungi and bacteria has increased considerably worldwide because many of them have no side effects on the human body or on the environment as they have bioactive compounds obtained by synthesis [1]. Plants with bioactive properties are part of the important group of plants traditionally used to prevent and treat the development of fungi and bacteria [2, 3]. Essential oils from plants are highly concentrated compositions in chemical compounds with important bioactivity, which have several properties: antiseptic, antibacterial, immunostimulant, regenerative, anticancer [4-10]. Essential oils are liquid, volatile, clear, or colored, soluble in lipids and organic solvents, having densities generally lower than water [11-13]. They can be synthesized by all the organs of the plant, like buds, flowers, leaves, stems, twigs, seeds, fruits, roots, wood or bark and are kept in secretory cells, cavities, channels, epidermal cells or glandular trichomes [11]. The antifungal and antibacterial effects of the essential oils extracted from the plants can inhibit their growth by different mechanisms initiated by the constituent compounds [14, 15]. Essential oils are complex mixtures of low molecular weight compounds extracted from plants by hydrodistillation and various solvents. Terpenoids and polyphenols are major components that give the characteristic aroma and biological properties of essential oils. Essential oils are prescribed for a variety of problems in traditional medicine around the world. They are assigned various biological and pharmaceutical activities such as antibacterial and antifungal properties. Extensive phytochemical analyses have led to the identification and characterization of the major components of the essential oils that are of great interest especially for the pharmaceutical and cosmetic industries [16-21]. The purpose of this research is to obtain antifungal and antibacterial treatments based on natural compounds extracted from different essential oils like *Aetheroleum pini sylvestris*, *Aetheroleum geranii*, *Rosmarinus officinalis* for cotton and leather linings that could be used to obtain leather and fur articles (gloves, caps) and shoes with essential bioactive properties for health and environmental protection.

MATERIALS AND METHODS

Materials

Aetheroleum pini sylvestris, *Aetheroleum geranii*, and *Rosmarinus officinalis* essential oils were acquired from S.C. Herbavit S.R.L. Oradea, Romania. "Flower" emulsion (dodecandioyl-diglycine / microcrystalline cellulose (1:1 ratio) / silica / ethanol / water) was obtained by the National Research and Development Institute for Textiles and Leather - Division: Leather and Footwear Research Institute (INCDTP-ICPI), Bucharest. Cotton cloth was obtained in the National Research and Development Institute for Textiles and Leather - INCDTP Bucharest. Sheepskin lining leather was processed at the National Research and Development Institute for Textiles and Leather - Division: Leather and Footwear Research Institute (INCDTP-ICPI), Bucharest. *Candida albicans* ATCC 10231 fungi, *Escherichia coli* ATCC 25922 (Gram-negative bacteria) and *Staphylococcus aureus* ATCC 25923 (Gram-positive bacteria) biological materials are purchased from SC Sanimed International Impex SRL.

Methods

Obtaining Cotton Cloth and Sheepskin Lining Leathers

In order to obtain the treated samples of cotton cloth or sheepskin lining leathers (Table 1), they were immersed in 200% aqueous float with 5% essential oil (and 15% "flower" emulsion respectively), relative to the weight of the lining materials, at 25°C for 30 minutes with stirring and then drying at 25°C.

Table 1: The description of samples tested

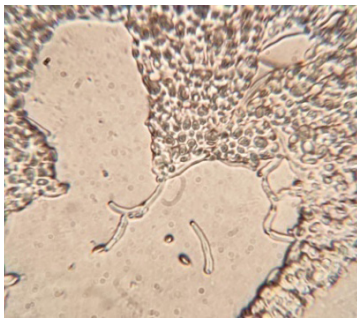
Control sheepskin lining leather	Sheepskin lining leather treated with geranium essential oil	Sheepskin lining leather treated with pine tree essential oil	Sheepskin lining leather treated with rosemary essential oil	Sheepskin lining leather treated with rosemary essential oil and "flower" emulsion
Control cotton cloth	Cotton cloth treated with geranium essential oil	Cotton cloth treated with pin tree essential oil	Cotton cloth treated with rosemary essential oil	Cotton cloth treated with rosemary essential oil and "flower" emulsion

Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR) Analysis

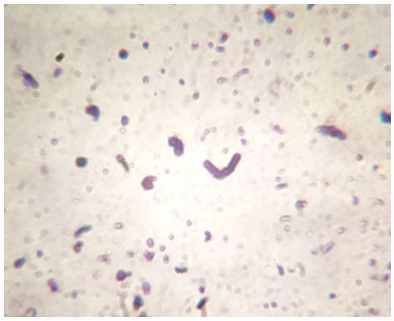
The chemical structures of investigated samples were investigated by use of FT-IR/ATR spectrometer (Jasco 4200) operating in the range of 4000-650 cm^{-1} with spectral resolution of 0.5 cm^{-1}. The device is equipped with a Michelson interferometer with incident angle of 45°, with Digital Signal Processing technology (DSP), cubic angular mirrors with self-aligning mechanism and standard thermostatic DLATGS Peltier detector used for the structure identification.

Microbiological Investigations

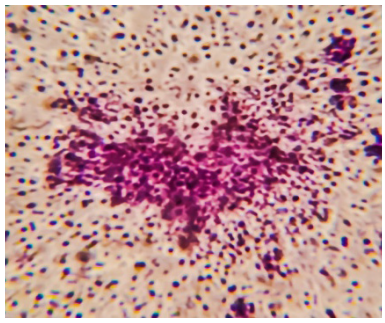
Antifungal activity was determined in the presence of Candida albicans ATCC 10231 according to ISO 20743: 2007 (Figure 1). The antibacterial activity was determined in the presence of Escherichia coli ATCC 25922 and Staphylococcus aureus ATCC 25923 (Figure 1) according to ISO 20743: 2007.



Candida albicans ATCC 10231



Escherichia coli ATCC 25922



Staphylococcus aureus ATCC 25923

Figure 1. Optical microscopy images for *Candida albicans*, *Escherichia coli*, and *Staphylococcus aureus*

Quantitative testing methods to determine the antifungal and antibacterial activity of the treated samples were performed according to ISO 20743:2007, Textiles — Determination of antibacterial activity of antibacterial finished products. The absorption method was used, which involves the inoculation of the bacteriological test inoculum directly on the treated samples.

The initial cell concentration was determined previously, by decimal dilutions (10^{-4}) in sterile deionized water, and from the last dilution, for each strain, 100 µL were taken and displayed on Sabouraud Dextrose Agar nutrient medium. The counts on the plate were carried out at 24h of incubation, these being kept as a reference for the cell developments in the control sample from the sample set. Thus, plates with a cell density similar to that of 10^{-4} dilution were considered to have similar Colony Forming Units (CFU) values (2.8x104 CFU/mL Escherichia coli, 3.42x104 CFU/mL for Staphylococcus aureus, and Candida albicans 2.48x104 CFU/mL).

The counts on the plate were made at 24h of incubation, in order to be able to detect the colony forming cellular units. The pictures

of the Petri dishes were made after 48h of incubation. To quantify the antibacterial and antifungal efficiency, the degree reduction of microorganisms and logarithmic reduction of each sample were calculated, based on the initial cell concentration.

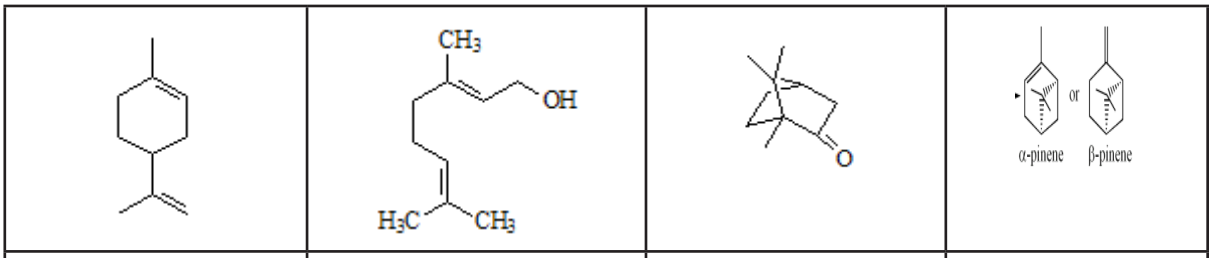
Optical Microscopy Investigation

Optical microscopy images were captured using a Leica stereomicroscope S8AP0 model with optical fiber cold light source, L2, with three levels of intensity, and 40X magnification.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR) Analysis

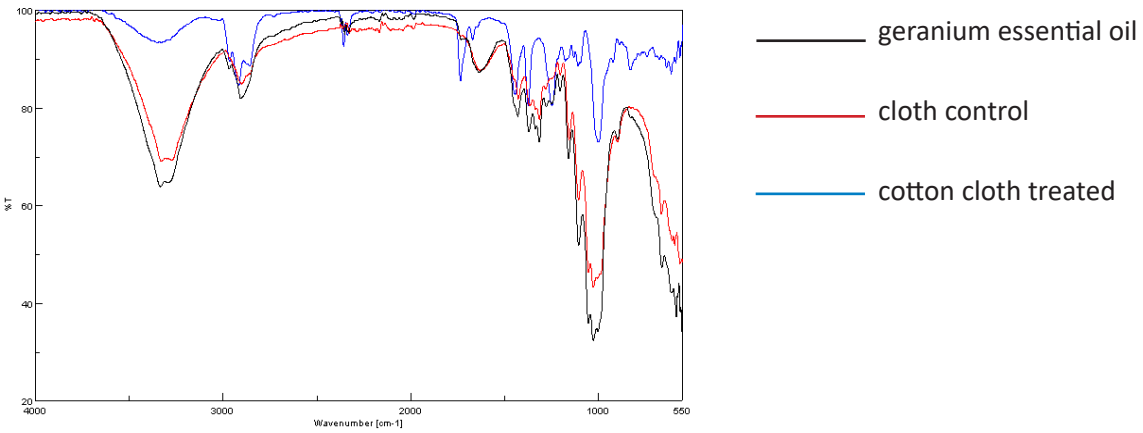
The essential oils used in these experiments are rich in compounds with antifungal and antibacterial activity. Thus, geranium essential oil is rich in citronellol and geraniol, pine essential oil has predominantly limonene and α-pinene, and rosemary essential oil is rich in eucalyptol and camphor and α-pinene [11, 16, 18, 20] (Figure 2). The characteristic absorption bands for the functional groups of geranium, pine and rosemary essential oil are shown in Figures 3, 5, and 7.



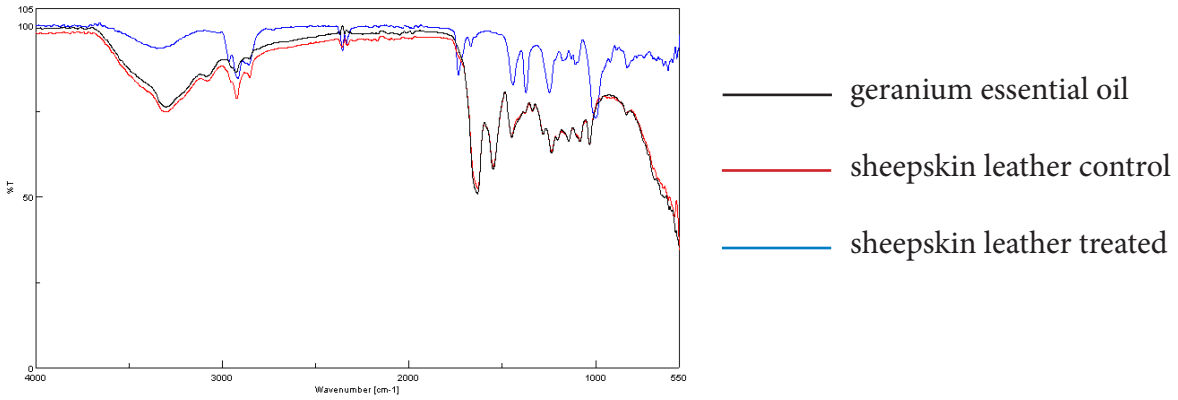
Limonene	Geraniol	Camphor	α-pinene

Figure 2. Main compounds of the essential oils used in experiments

From the FT/IR-ATR spectra in Figure 3(A) with geranium essential oil, control cotton cloth, cotton cloth treated with geranium essential oil and Figure 3(B) with geranium essential oil, control sheepskin leather, sheepskin leather treated with geranium essential oil the main peaks are recorded at: 830 cm^{-1} - corresponding to the C-H bond; 998 cm^{-1} - corresponding to the C-H bond; 1107 cm^{-1} - corresponding to the C-O bond, 1734 cm^{-1} - corresponding to the connection C = C; 2916 cm^{-1} - corresponding to the C-H bond; 3351 cm^{-1} - corresponding to the aromatic C-H bond.



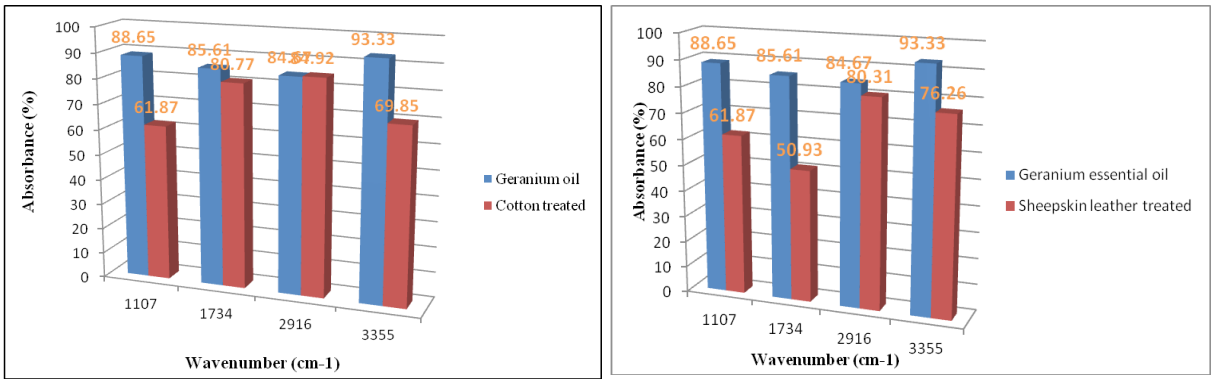
A



B

Figure 3. FTIR-ATR spectra for: (A) geranium essential oil, control cloth, cotton cloth treated with geranium essential oil, and (B) geranium essential oil, control sheepskin lining leather, sheepskin lining leather treated with geranium essential oil

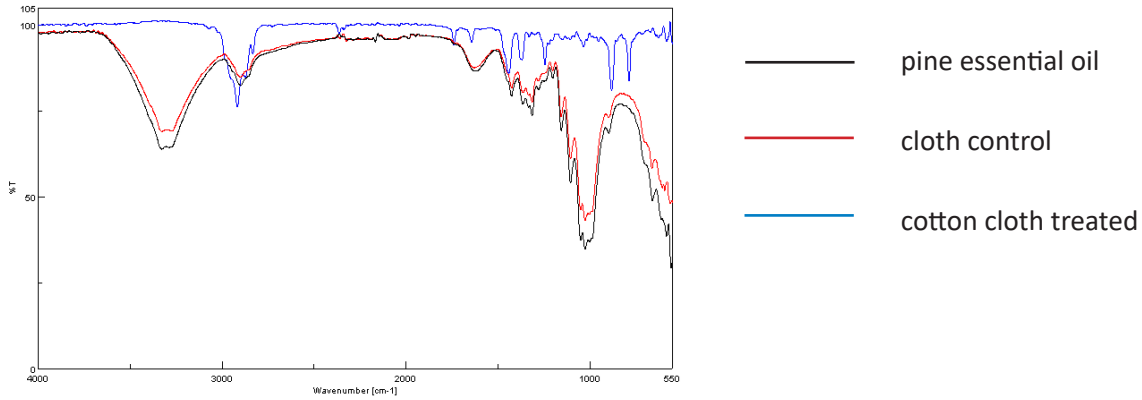
From the dependence of absorbance on the wavenumber, the fixation of the geranium essential oil compounds in the treated sample of cotton cloth (A) and sheepskin lining leather (B) is observed, through the decreasing of the absorbance values in the support samples compared to the value of the geranium essential oil (Figure 4).



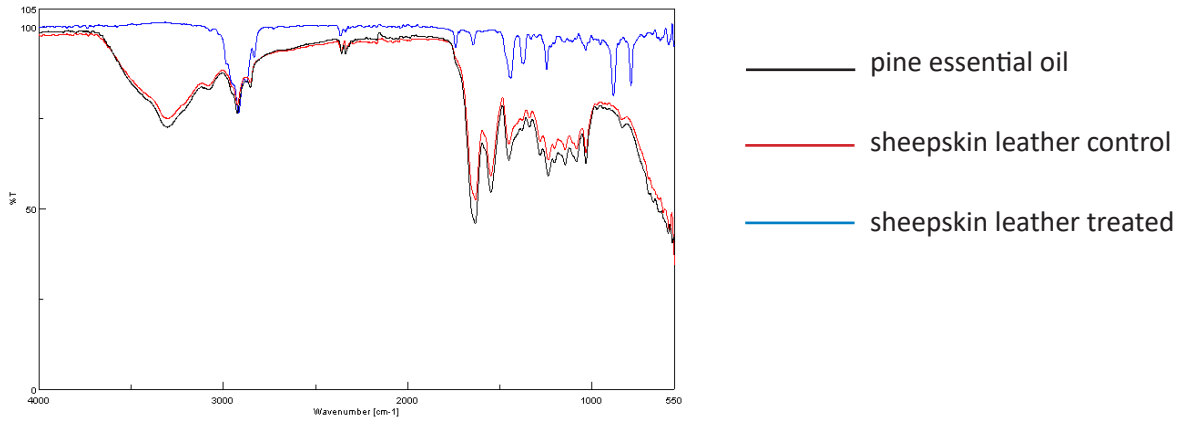
A) B)

Figure 4. Dependence of absorbance on the wavenumber for: (A) geranium essential oil, cotton cloth treated with geranium essential oil, and (B) geranium essential oil, sheepskin lining leather treated with geranium essential oil

From the FT/IR-ATR spectrum in Figure 5(A) with pine essential oil, control cotton cloth, cotton cloth treated with pine essential oil and Figure 5(B) with pine essential oil, control sheepskin leather, sheepskin leather treated with pine essential oil the main peaks are recorded at: 882 cm^{-1} - corresponding to the C-H bond; 954 cm^{-1} - corresponding to the C-H bond; 1033 cm^{-1} - corresponding to the C-O bond in the secondary alcohols; 1105 cm^{-1} - corresponding to the C-O-C bond; 1244 cm^{-1} - corresponding to the OH vibration; 1330 cm^{-1} - corresponding to the CH group and 1440 cm^{-1} - corresponding to the connection C = O.



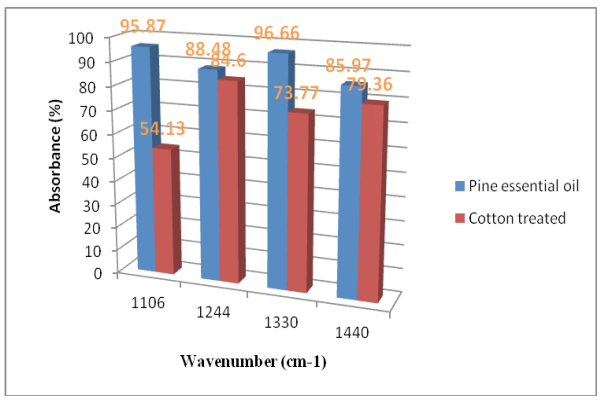
A



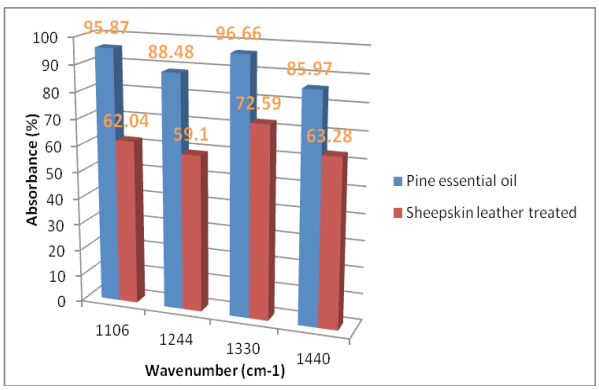
B

Figure 5. FTIR-ATR spectra for: (A) pine essential oil, control cloth, cotton cloth treated with pine essential oil, and (B) pine essential oil, control sheepskin lining leather, sheepskin lining leather treated with pine essential oil

From the dependence of absorbance on the wavenumber, the fixation of the pine essential oil compounds in the treated sample of cotton cloth (A) and sheepskin lining leather (B) is observed, through the decreasing of the absorbance values in the support samples compared to the value of the pine essential oil (Figure 6).



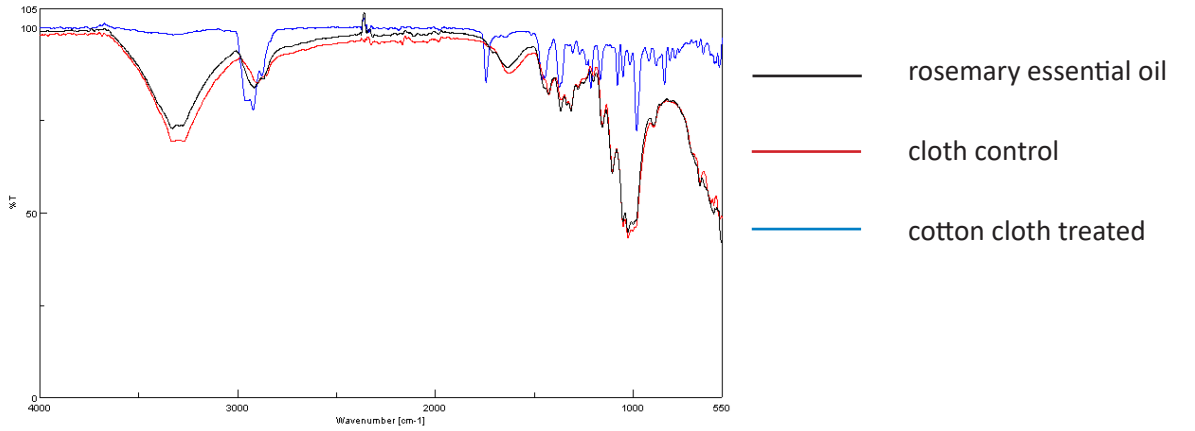
A)



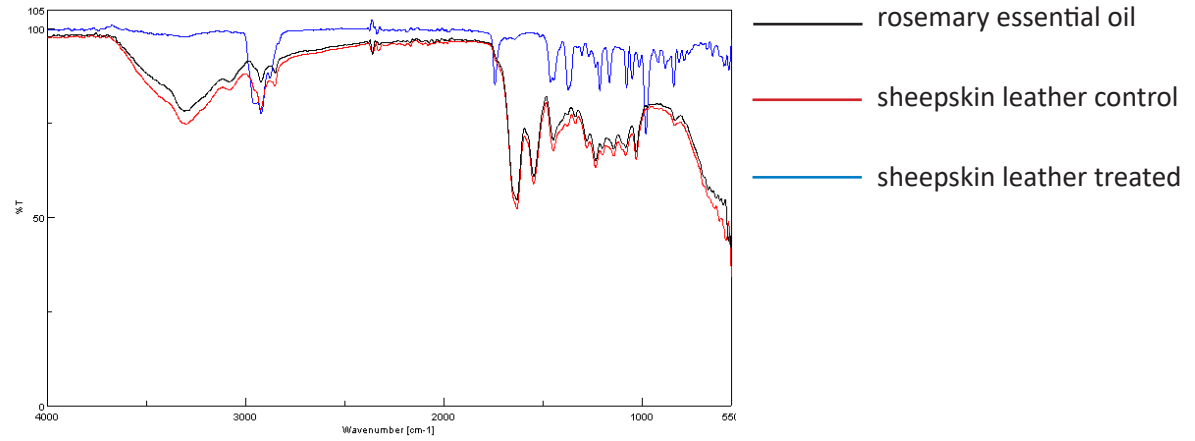
(B)

Figure 6. Dependence of absorbance on the wavenumber for: (A) pine essential oil, cotton cloth treated with pine essential oil, and (B) pine essential oil, sheepskin lining leather treated with pine essential oil

Figure 7 (A) showed the FTIR-ATR spectra with rosemary essential oil, control cotton cloth, and cotton cloth treated with rosemary essential oil, while Figure 7 (B) showed the spectra for rosemary essential oil, control sheepskin lining leather, and sheepskin lining leather treated with rosemary essential oil. The main peaks are recorded at: 885 cm^{-1}, and 992 cm^{-1}, 2878 cm^{-1}, and 3323 cm^{-1} (C-H bond); 1016 cm^{-1} (C-O bond in the secondary alcohols); 1166 cm^{-1} (C-O bond specific to terpenoids); 1743 cm^{-1} (C=C bond).



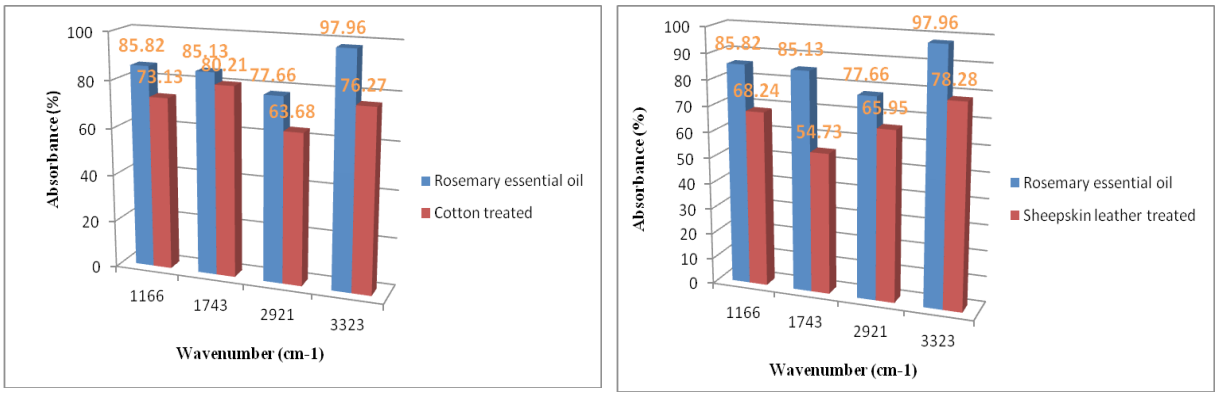
A



B

Figure 7. FTIR-ATR spectra for: (A) rosemary essential oil, control cloth, cotton cloth treated with rosemary essential oil (B) rosemary essential oil, control sheepskin lining leather, sheepskin lining leather treated with rosemary essential oil

From the dependence of absorbance on the wavenumber, the fixation of the rosemary essential oil compounds in the treated sample of cotton cloth (Figure 7(A) and sheepskin lining leather (Figure 7(B)) is observed, by decreasing of the absorbance values in the support samples compared to the value of the essential oil (Figure 8).



(A) (B)

Figure 8. Dependence of absorbance on the wavenumber for: (A) rosemary essential oil, cotton cloth treated with rosemary essential oil, and (B) rosemary essential oil, and sheepskin lining leather treated with rosemary essential oil

It is noted that the introduction of a mixture of tenside base constituted from a dodecandioyl-diglycine / sucrose diester (1:1 ratio) / ethanol / water in pine oil composition, as a nanostructured "flower" emulsion [22, 23], helps to fix the essential oil on both the cotton cloth and sheepskin lining leather treated (Figures 9 and 10).

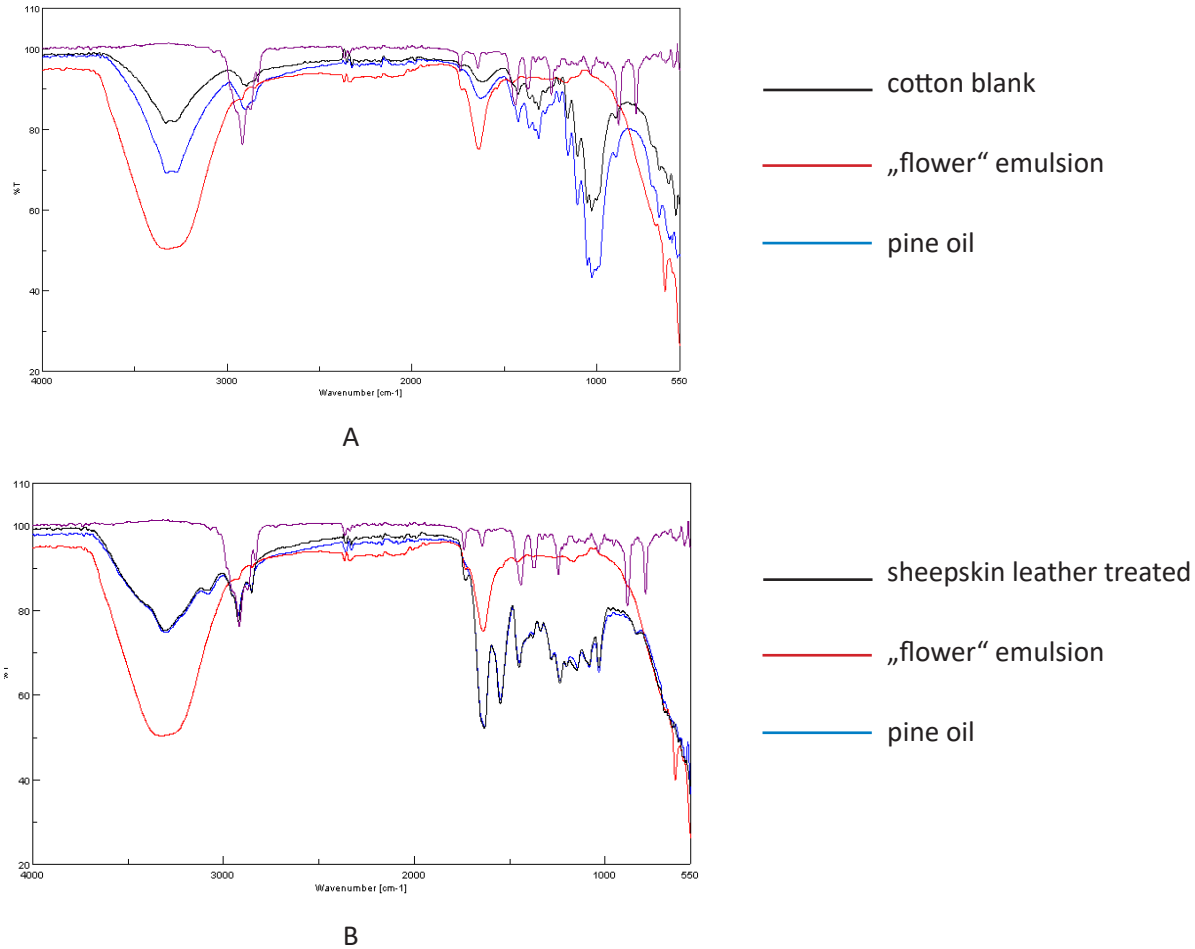


Figure 9. FT/IR-ATR spectra for: (A) pine essential oil, control cloth, cotton cloth treated with pine essential oil and "flower" emulsion, and (B) pine essential oil, control sheepskin lining leather, sheepskin lining leather treated with pine essential oil and "flower" emulsion

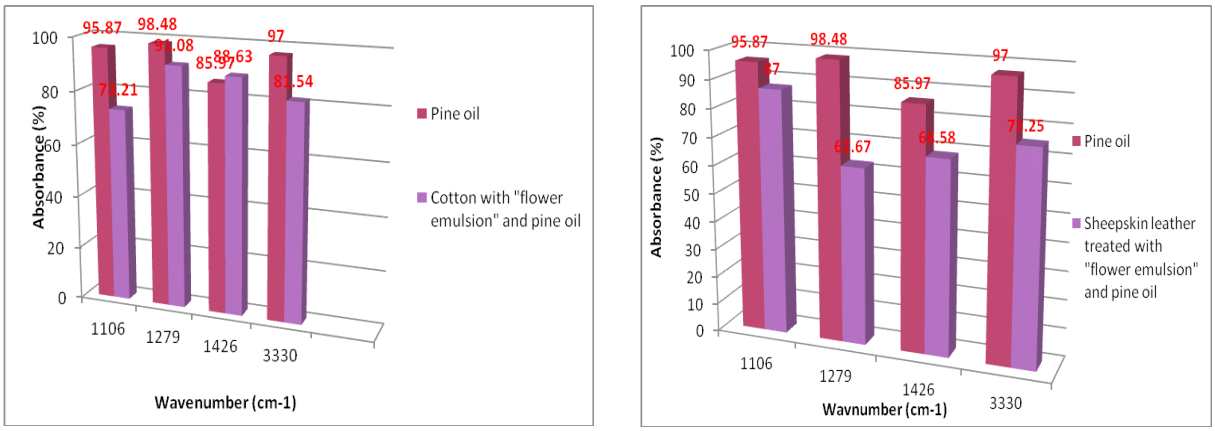


Figure 10. Dependence of absorbance on the wavenumber for: (A) pine essential oil, cotton cloth treated with pine essential oil and "flower" emulsion; (B) pine essential oil, sheepskin lining leather treated with pine essential oil and "flower" emulsion

Microbiological Investigations

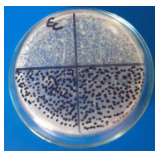
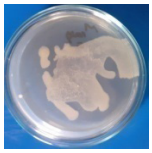
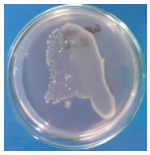
The microbiological tests were determined in the presence of *Candida albicans* fungus and *Escherichia coli* and *Staphylococcus aureus* bacteria.

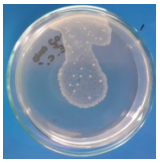
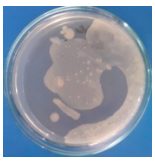
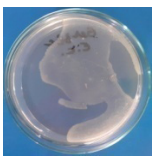
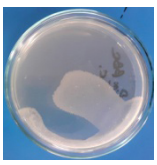
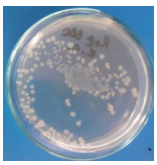
Tests on Escherichia coli

Escherichia coli (*E. coli*) is a group of gram-negative bacteria that normally resides in the gut of healthy people, but some strains can cause infections in the digestive tract and urinary tract [24]. *Escherichia coli* is the most common cause of urinary tract infections in the world, accounting more than 80%, both in the community and nosocomial cases [25]. In recent years, the emergence of same *Escherichia coli* resistant strains has made the treatment of patients infected with these organisms more difficult and complex [26, 27]. This *Escherichia coli* resistant strains have raised many concerns for physicians to choose the appropriate antibiotic in the treatment process [24].

The cotton cloth and sheepskin lining leather treated with geranium essential oil showed antibacterial properties against *Escherichia coli* with a reduction of 99.14% and 100% of colony forming units, followed by the essential oil of pine with a reduction of 98.43% and 99.96% and rosemary with a reduction of 98.21% and 94.86% (Table 2).

Table 2: Antibacterial activity of treated materials against *Escherichia coli*

Sample	Result	Image	R%	Log_{10} red.
Inoculum concentration	T_0= 2.8x10^4 CFU/mL		-	-
Control sample of sheepskin lining leather	T_0= 2.8x10^4 CFU/mL T_{24}= 2x10^2 CFU/mL		92.86	1.15
Sheepskin lining leather treated with geranium essential oil	T_0= 2.8X10^4 CFU/ML T_{24}= 4.4X10^1 CFU/ML		99.14	2.07

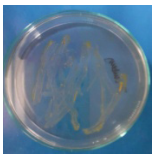
Sheepskin lining leather treated with pine tree essential oil	T_0= 2.8X10^4 CFU/ML T_{24}= 2.4X10^{1}CFU/ML		98.43	1.80
Sheepskin lining leather treated with rosemary essential oil	T_0=2.8x10^{4}CFU/mL T_{24}=5x10^{1}CFU/mL		98.21	1.75
Control sample of cotton cloth	T_0= 2.8x10^{4}CFU/mL T_{24}= 1.6x10^{2}CFU/mL		94.14	1.23
Cotton cloth treated with geranium essential oil	T_0=2.8x10^{4}CFU/mL T_{24}=0 CFU/mL		100	-
Cotton cloth treated with pine tree essential oil	T_0=2.8x10^{4}CFU/mL T_{24}=1x10^{1}CFU/mL		99.96	3.45
Cotton cloth treated with rosemary essential oil	T_0=2.8x10^{4}CFU/mL T_{24}=1.4x10^{2}CFU/mL		94.86	1.29

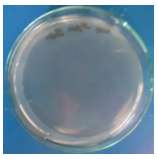
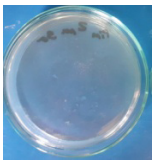
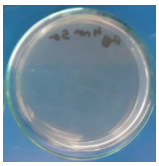
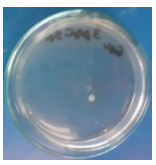
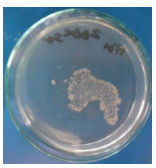
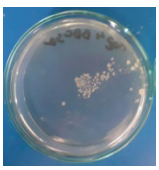
Tests on Staphylococcus aureus

Staphylococcus aureus is the most dangerous of all the many common staphylococcal bacteria. These gram-positive, sphere-shaped bacteria often cause skin infections, but they can cause pneumonia, heart valve infections and bone infections. These bacteria are spread by direct contact with an infected person, by the use of a contaminated object or by inhalation of infected drops dispersed by sneezing or coughing. Skin infections are common, but bacteria can spread through the bloodstream and can infect distant organs [28-34].

The cotton cloth and sheepskin lining leathers treated with geranium essential oil showed very good resistance against *Staphylococcus aureus* (with 100% reduction) followed by rosemary essential oil (with 100% and 96.20% reduction) and pine essential oil (with 100% and 81.29% reduction), as can be seen in Table 3.

Table 3: Antibacterial activity of treated materials against *Staphylococcus aureus*

Sample	Result	Image	R%	Log_{10} red.
Inoculum concentration	T_0= 3.42x10^4 CFU/mL		-	-

Control sample of sheepskin lining leather	T_0= 3.42x10^4 CFU/mL T_{24}=7.4x10^2 CFU/mL		78,36	0,66
Sheepskin lining leather treated with geranium essential oil	T_0= 3.42x10^4 CFU/mL T_{24}= 4.4x10^1 CFU/mL		100	-
Sheepskin lining leather treated with pine tree essential oil	T_0= 3.42x10^4 CFU/mL T_{24}= 2.4x10^{1}CFU/mL		100	-
Sheepskin lining leather treated with rosemary essential oil on leather	T_0= 3.42x10^4 CFU/mL T_{24}= 5x10^1 CFU/mL		100	-
Control sample of cotton cloth	T_0= 3.42x10^4 CFU/mL T_{24}=8.4x10^2 CFU/mL		75.44	0.61
Cotton cloth treated with geranium essential oil	T_0 = 3.42x10^4 CFU/mL T_{24} = 0 CFU/mL		100	-
Cotton cloth treated with pine tree essential oil	T_0 = 3.42x10^4 CFU/mL T_{24} = 6.4x10^2 CFU/mL		81.29	0.73
Cotton cloth treated with rosemary essential oil	T_0= 3.42x10^4 CFU/mL T_{24}= 1.3x10^2 CFU/mL		96.20	1.42

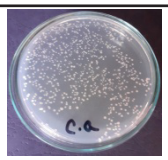
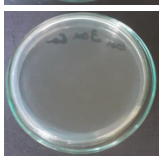
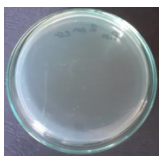
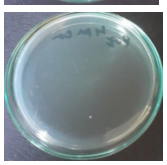
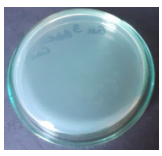
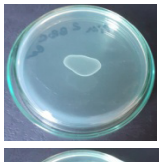
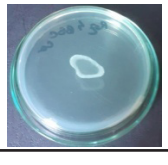
Tests on Candida albicans

Candida albicans is a diploid fungus that grows both as yeast and filamentous cell and a causative agent of opportunistic oral and genital infections in humans [35, 36], and candidal onychomycosis, a nail plate infection. At the same time, it can infect the skin, mucous membranes, nails and gastrointestinal tract. The incidence of candidal infection is increasing due to the increasing number of individuals with suppressed immune function caused by malignancy, antibiotic use, HIV infection, steroid use or chemotherapy [35, 36]. In addition, common health problems, including diabetes and obesity, may also predispose individuals to candidal skin infection [35, 36]. *Candida albicans* is a major cause of nosocomial infections (infections acquired during medical care); contaminated health workers and biomaterials are common sources of these infections [37]. *Candida albicans* is the most common fungus isolated from surgical wounds, so that candidal infection may delay wound

healing [38, 39]. In addition, *Candida albicans* is the most commonly isolated fungal species in patients in intensive care units (ICU); *Candida albicans* infection is associated with the mortality of patients in ICU [40].

Cotton cloths and sheepskin lining leathers treated with geranium essential oil showed a reduction of 100% of colony forming units of *Candida albicans* followed by the treated materials with pine essential oil with reduction of 99.68% and 100% respectively, and then rosemary with reduction of 98.79% and 100% respectively (Table 4).

Table 4: Antifungal activity of treated materials against *Candida albicans*

Sample	Result	Image	R%	Log_{10} red.
Inoculum concentration	T_0= 2.48x10^4 UFC/mL		-	-
Control sample of sheepskin lining leather	T_0= 2.48X10^4 CFU/ML T_{24}= 1.4X10^2 CFU/ML		94.35	1.25
Sheepskin lining leather treated with geranium essential oil	T_0= 2.48X10^4 CFU/ML T_{24}= 0 CFU/ML		100	-
Sheepskin lining leather treated with pine tree essential oil	T_0= 2.48X10^4 CFU/ML T_{24}= 0 CFU/ML		100	-
Sheepskin lining leather treated with rosemary essential oil	T_0= 2.48x10^4 CFU/mL T_{24}= 0 CFU/mL		100	-
Control sample of cotton cloth	T_0= 2.48x10^4 CFU/mL T_{24}= 1x10^2 CFU/mL		95.97	1.39
Cotton cloth treated with geranium essential oil	T_0= 2.48x10^4 CFU/mL T_{24}=0 CFU/mL		100	-
Cotton cloth treated with pine tree essential oil	T_0= 2.48x10^4 CFU/mL T_{24}= 8 CFU/mL		99.68	2.49
Cotton cloth treated with rosemary essential oil	T_0= 2.48x10^4 CFU/mL T_{24}=3x10^1 CFU/mL		98.79	1.92

CONCLUSIONS

Cotton cloth and sheepskin leather linings treated with geranium, pine and rosemary essential oils were obtained. FTIR-ATR analysis showed the characteristic absorption bands for the functional groups of compounds from geranium, pine and rosemary essential oils in the cotton cloth and sheepskin leather linings treated samples. Use of a nanostructured "flower" emulsion based on tensides in treatment fixed the essential oil on cotton cloth and sheepskin leather linings treated. Antifungal and antibacterial activity of essential oils of geranium (*Aetheroleum geranii*) pine (*Aetheroleum pini sylvestris*) and rosemary (*Rosmarinus officinalis*) were tested against *Candida albicans* fungus, Gram-negative bacteria *Escherichia coli* and Gram-positive bacteria *Staphylococcus aureus* on leather and cotton lining materials treated. The appearance and development of fungi and bacteria were inhibited by the high antifungal and antibacterial activity of the compounds of the essential oils used in experiments. The strongest biocidal activity was found for materials treated with geranium essential oil followed by pine and rosemary essential oils. The use of natural compounds with antifungal and antibacterial activity has high efficacy and is friendly to humans and the environment.

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CLEANER LEATHER TANNING PROCESS USING GAMBIR: THE INFLUENCE OF REBATING ON THE PROPERTIES OF LEATHER

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CLEANER LEATHER TANNING PROCESS USING GAMBIR: THE INFLUENCE OF REBATING ON THE PROPERTIES OF LEATHER

ABSTRACT. Gambir (*Uncaria gambir*) is a traditional plant from West Sumatera, Indonesia. Containing condensed tannin, gambir could be used as vegetable tanning agent in the leather making process. Sheepskin is usually used as materials for garment leather. Some industries in Indonesia use pickled sheepskin as raw material for the next process that the previous bating process is uncontrolled. Therefore, this study aims to determine the effect of rebating in the repickle stage on the leather tanned with *Uncaria gambir*. For alum-gambir tanned leather, rebating increased its softness, tear strength, and hydrothermal stability, while for glutaraldehyde-gambir tanned leather, rebating increased its tensile strength, degree of tannage, and tannin bound. The broad DSC peak revealed that the distribution of collagen molecules of all samples was unequal. Rebating could increase and decrease the quality of leather.

KEY WORDS: sheep leather, bating, vegetable tanning, gambir

UN PROCES DE TĂBĂCIRE A PIELII MAI CURAT PRIN UTILIZAREA GAMBIRULUI: INFLUENŢA RESĂMĂLUIRII ASUPRA PROPRIETĂŢILOR PIELII

REZUMAT. Gambirul (*Uncaria gambir*) este o plantă tradiţională din Sumatra de Vest, Indonezia. Datorită conţinutului de tanin condensat, gambirul poate fi utilizat ca agent de tăbăcire vegetală în procesul de fabricare a pielii. Pielea de oaie este folosită de obicei ca materie primă pentru îmbrăcămintea din piele. Unele industrii din Indonezia folosesc piele de oaie piclată ca materie primă pentru următorul proces, aşadar procesul de sămăluire anterior este necontrolat. Prin urmare, acest studiu îşi propune să determine efectul resămăluirii în etapa de repiclare asupra pielii tăbăcite cu *Uncaria gambir*. În cazul pielii tăbăcite cu alaun şi gambir, resămăluirea a condus la creşterea moliciunii, rezistenţei la sfâşiere şi stabilităţii hidrotermice, în timp ce în cazul pielii tăbăcite cu glutaraldehidă şi gambir, resămăluirea a condus la creşterea rezistenţei la rupere, gradului de tăbăcire şi o mai bună legare a taninului. Picul larg evidenţiat prin analiza DSC a arătat că distribuţia moleculelor de colagen a fost inegală în cazul tuturor probelor. Resămăluirea poate duce fie la creşterea, fie la scăderea calităţii pielii.

CUVINTE CHEIE: piele de oaie, sămăluire, tăbăcire vegetală, gambir

UN PROCÉDÉ DE TANNAGE DU CUIR PLUS ÉCOLOGIQUE UTILISANT LE GAMBIR: L'INFLUENCE DU RE-CONFITAGE SUR LES PROPRIÉTÉS DU CUIR

RÉSUMÉ. Le gambir (*Uncaria gambir*) est une plante traditionnelle de Sumatra occidental, en Indonésie. Contenant du tanin condensé, le gambir pourrait être utilisé comme agent de tannage végétal dans le processus de fabrication du cuir. La peau de mouton est généralement utilisée comme matériau pour les vêtements en cuir. Certaines industries indonésiennes utilisent la peau de mouton picklée comme matière première pour le processus suivant, de sorte que le processus de confitage précédent est incontrôlé. Par conséquent, cette étude a pour objectif de déterminer l'effet du re-confitage dans l'étape de repicklage sur le cuir tanné à l'*Uncaria gambir*. Pour le cuir tanné à l'alun-gambir, le re-confitage a augmenté sa douceur, sa résistance à la déchirure et sa stabilité hydrothermale, tandis que pour le cuir tanné au glutaraldéhyde-gambir, le re-confitage a augmenté sa résistance à la traction, son degré de tannage et le tanin lié. Le large pic de DSC a révélé que la distribution des molécules de collagène de tous les échantillons a été inégale. Le re-confitage peut également augmenter et diminuer la qualité du cuir.

MOTS CLÉS : cuir de mouton, confit, tannage végétal, gambir

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INTRODUCTION

Gambir (*Uncaria gambir*) is one of the traditional export plants from West Sumatera, Indonesia [1] that is traditionally used as vegetable tanning agent because it contains condensed tannin [2]. Gambir plant could be extracted by boiling the leaves and branches, then pressing it to take the gum out [1, 3]. Based on the percentage of tannin content, gambir has several kinds, such as coin, superior, brown cube, and galamai (black cube) [4]. Heating gambir could increase the solubility of tannin [5] and change catechin into tannin since the catechin loss the water molecules and the monomers are combined into tannin [4].

Nowadays, people are more concerned about the effect of industry on the environment and health [6] that makes them search the possibility of using plant materials [7, 8]. Some research was conducted to find the application of gambir as leather tanning agent. Kasim *et al*. [9] has tanned goat leather using gambir combined with alum to find the best concentration. His study found that the best result was generated by 3% of alum as pretanning agent and 3% of gambir as tanning agent because it has the highest degree of tannage and tannin bound. Another study of gambir showed that gambir has different characterization that caused different quality of tanned leather [3]. That study collected ten gambir from ten different locations, analyzed the characteristics, and applied as tanning agent for leather. The result concluded that the higher the tannin content of gambir, the higher degree of tannage of the leather, and the higher catechin content of gambir, the lower tannin bound of the leather.

Sheepskin is relatively small with 0.8 mm thickness [10] and commonly used for garment (jacket, coat, skirt, and pants). Among other animal skins, sheepskin was softer and more luxurious. To be made into garment that comes directly into contact with human skin, it needs to be processed using safe materials to replace chrome. Gambir is plant based material that could be used as natural tanning agent.

Leather tanning is a process to 'cook' raw skin into leather that consists of several stages: soaking, unhairing, liming, deliming, bating, pickling, tanning, dyeing, fatliquoring, and drying. After pickling stage, pickled sheep leather could be kept in a certain time. Processing pickled sheep leather means that the tanneries could not control the previous pre-pickling stages (usually called beamhouse stages). Bating stage is a stage in the leather tanning process where non-structural proteins from skins removed by protease that open up the structure of the collagen fiber and ease the fiber waves [11, 12]. Mostly, protease enzyme is produced from microorganism that contains no hazardous materials [13]. By adding more bating agent in the leather making process, more interfibrillary substances could be removed [11] that affect the physical properties [12], the penetration of tanning agent [14], and thermal stability. Therefore, this study determined the effect of rebating in the repickle stage on the leather tanned with gambir.

EXPERIMENTAL

Materials

Raw materials used in this research are processed pickled sheepskins from Sleman, Yogyakarta. Gambir used in this study is black cube gambir sourced from Sumatera Barat, Indonesia. Black cube gambir (pale catechin) is known as gambir extract that already proceeds. Chemicals used for the leather tanning process were of commercial grade from a chemical reseller in Yogyakarta.

Table 1: Samples description

Sample Identification	Description
Gam-Al	Alum – gambir tanning combination without rebating
Gam-Alx	Alum – gambir tanning combination with rebating
Gam-Glu	Glutaraldehyde - gambir tanning combination without rebating
Gam-Glux	Glutaraldehyde - gambir tanning combination with rebating
Gam	Gambir tanning without rebating
Gamx	Gambir tanning with rebating

Once received from the seller in Bantul, Yogyakarta, Indonesia, pickled sheep skin was rebated. The rebating formulation is described in Table 2. The percentage of the product was calculated based on the pelt weight. In this process, the sheepskin was added with 8% of salt and 80% of water and ran for 20 minutes in the rotating drum (Otto Specht serial number 80304). After that, 1% of bating agent for the acid bate was added and ran for 60 minutes.

Table 2: Formulation of rebating process

Process	Product	%	Duration (min)
Rebating	Salt	8	20
	Water	80	
	Feliderm Bate AB, Clariant	1	60

Rebated sheepskins were then subjected to the formulation shown in Table 3. This formulation was modified formula from Musa *et al.* [7] and Sreeram *et al*. [15]. Similar with the Table 2, the percentage of the product in Table 3 was calculated based on the pelt weight.

Table 3: Formulation of the tanning process

Process	Product	%	Duration (min)
Repickle	Salt	10	10
	Water	80	
Pretanning	Sodatan SB, Selic chemical company	2	30
	Sodatan TSN, Selic chemical company	2	30
	Tannit LSW, Dr Bohme	0,5	30
Tanning	Gambir extract	25	4 x (30 Ø 15)
Tanning combination	Alum/glutaraldehyde	6	60
Drained, aged, and shaved			
Wetting back	Water	200	
	Wetting agent	0,5	30
	Oxalic acid	0,3	
Neutralization	Water	150	
	Novaltan PF	2	60
	Sodatan TSN, Selic chemical company	1	
	Sodium Formate (HCOONa)	2	2 x 30
	Baking Soda ($NaHCO_3$) (Optional)	0,5	2 x 15
Retanning	Acrylic Syntan (R40), Abhilash chemicals Pvt., Ltd., India	6	60
	40°C water	70	
Fatliquoring	Water 50°C	40	40
	Tannit LSW, Dr Bohme	2	
	Seroil LL, Quimser S.A	2	
	Garboil BS, Selic chemical company	6	30
	Coriol FBD	4	
	Leathernol BLM, Allied chemicals international company limited	2	
Fixating	Formic acid (HCOOH)	1,5	2 x 30
Antifungal	Antifungal agent	0,05	30
Masking	Catalix GS, Clariant	1	15

Analytical Procedures

Physical Properties

The softness, tear strength, tensile strength, and elongation was determined. Measurement of softness used 20 mm diameter of the sample. Measurement of the physical properties was performed as per standard procedures [16, 17].

Chemical Properties

Chemical properties tests of crust leather were used to investigate the tannin bound and degree of tannage that were calculated using equations 1 and 2.

$$\text{Tannin bound} = 100\% - (\text{water content} + \text{fat content} + \text{water soluble subtances} + \text{insoluble ash} + \text{hide substances})\% \quad (1)$$

$$\text{Degree of tannage} = \frac{\text{tannin bound}}{\text{hide substance}} \times 100\% \quad (2)$$

Hydrothermal Stability

Using DSC-60, the thermal denaturation of each sample was determined. The heating rate was maintained at 10°C/min. Sample weighed around 5 mg.

Organoleptic Properties

All of the samples were assessed for general appearance, grain smoothness, and fullness by hand and visual examination of three experienced tanners. Those tanners gave a score for each parameter on a scale of 0-10 points. Higher points mean better property.

Scanning Electron Microscopy

Scanning Electron Microscopy SEC type SNE 3200 M was used to analyze samples before and after acid bating addition and crust leather samples. Samples were cut into specimens without pre-treatment and were coated with gold. The grain surface and cross section were obtained by SEM operation at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSIONS

Physical Properties

From the Figure 1, it is observed that leather tanned with glutaraldehyde-gambir was the softest leather. Glutaraldehyde followed by gambir leather without rebating has a higher value of softness than that with rebating, while alum-gambir leather without rebating has a lower value of softness than that with rebating.

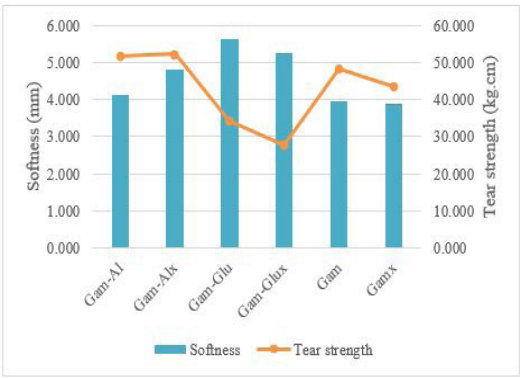


Figure 1. Graphical presentation of softness and tear strength of the leather samples

Crust leather from control leather and experimental leather showed different tear strength and given in Figure 1. Leather samples of alum followed by gambir showed the highest tear strength, while leather samples tanned with glutaraldehyde followed by gambir showed the lowest. From the same figure, it is observed that rebating slightly increased the tear strength of gambir followed by alum tanned leather. On the other hand, rebating decreased the tear strength of gambir-glutaraldehyde and control leather samples. Tear strength could be defined as the toughness of the leather because it is strongly correlated with the ability of leather to 'survive' from the tear [18]. Sizeland *et al.* [18] also found that tear strength is influenced by the strength perpendicular to the axis of fibril collagen which is affected by the strength of the cross-link.

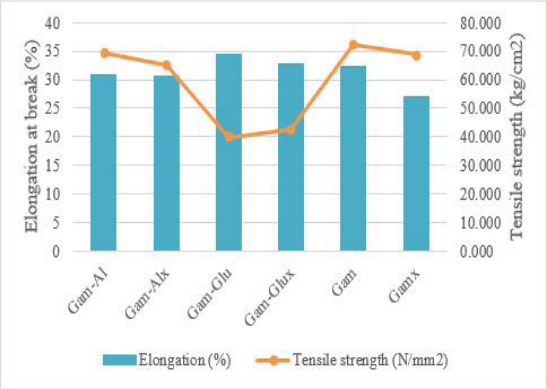


Figure 2. Graphical presentation of tensile strength and elongation of the leather samples

Leather tanned with gambir-glutaraldehyde showed the highest tensile strength, while the elongation was the opposite. Graphical presentation in the Figure 2 also revealed that the tensile strength value of the leather tanned with gambir and glutaraldehyde were the highest. However, this combination showed the lowest elongation. Gambir-glutaraldehyde tanned leather with rebating showed higher tensile strength value than that without rebating, while the other samples were the opposites. Elongation test results revealed that rebating decreased the elongation value of gambir-glutaraldehyde and control leather, whereas in the gambir-alum leather was almost equal.

Adding more bating agent in the leather making process could have two different effects, first, it can increase the quality of the leathers, and the second is the collagen could be overworked caused by the hydrolyzing effect of the bating agent on the collagen [11]. This study [11] also found that after bating stage, the fibres were separated and opening up. When the skin was added with more bating agent, the opening up was bigger and there were some fibrils splitting-up.

Chemical Properties

The chemical analysis result is given in Table 4. The hide/skin substance value is the quantification of the collagen (the skin protein). In the bating stage, non-fibrous protein, including collagen types that do not form collagen fibrils, were also removed [11]. Rebating means removing more interfibrillary protein in the skin.

Table 4: Analysis results of the chemical properties testing

Parameter Uji	Gam-Al	Gam-Alx	Gam-Glu	Gam_Glux	Gam	Gamx
Moisture (%)	11.66	11.02	13.57	11.78	12.92	11.17
Insoluble ash (%)	1.110	2.020	1.39	1.085	1.250	1.430
Fats/oils (%)	18.99	17.23	12.27	11.30	14.79	14.42
Hide substance	52.15	56.31	55.84	56.01	52.55	56.62
Tannin bound (%)	14.29	12.51	14.55	18.65	17.31	14.85
Degree of tannage (%)	27.42	22.22	26.06	33.3	32.95	26.22

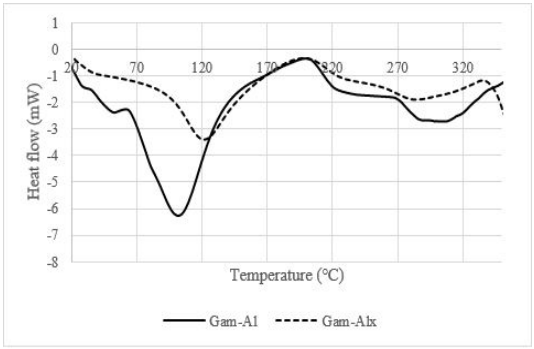
From the same table, it is clearly observed that the tannin bound and the degree of tannage were linear. Leather tanned with gambir followed by glutaraldehyde (rebated) showed the highest tannin bound and degree of tannage, whereas leather tanned with gambir followed by alum (rebated) showed the lowest. Rebating increased the tannin bound and the degree of tannage of gambir-glutaraldehyde leather, while in the gambir-alum and control leather decreased. The percentage of degree of tannage presents the tannin content in the leather that it could determine the stabilization of the chemicals in the collagen and affect the properties of the finished leather [19].

Hydrothermal Stability

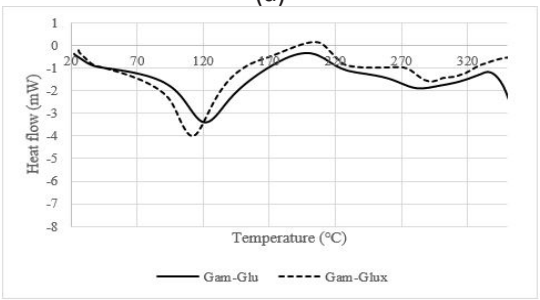
Hydrothermal stability is one of the methods to measure the efficiency of the tanning process based on phase transition and denaturation process of the collagen using differential scanning calorimetry (DSC) [20]. All of the samples in this study have two peaks (Figure 3).

From the Figure 3, all of the samples undergo thermal denaturation and it is clearly showed that rebating has an impact on the collagen stability of leather tanned with gambir-alum (Figure 3(a)), gambir-glutaraldehyde (Figure 3(b)), and gambir (Figure 3(c)). Compared with the literature [21], the thermogram peaks of all

samples in this study were broader and narrower. It is showed that gambir, with or without tanning agent combination, has low tannin diffusion that caused diverse cross-linking [22]. DSC peak showed the unique population of the collagen molecules [22, 21]. The broader the peak the broader the distribution of collagen molecules which have hydrothermal stability. Moreover, the two peaks of all the samples revealed that the collagen molecules distribution across the thickness of the leather has unequal thermal stability [22].



(a)



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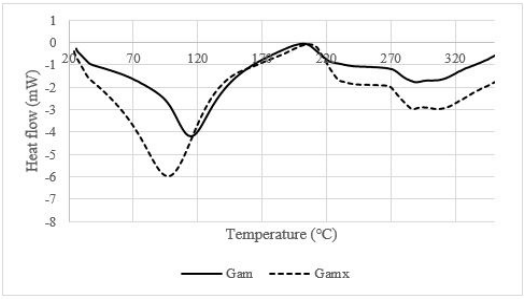

(c)

Figure 3. DSC thermogram of the rebated and unrebated leather samples (a) gambir-Alum; (b) gambir-glutaraldehyde; (c) gambir

Each peak has the temperature of denaturation called T_{max} where the hydrothermal stability of the collagen is presented. On the other hand, the shrinkage temperature (T_s) that usually used as the 'cook proof' in the leather tanning industry is the onset temperature (T_i) in the DSC [22]. From the Table 5, the first onset temperature varied between 65.9 and 99.06°C. Rebated gambir-alum tanned leather was higher than that unrebated leather. However, gambir-glutaraldehyde and control leather showed the opposites. Surprisingly, the unrebated gambir tanned leather revealed the highest onset temperature. For the second onset temperature, the gambir-glutaraldehyde tanned leather showed the highest value.

Table 5: Hydrothermal stability data of the samples using DSC

Sample	T_{onset1} (°C)	T_{onset2} (°C)	T_{max1} (°C)	T_{max2} (°C)
Gam-Al	65.9	269.34	101.94	305.79
Gam-Alx	94.81	259.27	121.62	283.73
Gam-Glu	94.81	259.27	121.62	283.73
Gam-Glux	90.19	273.75	112.01	292.25
Gam	99.06	205.97	114.9	289.2
Gamx	77.17	269.31	96.65	306.72

The higher the denaturation temperature (T_{max}), the more stable the skin collagen. Rebated gambir-alum tanned leather showed higher T_{max1} than the unrebated one, while other samples showed the opposites. Gambir-alum leather with rebating showed the same DSC parameters value with gambir-glutaraldehyde leather without rebating. In the tanning process, aluminum salt performed weaker and longer covalent bond with the collagen, unstable, and easily hydrolyzed [20].

Organoleptic Properties

The combination tanning agent affected the color of the crust leather. From Figure 4, it is clearly seen that the grain surface of gambir-glutaraldehyde leathers were the smoothest ones with less looseness than others. While the gambir leather with rebating was the darkest and unclear surface.

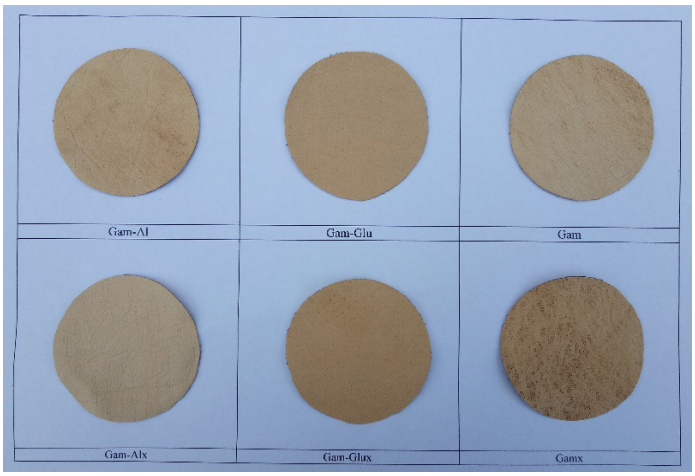

Figure 4. Gambir tanned leather

The organoleptic properties of crust leathers from the experiment are presented in the Figure 5. From the graphical presentation, the gambir-glutaraldehyde leather without rebating was the softest. It was similar to the softness testing results. From the same figure, it is shown that unrebated gambir-glutaraldehyde leather exhibited better fullness than other samples, whereas rebated gambir-glutaraldehyde leather exhibited better grain smoothness and general appearance.

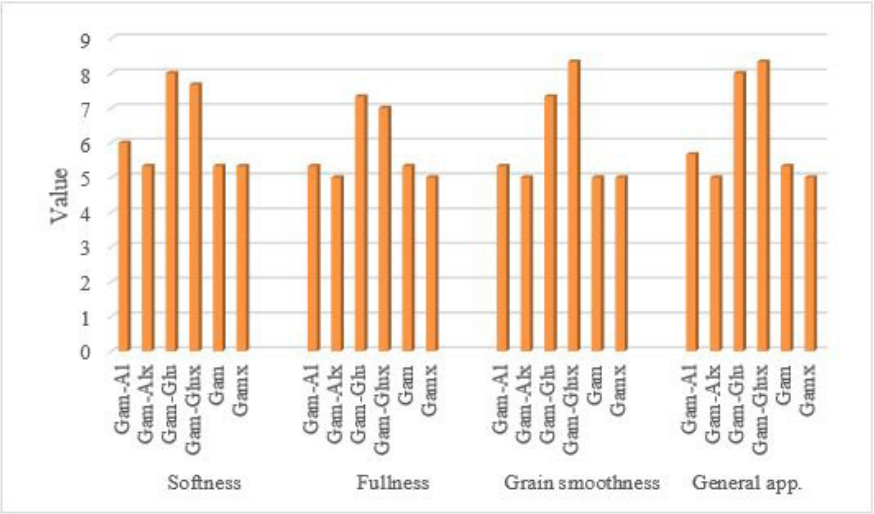

Figure 5. Graphical presentation of organoleptic properties of the leather samples

Scanning Electron Microscopy Analysis

Scanning electron micrograph of the samples is shown in Figure 6(a)-(f) to investigate the grain characteristics. It is seen that the grain surface of crust leather at a magnification of X 80 was clean without tannin deposition. The pores of all the leather samples were clearly visible but the gambir-glutaraldehyde tanned leather. The grain surface of gambir-glutaraldehyde (Figure 6(c) and 6(d)) tanned leather was smoother than others. The pores of Gam-Alx leather (Figure 6(b)) were smaller and neater than Gam-Al. The grain surface of gambir-alum tanned leather (Figure 6(a) and (b)) also looks smoother than gambir tanned leather (control).

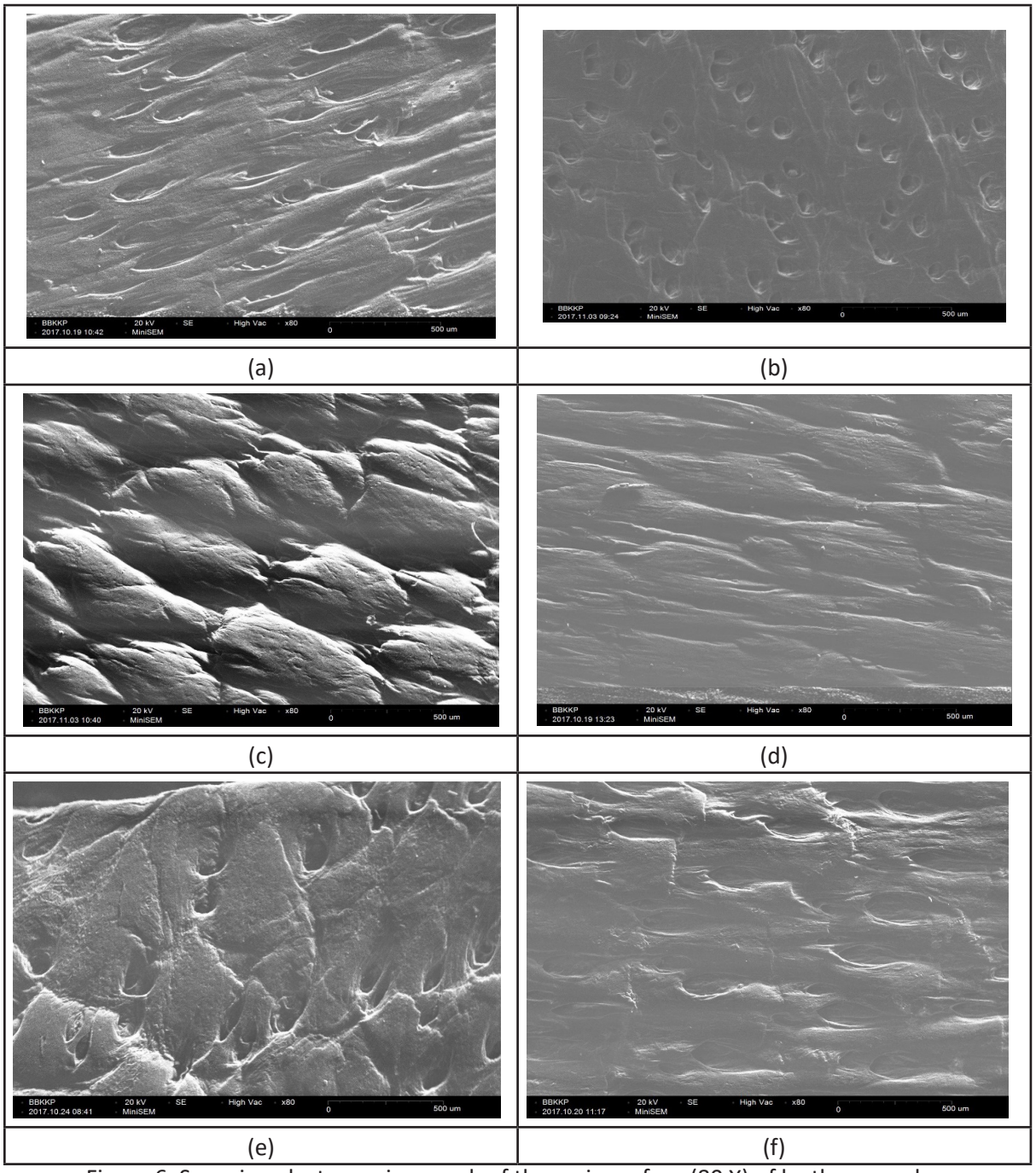

Figure 6. Scanning electron micrograph of the grain surface (80 X) of leather samples: (a) Gam-Al; (b) Gam-Alx; (c) Gam-Glu; (d) Gam-Glux; (e) Gam; (f) Gamx

CONCLUSIONS

Gambir (*Uncaria gambier*) is a traditional plant from West Java, Indonesia which contains tannin to offer environmentally benign leather tanning methodology. This study reported that rebating using acid bate before repickling increased softness, tear strength, and hydrothermal stability of gambir-alum tanned leather. Alum has weaker covalent bond with skin collagen that rebating helped the fiber to split up to strengthen the interaction with skin collagen. Even though gambir-glutaraldehyde tanned leather showed the best organoleptic properties, rebating only increased its tensile strength, degree of tannage, and tannin bound. The broad DSC peak revealed that the distribution of tanning agent molecules of all samples was not

uniform. In this study, rebating could increase and decrease the quality of leather.

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ANTIBACTERIAL NANOCOMPOUND BASED ON SILICONE RUBBER. PART II – BIOLOGICAL CHARACTERISATION

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ANTIBACTERIAL NANOCOMPOUND BASED ON SILICONE RUBBER. PART II – BIOLOGICAL CHARACTERISATION

ABSTRACT. The aim of this work is to characterize an antibacterial polymeric nanocompound based on silicone elastomer (silicone rubber), reinforced with TiO2 nanoparticles, crosslinked with dicumyl peroxide (PD). The antibacterial polymer nanocompound was obtained by vulcanization on a laboratory roll (vulcanization is a main step, with a major impact on the final properties of the products), in the form of a 3-5 mm sheet, in order to be biologically characterized, as well as physico-mechanically and morpho-structurally characterized, according to the standards in force, in specific environments for the food and pharmaceutical fields. Vulcanized silicone elastomers have uses in the food, medical, pharmaceutical industries, etc., because they do not contain substances that are not toxicologically admitted. The dispersion of TiO2 nanopowders (with antifungal, antibacterial and antimicrobial properties) in the nanocompound mass has a decisive role in influencing its antimicrobial and antibacterial sterilization properties. The polymeric nanocompound based on silicone rubber contributes to improving the quality of the products, but also to environmental protection and, of course, protection of human health.

KEY WORDS: biological characterisation, antibacterial nanocompound, silicone rubber, nanoparticles

NANOCOMPOUND ANTIBACTERIAN PE BAZĂ DE CAUCIUC SILICONIC. PARTEA II – CARACTERIZARE BIOLOGICĂ

REZUMAT. Scopul acestei lucrări este caracterizarea unui nanocompound polimeric antibacterian pe bază de elastomer siliconic (cauciuc siliconic), ranforsat cu nanoparticule de TiO2, reticulat cu peroxid de dicumil (PD). Nanocompoundul polimeric antibacterian a fost obţinut prin vulcanizare pe un valţ de laborator (vulcanizarea este o etapă principală, cu un impact major asupra proprietăţilor finale ale produselor), sub forma unei foi de 3-5 mm, pentru a putea fi supus caracterizării biologice, dar şi caracterizărilor fizico-mecanice şi morfo-structurale, conform standardelor în vigoare în medii specifice domeniilor alimentar şi farmaceutic. Vulcanizatele din elastomer siliconic au utilizări în domeniul alimentar, medical, farmaceutic etc., deoarece nu conţin substanţe care nu sunt admise din punct de vedere toxicologic. Dispersarea nanopulberilor de TiO2 (cu proprietăţi antifungice, antibacteriene şi antimicrobiene) în masa nanocompoundului au un rol determinant în influenţarea proprietăţilor de sterilizare antimicrobiană şi antibacteriană a acestuia. Nanocompoundul polimeric pe bază de cauciuc siliconic contribuie la îmbunătăţirea calităţii produselor, dar şi la protecţia mediului şi, bineînţeles, a sănătăţii omului.

CUVINTE CHEIE: caracterizare biologică, nanocompound antibacterian, cauciuc siliconic, nanoparticule

NANOCOMPOSITE ANTIBACTÉRIEN À BASE DE CAOUTCHOUC DE SILICONE. PARTIE II – CARACTÉRISATION BIOLOGIQUE

RÉSUMÉ. Le but de cet article est de caractériser un nanocomposite polymère antibactérien à base d'élastomère de silicone (caoutchouc de silicone), renforcé de nanoparticules de TiO2, réticulé au peroxyde de dicumyle (PD). Le nanocomposite polymère antibactérien a été obtenu par vulcanisation sur un rouleau de laboratoire (la vulcanisation est une étape principale ayant un impact majeur sur les propriétés finales des produits), sous la forme d'une feuille de 3 à 5 mm, afin d'être caractérisé du point de vue biologique, mais aussi physico-mécanique et morpho-structurel, selon les normes en vigueur dans des environnements spécifiques pour les domaines alimentaire et pharmaceutique. Les élastomères de silicone vulcanisés ont des utilisations dans les domaines alimentaire, médical, pharmaceutique, etc., car ils ne contiennent pas de substances qui ne sont pas toxicologiquement admises. La dispersion de nanopoudres de TiO2 (aux propriétés antifongiques, antibactériennes et antimicrobiennes) dans la masse de nanocomposites joue un rôle déterminant dans l'influence de ses propriétés de stérilisation antimicrobiennes et antibactériennes. Le nanocomposite polymère à base de caoutchouc silicone contribue à l'amélioration de la qualité des produits, mais également à la protection de l'environnement et, bien sûr, de la santé humaine.

MOTS-CLÉS : caractérisation biologique, nanocomposite antibactérien, caoutchouc de silicone, nanoparticules

INTRODUCTION

Silicone elastomers are polymers with special characteristics due to their high resistance to temperatures from -100°C to above +300°C [1, 2]. These are high temperatures specific to sterilization, used to make products for the food, pharmaceutical and medical industries. Items made of silicone elastomers (silicone rubber) are preferred in medicine and pharmaceutical products because they do not contain substances such as antioxidants and other restricted ingredients [3-6].

Staphylococcus (*S.*) *aureus* (as a model for Gram-positive bacteria), *Escherichia* (*E.*) *coli* (prototype for Gram-negative bacteria) and *Candida albicans* (as a representative of fungi) are among the most commonly isolated in clinics, with an increased incidence in nosocomial infections. In addition, antibiotic resistance in these strains, namely MRSA strains (methicillin-resistant *Staphylococcus aureus*) and *E. coli* ESBL strains (extended spectrum beta lactamase), pose major problems in the therapeutic approach [7, 8]. One solution in this regard may be the development of new materials coated with various nanoparticles in order to inhibit bacterial adhesion to the substrate, thus eliminating their chance of triggering an infectious process. Antibacterial activity of nanoparticles has been intensely studied recently. *Escherichia coli* is the most prevalent facultative anaerobic species from the gastrointestinal tract of human and animals, so a commensal species, but is also one of the most involved bacteria in medical conditions, causing a number of significant illnesses. Antibiotic resistance in *Escherichia coli* is a great concern because it is one the most common Gram-negative pathogen, and the number of resistant strains is increasing, most of them being *Escherichia coli* ESBL (extended spectrum beta lactamase) strains [9-11]. *Pseudomonas aeruginosa* is also an important pathogen especially in immunocompromised patients, with an intrinsic resistance to many antibiotic classes, and a high capacity to develop biofilms (microbial cells associated between them and from a substrate enclosed in an extracellular polymeric matrix secreted by them), in which microorganisms are safe from antibiotic treatment becoming more resistant and capable to determine persistent infections [11-15].

In the medical field, all indwelling prosthetic devices such as catheters, heart valves, ocular lenses, but also all the surfaces from medical units are predisposed to be colonized by biofilms. Staphylococcus aureus is another most frequent species that causes nosocomial infections and biofilm associated infections on indwelling medical devices.

Although fungal biofilms have not received so much attention comparing with bacterial ones, some conditions such as immunosuppression, the prolonged use of indwelling devices, high periods of hospitalization increased the prevalence of fungal disease, most commonly associated with infections being *Candida albicans*, responsible for both superficial and systemic disease [9-11].

This paper presents the development of polymer nanocompounds based on Elastosil R701/70-OH (silicone rubber) [16-18] reinforced with TiO_2 – nanometric particles (with antifungal, antibacterial and antimicrobial properties), filled with $CaCO_3$ (chalk), with stearin as plasticizer and crosslinked with PD – dicumyl peroxide reinforced, which were biologically characterized in specific environments for the pharmaceutical and food industries according to standards in force.

EXPERIMENTAL

Materials

The following materials were used to make the antibacterial polymer nanocompound:

(1) Elastosil R701/70-OH – silicon rubber: polydimethylsiloxane with vinyl groups, dynamic viscosity over 9.000.000 mPa*s, in the form of paste, density – 1.32 g/cm^2, colour – opaque;

(2) stearin, white flakes, moisture - 0.5% max, ash – 0.025 % max;

(3) ZnO – zinc oxide microparticles: precipitate 93-95%, in the form of white powder, density – 5.5 g/cm, specific surface – 45-55 m^2/g;

(4) TiO_2 - titanium dioxide nanoparticles: white nanopowder, assay ≥ 99.5 % trace metals basis;

(5) chalk: $CaCO_3$ precipitate – white powder, molecular weight 100.09;

(6) PD – di(tert-butylperoxyisopropyl) benzene: powder 40% with calcium carbonate and silica - Perkadox 14-40B (1.65 g/cm^3 density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%).

For the antibacterial tests the following were used:

(1) *Staphylococcus aureus* ATCC 25923;

(2) *Escherichia coli* ATCC 25992;

(3) *Candida albicans* ATCC 1023, and were preserved on glycerol medium, seeded on nutrient gelatin agar medium and Sabouraud with chloramphenicol (for *Candida*), respectively, to obtain 24h cultures.

Methods

Composites Processing

The antibacterial polymer nanocompound based on elastomer (silicone rubber – Elastosil R701/70-OH), reinforced with TiO_2 – nanometric particles, filled with $CaCO_3$ (chalk) and crosslinked with PD – dicumyl peroxide was developed by electric laboratory roll mill mixing and the rolls were water-cooled. The Elastosil R701/70-OH (silicone rubber) was plasticized between the rolls for approximately 3 minutes, the stearin (plasticizer) was added and mixing continued for 1.5 minutes; the microparticle of zinc oxide was then added and embedded into the mixture until homogenisation; TiO_2 nanoparticles were added, continuing to mix for 3 minutes until the nanometric component was embedded; the $CaCO_3$ filler was then added and mixing continued for 2.5 minutes and the dicumyl peroxide (last ingredient) is embedded into the mixture for 2 minutes. After adding all the ingredients, the mixture is homogenized on the roll mill for maximum 3 minutes and taken off in the form of a 3-4 mm thick sheet. The order of adding ingredients was strictly observed, according to Table 1. The nanocompound resulting after 24 h stabilization at room temperature was biologically, physico-mechanically, chemically and morpho-structurally characterized according to standards in force.

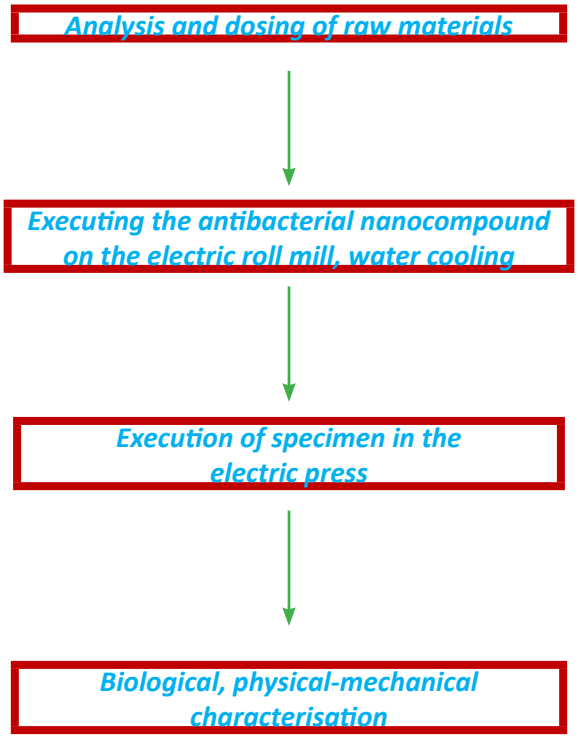

Figure 1. Technological process for obtaining the antibacterial elastomeric nanocompound reinforced with TiO_2 nanoparticles [19]

Table 1: Formulations of antibacterial polymer nanocompounds based on silicone rubber reinforced with TiO_2 [19]

Component	MU	CS_1 (control)	P_5	P_6	P_7
Silicone rubber	g	150	150	150	150
Stearin	g	7.5	7.5	7.5	7.5
Zinc oxide (microparticles)	g	6	4.5	3	1.5
Titanium dioxide (nanoparticles)	g	-	1.5	3	4.5
Chalk ($CaCO_3$)	g	15	15	15	15
PD (dicumyl peroxide – 40% - on silica and $CaCO_3$ substrate)	g	11.25	11.25	11.25	11.25

Biologic Setup

Staphylococcus aureus ATCC 25923, *Escherichia coli* ATCC 25992 and *Candida albicans* ATCC 10231 strains from the American Type Culture Collection (ATCC, US), stored on glycerol medium, were seeded on nutrient gelatin agar medium and Sabouraud with chloramphenicol (for *Candida*), respectively to obtain 24h cultures that were further used in the experiment.

The sterilized samples were placed in six-well plates (Nunc) with 2 ml broth (Sabouraud, respectively) and 200 µl microbial suspension with 0.5 McFarland density (1.5 x 108 CFU/mL) for bacteria and 1 McFarland density for fungi (3 x 108 CFU/ml). After 24 h incubation at 37°C the colonized materials were washed with sterile distilled water to remove non-adherent microorganisms and introduced into Eppendorf tubes with 1 ml sterile saline (AFS), sonicated for 15 s at maximum power and then vortexed for 15 s at 3000 rotations/min. From the suspension recovered in AFS, decimal dilutions were performed, which were seeded in triplicate (3 replicates of 10 µl each) on nutrient gelatin medium (and Sabouraud with chloramphenicol, respectively) to calculate the number of UFC (colony forming units)/ml.

RESULTS AND DISCUSSIONS

Biological Characterization of Antibacterial Polymer Nanocompounds

In recent years, the antibacterial activity of nanoparticles and many surfaces coated with nanoparticles has been intensively studied, therefore a solution in this regard was the development and use of new materials with different types of nanoparticles to inhibit bacterial adhesion to surfaces, thus eliminating the possibility of triggering an infectious process.

In this study, the antimicrobial activity of some polymeric antimicrobial nanocompound surfaces based on silicone rubber, reinforced with TiO_2 nanoparticles (with antifungal, antibacterial and antimicrobial properties) and cross-linked with dicumyl peroxide (Percadox - PD) is tested. The antibacterial polymer nanocompounds were tested and characterized according to standard ASTM: E 2149-10. The samples were tested for 24 h with the above mentioned strains: *Staphylococcus aureus* ATCC 25923; *Escherichia coli* ATCC 25992; *Candida albicans* ATCC 1023, Figures 2-4.

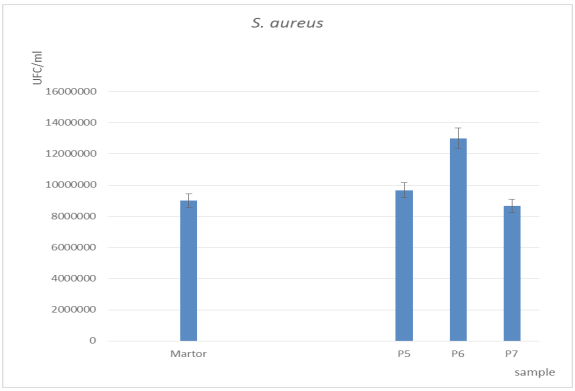

Figure 2. Biological characterization of samples with TiO_2 nanoparticles on *Staphylococcus aureus* ATCC 25923 strains

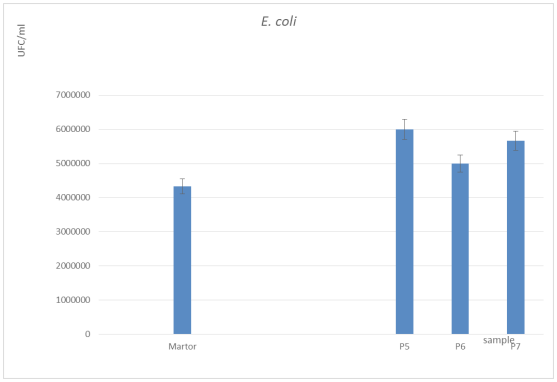

Figure 3. Biological characterization of samples with TiO_2 nanoparticles on *Escherichia coli* ATCC 25992 strains

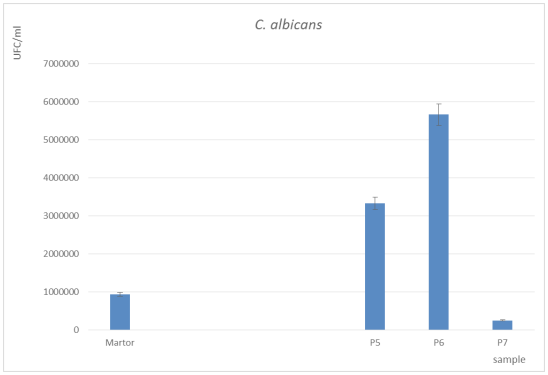

Figure 4. Biological characterization of samples with TiO_2 nanoparticles on *Candida albicans* ATCC 10231 strains

The results showed that the materials treated with nanoparticles show an inhibition adhesion capacity compared to the control sample, except for *E. coli* for which the results were not significantly different. The effect was dependent on bacterial strains and also on the concentration of TiO_2 nanoparticles introduced into the polymeric compound.

P7 samples have been shown to be very effective especially against fungus species - *Candida albicans*, but also against gram positive bacteria - *Staphylococcus aureus*, compared to the control sample.

In the case of *Escherichia coli* strains, P7 and P5, P6 showed no antimicrobial activity (against this strain), it rather seems that a small amount of TiO_2 favours bacterial adhesion, as the UFC values are higher than those of the control sample.

CONCLUSIONS

This paper presents the development of polymer nanocompounds based on Elastosil R701/70-OH (silicone rubber), reinforced with TiO_2 – nanometric particles (with antifungal, antibacterial and antimicrobial properties), filled with $CaCO_3$ (chalk), with stearin as plasticizer and crosslinked with PD – dicumyl peroxide reinforced, which were biologically characterized in specific environments for the pharmaceutical and food industries according to standards in force.

The antibacterial polymer nanocompounds were tested and characterized according to standard ASTM: E 2149-10. Samples were tested for 24 h, using the following strains: *Staphylococcus aureus* ATCC 25923; *Escherichia coli* ATCC 25992; *Candida albicans* ATCC 1023.

Due to the high temperature resistance properties, above +300°C, specific for the sterilization operation and the use of TiO2 nanoparticles, with antimicrobial, antibacterial and antifungal role, polymeric nanocomposites can be used in the food and pharmaceutical industry.

As a result of biological characterization, the P7 sample was selected as having potential applications in the food and pharmaceutical industry.

Acknowledgements

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FABRICATION OF COLLAGEN HYDROLYSATE NANOFIBERS BY THE ELECTROSPINNING METHOD

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FABRICATION OF COLLAGEN HYDROLYSATE NANOFIBERS BY THE ELECTROSPINNING METHOD

ABSTRACT. Nanotechnology is a ground-breaking technology which has found applications on many areas of daily life. Fibers with nanometer diameters are the most suitable candidates for a large number of applications since they have high surface area to volume ratio and different surface characteristics. Among the various nanofiber production techniques, the most advanced and efficient is the electrospinning technique. In our study, nanofibers were obtained from collagen hydrolysate by the electrospinning method. For this purpose, collagen hydrolysate was dissolved at different concentrations in 2,2,2-trifluorethanol and stirred for six hours at room temperature. The turbidity, viscosity, conductivity and pH of the solutions were determined. According to the results obtained, it was observed that viscosity and conductivity values rose as the amount of collagen hydrolysate increased. Nanofibers of collagen hydrolysate with 103 nm and 384 nm obtained by the electrospinning method were examined by SEM, and their morphological characteristics were discussed.

KEY WORDS: electrospinning, collagen hydrolysate, nanofiber, leather

FABRICAREA NANOFIBRELOR DIN HIDROLIZAT DE COLAGEN PRIN METODA ELECTROSPINNING

REZUMAT. Nanotehnologia este o tehnologie de ultimă oră, care a găsit aplicaţii în multe domenii ale vieţii de zi cu zi. Fibrele cu diametru de ordin nanometric sunt cele mai potrivite candidate pentru un număr mare de aplicaţii, deoarece au raport suprafaţă/volum ridicat şi caracteristici diferite ale suprafeţei. Printre diferitele tehnici de producţie a nanofibrelor, cea mai avansată şi eficientă este tehnica electrospinning. În studiul nostru, s-au obţinut nanofibre din hidrolizat de colagen prin metoda electrospinning. În acest scop, hidrolizatul de colagen a fost dizolvat la diferite concentraţii în 2,2,2-trifluoretanol şi agitat timp de şase ore la temperatura camerei. S-au determinat turbiditatea, vâscozitatea, conductivitatea şi pH-ul soluţiilor. Conform rezultatelor obţinute, s-a observat că valorile vâscozităţii şi conductivităţii au crescut odată cu creşterea cantităţii de hidrolizat de colagen. Nanofibrele din hidrolizat de colagen cu 103 nm şi 384 nm obţinute prin metoda electrospinning au fost examinate prin SEM şi s-au discutat caracteristicile morfologice ale acestora.

CUVINTE CHEIE: electrospinning, hidrolizat de colagen, nanofibră, piele

LA FABRICATION DE NANOFIBRES D'HYDROLYSAT DE COLLAGÈNE PAR LE PROCÉDÉ D'ÉLECTROFILAGE

RÉSUMÉ. La nanotechnologie est une technologie révolutionnaire qui a trouvé des applications dans de nombreux domaines de la vie quotidienne. Les fibres de diamètre nanométrique sont les candidats les plus appropriés pour un grand nombre d'applications car elles ont un rapport surface/volume élevé et des caractéristiques de surface différentes. Parmi les différentes techniques de production de nanofibres, la plus avancée et la plus efficace est la technique d'électrofilage. Dans notre étude, les nanofibres ont été obtenues à partir d'hydrolysat de collagène par la méthode d'électrofilage. Dans ce but, l'hydrolysat de collagène a été dissous à différentes concentrations dans le 2,2,2-trifluoréthanol et agité pendant six heures à température ambiante. La turbidité, la viscosité, la conductivité et le pH des solutions ont été déterminés. Selon les résultats obtenus, on a observé que les valeurs de viscosité et de conductivité augmentaient à mesure que la quantité d'hydrolysat de collagène augmentait. Les nanofibres d'hydrolysat de collagène à 103 nm et 384 nm obtenues par la méthode d'électrofilage ont été examinées par SEM, et leurs caractéristiques morphologiques ont été discutées.

MOTS CLÉS : électrofilage, hydrolysat de collagène, nanofibre, cuir

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INTRODUCTION

Nanotechnology is a ground-breaking technology which has found applications in many areas of daily life. The basic reason for the rapidly growing interest in nanotechnology is that studies of nanotechnology have shown materials to have different characteristics at very small dimensions, thus completing deficiencies in basic knowledge. Fibers with nanometer diameters are the most suitable candidates for a large number of applications since they have high surface area to volume ratio and different surface characteristics and have shown much better mechanical performance than materials in other forms in terms of hardness and mechanical strength [1].

Nanofibers fabrication can be performed by bicomponent extrusion, template synthesis, self-assembly, phase separation, melt-blowing, drawing, centrifugal spinning and electrospinning [2]. However, the electrospinning method is easy and cheap, and fibers can be produced from many polymers, making it the most flexible and most preferred method [3]. In the electrospinning method, a polymer solution or a molten polymer is exposed to a high voltage, which gives it an electric charge. A jet of the polymer solution from a fine nozzle is directed towards a target with the opposite charge, placed opposite the nozzle. During this process the solvent evaporates, or if molten polymer is being used it begins to solidify. The jet of polymer is scattered as very fine fibers, and in this way fibers with a diameter on the nano scale can be obtained [4-6].

A large number of studies on the production of nanofibers by the electrospinning method deal with the use of many different polymers for various purposes. These studies have shown that polyurethane [7, 8], PVA/sodium alginate [9] and PEO/sodium alginate [10], chitin [11], cellulose [12], PVA [13], polyacrylic acid [14], PMMA [15], polystyrene [16], nylon-6 [17] and all other polymers which can be used in nanofiber production techniques are suitable for electrospinning.

The main source of natural polymer collagen is the skins of various animals. Among the fibrous proteins in the skin structure, the amount of collagen is 98% [18]. Collagen hydrolysate (CH) is produced by the controlled hydrolysis of collagen and consists of a mixture of polypeptides that are dispersed by molecular weight [19]. CH shows technological advantages such as good resolution, heat stability and high resistance to precipitation with metal ions or pH [20]. It is used in different fields such as food, medicine, pharmaceuticals, cosmetics and biomaterials due to its bioactivity, biocompatibility and penetration as well as its excellent digestibility and high consumer tolerance [19].

Today, as well as intense research into nanofibers, more importance is being accorded to studies on developing new products and materials containing collagen to be used for different purposes, in order to increase the opportunities for making use of collagen-based products. In a scan of the literature, it was found that gelatin, a biopolymer with known advantages for use especially in the biomedical field [21, 22], collagen [23-25], and mixtures of collagen with other polymers had been used in a number of studies of electrospinning [26-29]. Collagen and chitin derivate nanofibers were obtained by electrocapillary, electrocentrifugal, Nanospider™ methods [30]. Also, it was found that in these studies, different cross-linkers or hardening polymers had been used in the production of collagen-based nanofibers. In this study therefore, the topic of the production of collagen hydrolysate nanofibers by the electrospinning method without the use of cross-linkers or hardening polymers was considered, and the morphological characteristics of the collagen hydrolysate nanofibers obtained were discussed.

MATERIALS AND METHODS

Materials

Collagen hydrolysate was provided by Sigma-Aldrich and the TFE (2,2,2-trifluorethanol) used as a solvent was supplied by Fluka (Germany).

Method

Setting up the Apparatus for Electrospinning

The main apparatus used in this study was an electrospinning unit used in the production of nanofibers. The most important parts of this

were the feed unit and spinning collector cylinder, designed by the Küçüker company (Turkey) with the support of the Scientific Research Projects Coordinatorship of Pamukkale University, a high voltage source (Simco, UK), and a syringe perfusion pump (New Era 1100, USA), obtained from the distributor companies.

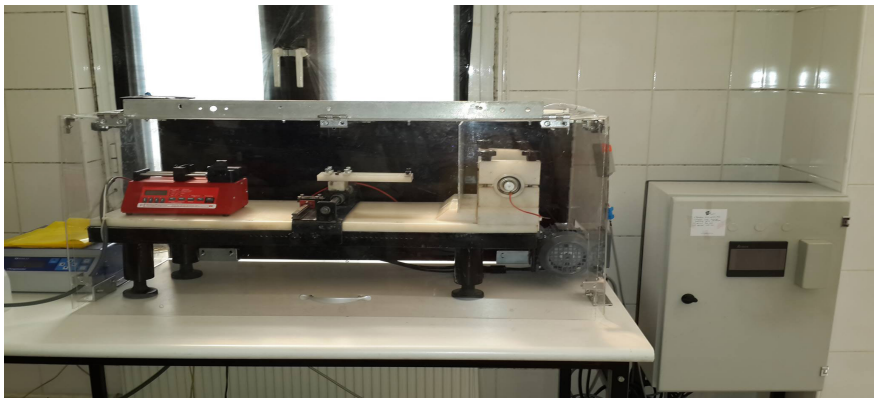

Figure 1. Electrospinning apparatus used in nanofiber production

Preparation of Solution, Optimization and Nanofiber Production

Collagen hydrolysate (CH) at various concentrations (10%, 15%, 20%, 25%, 30% w/v) was dissolved in 2,2,2-trifluoroethanol (10% v/v) and stirred for six hours at room temperature (relative humidity 40%). The resulting solution was loaded into a plastic syringe (Ayset Plastik, Turkey) of volume 10 mL and diameter 0.9 mm with a metal syringe needle tip, and optimization of the parameters for the production of nanofibers by electrospinning was carried out at room temperature.

First of all, the distance between the end of the syringe and the collector plate were examined in the range of 8-12 cm. The parameters in the electrospinning process to obtain nanofibers of the voltage applied and the flow rate of the feed solution were accepted as experimental variables. In order to determine the effect on nanofiber yield of these parameters, different voltages and different flow rates were applied for concentrations of collagen hydrolysate (Table 1). Optimization studies showed that optimum values were a concentration of 20%, 25% and 30% w/v of CH, a stirring time of 6 hours, a voltage value of 20kV and a flow rate of 0.8 mL/hour. The distance between the metal tip of the syringe and the collector plate was determined as 12 cm. The duration of all experiments was set at 120 and 180 minutes (for obtaining thicker nanofiber mats).

Table 1: Electrospinning parameters

Electrospinning parameters	
Different voltages, kV	13, 15, 17, 20
Flow rates, mL/h	0.8, 1.0, 1.5, 2.0
Distance, cm	8, 10, 12
Duration, min	120, 180
Solution parameters	
Concentration, % (w/v)	10, 15, 20, 25, 30

Characterization of Solution

The pH measurements of the working solutions were performed using a digital pH meter (WTW, Germany). The viscosity of the working solutions was determined by using a rheometer (Fungilab, Spain). The turbidity of the working solutions was measured with a turbidimeter (Velp TB1, Italy). The conductivity of the solution was determined by testing its ability to carry an electric current, and conductivity affects the rate of movement of a polymer solution during electrospinning. The electrical conductivities of the solutions to be fed to the electrospinning device were determined with an electrical conductivity meter (WTW MULTI 9310, Germany). Measurement of the viscosity, turbidity and conductivity of the feed solutions were conducted at room temperature (25˚C) triplicate. The results are given as the mean ± standard deviation of the three measurements.

FTIR Analysis of Nanofibers

A Fourier Transform Infrared (FTIR) spectrophotometer (Perkin Elmer, USA) was used in order to determine the chemical structure of the surfaces of the nanofibrous matrices. Spectra were recorded with a resolution of 4 cm^{-1} and at wavelengths of 400-4000 cm^{-1}, and were analyzed using an FTIR software program.

Scanning Electron Microscope Analysis of Nanofibers

A SEM device (JEOL 840, USA) was used to examine the morphological properties of the nanofibers and to obtain information about their diameters. Small sections of nanofibers on aluminum foil obtained by electrospinning were taken and gold-plated, after which SEM images were obtained. SEM images with 40 kX enlargement were taken for analysis of the dimensions and morphological characteristics of the nanofibers. The mean diameter value was determined by performing 50 different measurements from the SEM images of each sample.

RESULTS AND DISCUSSIONS

Analysis of Solutions

pH Value

The acidic characteristics and the degree of reactivity of a solution as well as other important characteristics can be determined by a correctly measured pH value. In addition, many chemical characteristics and processes such as the solubility of a compound are to a large extent connected to the pH value of the solution. Table 2 shows the pH values of 20%, 25% and 30% solutions of collagen hydrolysate. The results of tests performed with a pH meter showed that solutions of collagen hydrolysate had a weak acidic character with pH values of between 5.4 and 5.6.

At the isoelectric point of protein there is no net charge on it, whereas above the isoelectric point, the protein should carry a net negative charge. It was observed that fibers with protein are obtained if the pH of the electrospinning solution is adjusted to the isoelectric point of the protein [31]. The pH values of the collagen hydrolysate solutions (pH 5.4-5.6) used in this study were in the range of the isoelectric point of collagen peptides (pH 5-6).

Turbidity Results

Turbidity test results were used to ascertain whether the solutions had dissolved before electrospinning, and further tests furnished information on the morphology of the nanofibers. Turbidity was measured between 0 and 1000 NTU. The production of homogeneous, continuous and fine solutions is directly related to a turbidity value of 0 NTU. Table 2 gives the turbidity values of collagen hydrolysate solutions. It was determined from tests conducted using a turbidimeter that the solutions were very transparent in appearance and homogeneous. If solutions contain undissolved solid materials, a clear solution is not produced, and the morphology of the nanofibers obtained will not be regular. This can give unwanted results. Turbidity values of between 19.4 and 22.7 NTU were determined for the solutions in the study.

Viscosity Results

Gelling occurs under the effect of van der Waals forces, with aggregation between particles or molecules in a liquid. The gelling process is studied using rheological measuring techniques. The viscosity characteristics of the solutions in our study were determined in this way. As seen in the Table 2, mean viscosity values of the solutions at room temperature were found to be generally between 15.4 and 21.0 mPa.s. The viscosity values of the collagen hydrolysate solutions were found to increase with increasing CH concentration, which was resulted in a greater number of polymer chain entanglements within the solution [32]. An increase in the viscosity values of the solutions is undesirable because they become lumpy in the nozzle of the electrospinning apparatus, and this causes the formation of non-homogeneous beaded nanofibers. The viscosity values determined in the study are showed the suitability of solutions with low viscosity values for entanglement to be electrospun.

Conductivity Results

Electrical conductivity is a parameter which greatly affects the diameter of the nanofibers. Table 2 gives the conductivity values

of the collagen hydrolysate solutions. These were found to vary between 3.3 and 4.6 mS/cm. In our study, it was observed that conductivity increases with the increase of solution concentration. This situation can be explained by the increase in the total amount of ions in solution. It was thought that an increase in conductivity values by an increase in collagen hydrolysate concentration would make the diameters of the nanofibers obtained low and in this way these values would provide an advantage in the electrospinning process. It has been seen in some studies that solutions with high conductivity produced nanofibers with smaller diameters [33, 34]. However, some other studies support the hypothesis that high conductivity results in fibers with large diameters [35]. The conductivity results obtained in this study contributed to the formation of CH nanofibers without formation of beads.

Table 2: Properties of collagen hydrolysate solutions

Concentration	pH	Turbidity (NTU)	Viscosity (mPa/s)	Electrical conductivity, (mS/cm)
%20	5.4	19.4±6.7	15.4±0.3	3.3±0.4
%25	5.5	20.2±1.7	17.2±0.8	4.4±0.2
%30	5.6	22.7±3.2	21.0±0.2	4.6±0.2

Characterization of Nanofibers

FTIR Results

Figure 2 gives the FTIR spectra of nanofibers obtained from 20%-30% collagen hydrolysate. The graphics obtained are very close to the FTIR spectra of collagen obtained by many other researchers [36-38]. Examining spectra obtained after spectral scans, it was determined that the bands emerging in connection with tension vibration of the (0) C-O, (1) C-O-C, (2) OR-C-C, (3) $COO-CH_3$ (asymmetric), (4) C=C and (5) C=O groups on the structure chain of the collagen hydrolysate nanofiber samples were at wavenumbers of (0) 1035 cm^{-1}, 1082 cm^{-1} (1) 1064 cm^{-1}, (2) 1140 cm^{-1}, 1174 cm^{-1}, (3) 1454 cm^{-1}, (4) 1633 cm^{-1}-1647 cm^{-1}, and (5) 1723 cm^{-1}-1735 cm^{-1} respectively (Figure 2).

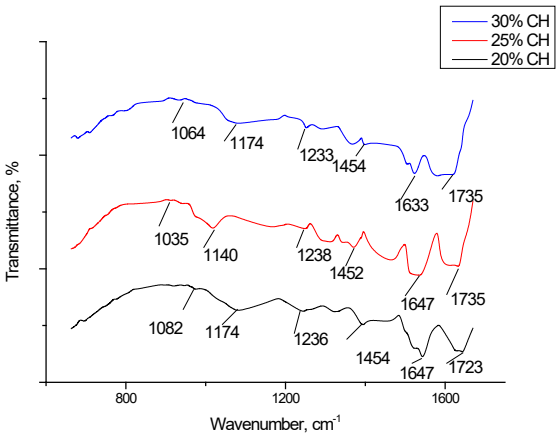

Figure 2. FTIR spectra of collagen hydrolysate nanofibers

In addition, it was determined that in all samples peaks between wavenumbers of 1233 cm^{-1} and 1236-1237 cm^{-1} belonged to the amide I band, and those between 1452 cm^{-1} and 1454 cm^{-1} belonged to the amide II band. It was observed that the carboxyl band which appeared in connection with the C=O absorption band was at wavenumbers of 1723 cm^{-1}-1735 cm^{-1} in all samples. Absorption bands between 1238 cm^{-1} and 1452 cm^{-1} are bands which appear in relation to the existence of a helix structure [37]. Thus FTIR examination showed that the

helix structures in CH nanofibers obtained could be preserved without destruction.

Results from the Scanning Electron Microscope

Figure 3 shows 40 kX magnified SEM images of nanofibers obtained from 20%, 25% and 30% collagen hydrolysate solutions. It was seen that the diameters of the nanofibers obtained as a result of 2 hours spinning of a 20% collagen hydrolysate solution varied between 111 nm and 273 nm, while the nanofibers obtained as a result of 3 hours' spinning of a 20% solution of CH had diameters of 103 nm to 384 nm. The nanofibers obtained from a 25% collagen hydrolysate solution after 2 hours of electrospinning had diameters of 116 nm-133 nm, and after 3 hours of electrospinning 157 nm-235 nm. With a 30% CH solution, the diameters of the nanofibers obtained were 140 nm-313 nm with 2 hours of electrospinning and 176 nm-260 nm with 3 hours. It was determined from SEM images that the smallest diameter of nanofibers obtained from CH solutions of 20%-30% was 103 nm, and the largest was 384 nm.

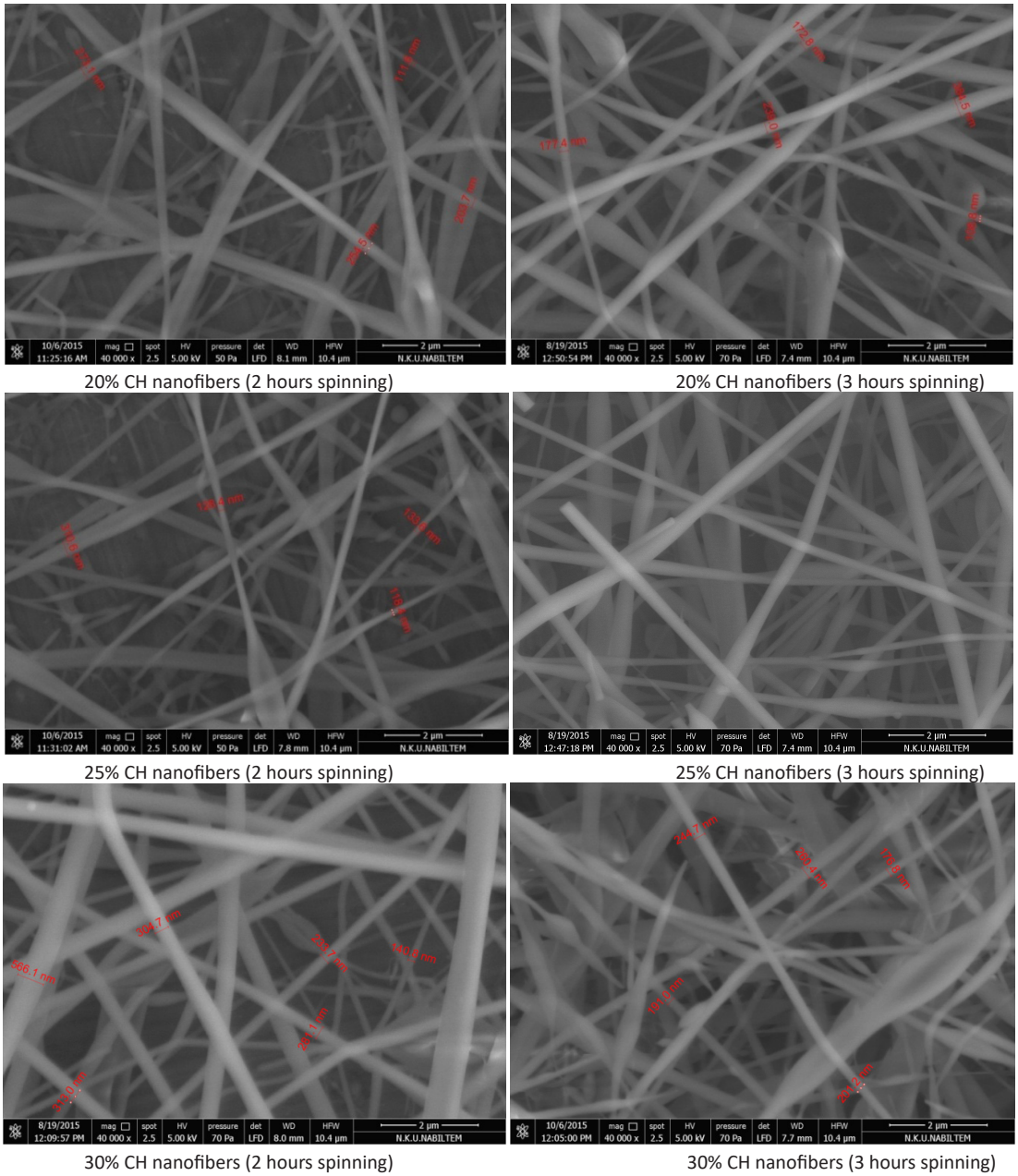

Figure 3. SEM images of nanofibers obtained from 20%, 25% and 30% solutions of CH

In previous studies conducted on collagen, nanofibers in the range of 100-700 nm in diameter were obtained [23, 24, 39, 40], but when collagen hydrolysate mixed with chitin derivate and polyvinyl alcohol was used, nanofibers of between 200 nm and 600 nm were obtained [30]. In the present study, collagen hydrolysate nanofibers with small diameters of 103 nm-384 nm were obtained using no other material than a solvent. It is thought that more homogeneous nanofibers could be obtained in future studies by adding salt and large-molecule polymers or a plasticizer.

CONCLUSIONS

In conclusion, collagen hydrolysate nanofibers were successfully produced by the electrospinning method. First, it was determined that the 10%, 15% CH solutions beaded, 20%, 25% and 30% CH solutions used had pH values of 5.4-5.6, viscosities of 15.4-21.0 mPa.s, turbidities of 19.4-22.7 ntu, and conductivities of 3.3-4.6 mS/cm according to concentration. This clearly showed that nanofibers can be obtained from collagen hydrolysate at concentrations of between 20% and 30%. Studies are being carried out in many different scientific fields today in connection with the potential advantages of using collagen hydrolysate to develop new products and materials containing collagen which can be put to various different uses. In the light of the results of the present study, nanofibers obtained by the use of collagen hydrolysate can be accepted as a new collagenic material, and after improvement and development in future studies, will form a new material of industrial and economic importance. This also provides an alternative opportunity to make use of collagen hydrolysate, a solid waste of the leather industry, which will also provide ecological benefits.

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TESTING THE NEW PRODUCTS FOR FINISHING FOOTWEAR MADE OF NATURAL LEATHER

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TESTING THE NEW PRODUCTS FOR FINISHING FOOTWEAR MADE OF NATURAL LEATHER

ABSTRACT. In order to create a footwear model, it is necessary to take into account the chosen materials, the manufacturing system and, last but not least, fashion trends, because fashion can be a determining factor for the industry. Finishing improves the appearance of the shoe and preserves it. Various wax mixtures combined with natural and synthetic oils are used to finish footwear, such as water-resistant mixtures and leather polishing products, with the purpose of improving the appearance of footwear uppers made of natural leather finished by polishing. The obtained ecologic wax emulsion may be used in surface finishing of natural bovine leather and footwear, in the final dressing composition. This paper presents the technological process of footwear manufacturing and the finishing composition for footwear made of natural leather based on complex metal dyes, ethyl alcohol, nitrocellulose aqueous emulsion, wax emulsion (made from triethanolamine monostearate and paraffin oil), used to obtain glossy finish.

KEY WORDS: natural leather, finishing footwear

TESTAREA NOILOR PRODUSE PENTRU FINISAREA ÎNCĂLŢĂMINTEI FĂCUTE DIN PIELE NATURALĂ

REZUMAT. Pentru a crea un model de încălţăminte, este necesar să se ţină cont de materialele alese, de sistemul de fabricaţie şi, nu în ultimul rând, de tendinţele modei, deoarece moda poate fi un factor determinant pentru industrie. Finisajul îmbunătăţeşte aspectul încălţămintei şi îl păstrează. Pentru finisarea articolelor de încălţăminte, se utilizează diverse amestecuri de ceruri combinate cu uleiuri naturale şi sintetice, cum ar fi cele rezistente la apă şi pentru lustruit produse din piele, cu scopul îmbunătăţirii aspectului feţelor de încălţăminte din piele naturală finisate prin lustruire. Emulsia de ceară ecologică obţinută poate fi folosită la finisarea suprafeţei pielii naturale de bovine şi încălţămintei realizate din această piele, în compoziţia apretului final. Această lucrare prezintă procesul tehnologic de fabricare a încălţămintei şi compoziţia de finisare pentru încălţăminte din piele naturală pe bază de coloranţi metalici complecşi, alcool etilic, emulsie apoasă pe bază de nitroceluloză, emulsie de ceară (fabricată din monostearat de trietanolamină şi ulei de parafină), folosită pentru obţinerea unui finisaj lucios.

CUVINTE CHEIE: piele naturală, finisarea încălţămintei

ESSAI DES NOUVEAUX PRODUITS POUR LA FINITION DE CHAUSSURES EN CUIR NATUREL

RÉSUMÉ. Pour créer un modèle de chaussures, il est nécessaire de tenir compte des matériaux choisis, du système de fabrication et, enfin, des tendances de la mode, car la mode peut être un facteur déterminant pour le secteur. La finition améliore l'aspect de la chaussure et la préserve. Différents mélanges de cires combinés avec des huiles naturelles et synthétiques sont utilisés pour la finition des chaussures, tels que des mélanges résistants à l'eau et des produits pour le polissage du cuir, dans le but d'améliorer l'apparence des tiges de chaussures en cuir naturel finies par polissage. L'émulsion de cire écologique obtenue peut être utilisée pour la finition de la surface du cuir bovin et des chaussures réalisées en utilisant ce cuir, dans la composition de la couche finale. Cet article présente le processus technologique de fabrication de la chaussure et la composition de finition pour la chaussure en cuir naturel à base de colorants métalliques complexes, alcool éthylique, émulsion aqueuse de nitrocellulose, émulsion de cire (à base de monostéarate de triéthanolamine et d'huile de paraffine), utilisé pour obtenir un fini brillant.

MOTS CLÉS : cuir naturel, finition de la chaussure

INTRODUCTION

In order to create a footwear model, it is necessary to take into account the chosen materials, the manufacturing system and, last but not least, fashion trends, because fashion can be a determining factor for the industry. Obtaining a high quality product is also conditioned by the designing and manufacturing preparation activity, in terms of providing technical and technological parameters and high economic efficiency. The manufacturing process comprises a series of distinct operations, executed in a given order, determined according to:

- the characteristics of the product to be executed;
- the characteristics of raw materials;
- the characteristics of the equipment used.

The technological manufacturing process must ensure:

- high productivity indices;
- reduced consumption of materials;
- high quality products.

The technological process of footwear manufacturing comprises the following groups of operations [1-3]:

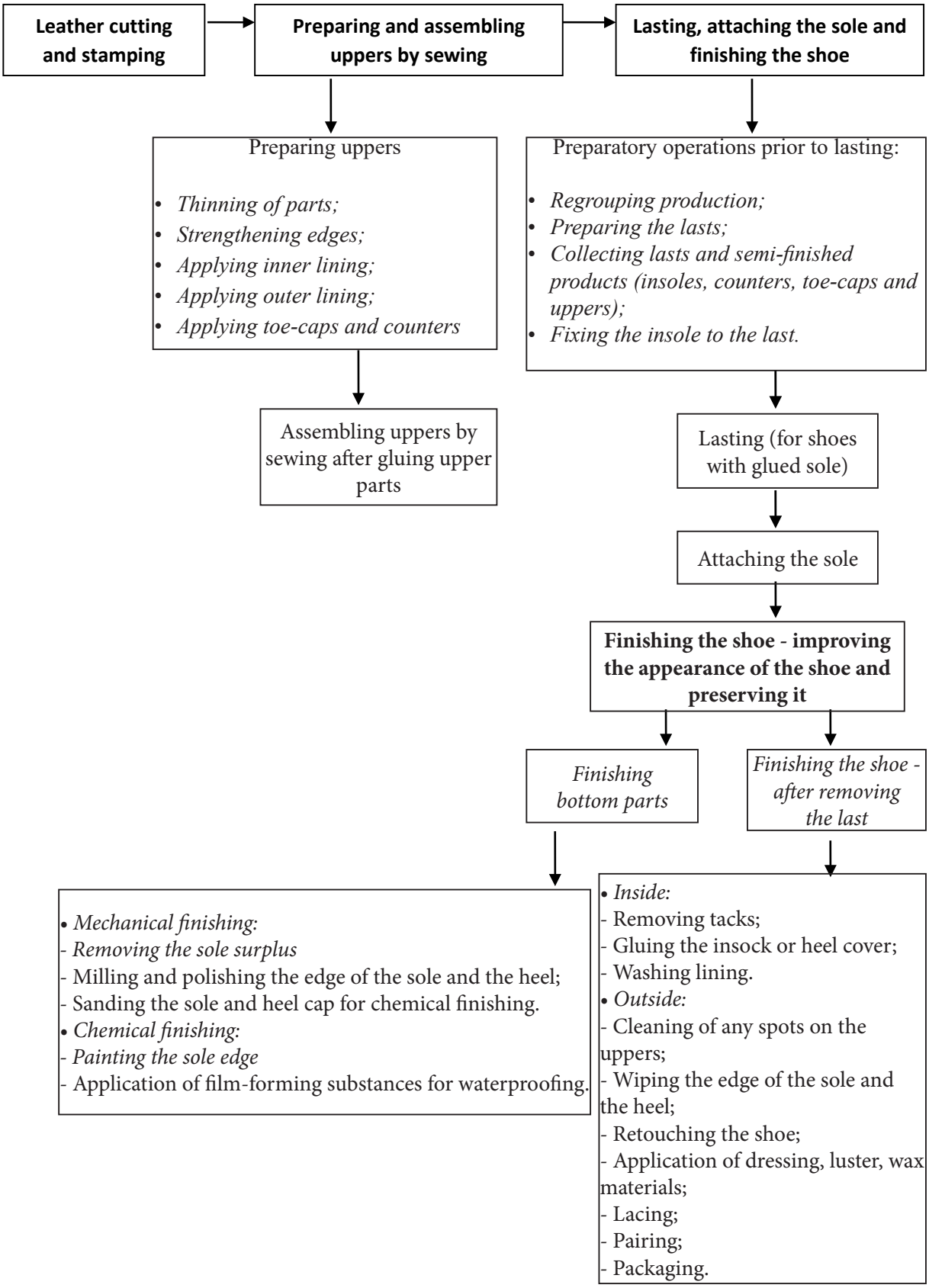


Figure 1. Technological process of footwear manufacturing

Types of Natural Leather Assortments Used in Making Footwear

The main types of leather used in footwear manufacturing are the following:

- Natural grain box leather is made of bovine hides, it has a smooth, evenly finished grain, fullness, medium softness, at least 10% section dyeing, coating dye colour close to full dyeing colour, well polished velour side. It is a mineral tanned assortment and is most often used. The finest box leathers come from calfskins;
- Natural grain nappa, made from bovine hides (mineral tanned), has a smooth, uniformly finished, full grain, accentuated softness, at least 10% section dyeing, coating dye colour close to full dyeing colour, well polished velour side;
- Bison leather is a mineral tanned leather, with a pressed grain (to form a characteristic design on the leather surface to cover some imperfections), uniformly finished, full and thicker than box leathers. It is used for making men's footwear;
- Buffo is a mineral tanned bovine leather with polished grain, fullness and 100% section dyeing. It is used for making men's footwear;
- Suede is a velvet-like assortment of leather obtained by polishing mineral tanned leather on the flesh side (velour). The smoothness, uniformity and size of the nap define the quality of the suede. The best varieties of suede are obtained from calfskins [4-7].

The Finishing of Footwear Made of Natural Leather

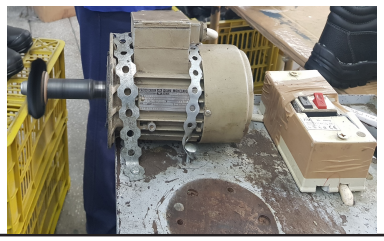
For the finishing of footwear, various mixtures of waxes combined with natural and synthetic oils, such as water-resistant ones and for polishing leather products, are used to improve the appearance of polished leather for footwear uppers. Both natural and synthetic waxes are used to finish the natural leathers, to reduce the stickiness of the thermoplastic binders and to obtain a certain handle or color darkening effect (in the waxed leather varieties, which are fashionable) [8, 9]. Also, for the finishing of footwear, various mixtures of waxes combined with natural and synthetic oils, such as water-resistant ones and for polishing leather products, are used to improve the appearance of polished leather for footwear uppers. As the aqueous finishing dispersions used to finish the natural leathers are fluid, they are suitable for rheological measurements. Finishing systems are applied to the surface of leather by spraying or by means of roll-coating and reverse-coating machines. The correct determination of their composition, as well as the control of rheological behavior, leads to obtaining adherent finishing films uniformly set on the surface of leather, with suitable physical-mechanical resistance, and to the prevention of undesirable effects, especially in the case of aqueous systems with deviations from the ideal or Newtonian flow.

Obtaining a uniform finish of the leather, as well as of footwear made of natural leather, is determined by a number of factors such as: evaporation rate of volatile components, quality of volatile components (solvation power, surface tension), viscosity of aqueous dispersion of pigments, viscosity of the binders, surface tension, the heat of vaporization, the coalescence of droplets in the case of emulsions, the evaporation rate of the emulsions [10, 11]. One of the most important factors is the viscosity of the aqueous finishing systems. In order to obtain a uniform finish, each system must have a specific viscosity profile, and the finishing technician must take into account each component of the viscosity to obtain the desired and correct finish of the natural leather, as well as footwear made of natural leather.

Machines Used for Footwear Finishing

Table 1 presents the main machines used to finish footwear [12].

Table 1: Machines used for footwear finishing

No.	Footwear finishing chamber	No.	Equipment with brushes for footwear finishing
1		2	
3	Equipment with brushes for footwear finishing 	4	Hot air blower for drying footwear after finishing 

EXPERIMENTAL

Materials

- Stearin (S.C. Stera Chemicals S.R.L., Bucharest) – solid substance, with specific grease odour, white colour, melting point 69-70°C;
- Triethanolamine (SC Stera Chemicals S.R.L., Bucharest) – colourless liquid, melting point – 20-21°C, boiling point – 277-279°C, density – 1.124 g/cm3, refractive index – 1.4852;
- Paraffin oil (MOL, company, Hungary) – colourless, odorless, non-fluorescent and free of aromatic compounds;
- Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (SC Elton Corporation SA., Bucharest), density – 0.95 g/cm3 at 40°C, pH (10% solution) – 7-8;
- Wax emulsion (marked TP) used as handle modifier: dry substance – 14-16%, pH (10% solution) – 6.0-7.0 (INCDTP–Division Leather and Footwear Research Institute Bucharest, Romania) [13, 14];
- Roda lacquer 93 (Triderma, Germany), nitrocellulose emulsion used as a fixing agent (final dressing) for finishes applied to natural leather: dry substance –15%, pH (10% solution) – 5.5, Ford cup viscosity Φ4 – 125, flash point – 82°C;
- Finishing composition (marked FC-1, black and FC-2, brown) based on nitrocellulose emulsion, wax emulsion (TP), metal complex dyes and ethyl alcohol, for footwear made of natural leather: dry substance – 10-12%, pH (10% solution) – 7.0-8.0 (INCDTP–Division Leather and Footwear Research Institute Bucharest, Romania);
- The footwear made of natural leather (mineral tanned and wet finished by retanning, fatliquoring and dyeing, 1.2-1.4 mm thick, dyed black and brown (INCDTP – Division Leather and Footwear Research Institute Bucharest, Romania).

Methods

- Chemical characteristics of the finishing composition for footwear, and of the wax emulsion were determined according to the following standards: dry substance (%) – SR EN ISO 4684:2006; pH (10% solution) – SR-EN ISO 4098: 2006.

- Optical microscopy images were captured using a Leica stereomicroscope S8AP0 model with optic fiber cold light source, L2, with three levels of intensity [13]. Magnifying was 100X for the wax emulsions and 20X for surface of finished leather and footwear made of natural leather.
- Physical-mechanical characteristics of footwear made of natural leather were determined according to the following standards: elongation at a load of 10 N/mm2 (%) and tensile strength (N/mm2) – SR EN ISO 3376:2012; tear strength (N/mm) – SR EN ISO 3377:2012; resistance to repeated bending, number of flexions – SR EN ISO 5402:2012; strength to dry and wet abrasion (1-5 ranking) – SR EN ISO 11640:2002; water vapour permeability, (mg/cm2) – SR EN ISO 3377-1: 2012.
- Finishing composition for footwear viscosities were determined with Ubbelohde KPG capillary viscometers, Schott, Jenaer Glaswerk Schott & Gen. Mainz, Germany [10, 11].

Obtaining the Wax Emulsion for Finishing the Footwear

The wax emulsion obtained by emulsifying a mixture of triethanolamine monostearate, paraffin oil and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide. The wax emulsion (TP) was added into the nitrocellulose final dressing.

Finishing Composition for Footwear Made of Natural Leather (FC)

It is made of the following components:

- 5-10 g/L metal complex dyes (black, brown);
- 10-20 g/L ethyl alcohol;
- 700 g/L nitrocellulose aqueous emulsion;
- 30-50 g/L wax emulsion (TP);
- and water.

The finishing composition FC can be applied to film-coated leather shoes using a hand spray gun as final operation using an amount of 100% finishing composition on the entire leather surface of the shoe, to get a glossy effect. This operation is repeated two to three times, until the desired effect is achieved, after which the shoes are dried in the hot-air drying machine and polished in the polishing machine.

RESULTS AND DISCUSSIONS

Characterization of Wax Emulsion for Finishing the Footwear

The physico-chemical properties of the wax emulsion TP are: dry substance – 14-16%, pH (10% solution) – 6.0-7.0. The microscopic image obtained for the prepared emulsion is presented in Figure 2.

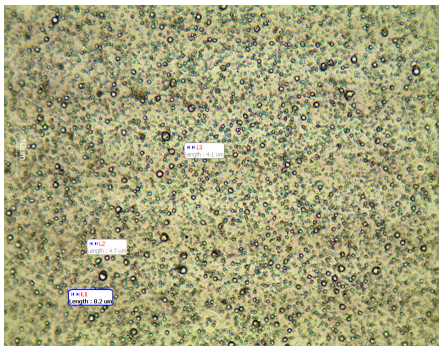


Figure 2. Optical image, 100X, of TP wax emulsion

The wax emulsion obtained by emulsifying a mixture of triethanolamine monostearate, paraffin oil and stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide has homogenous appearance and particle sizes ranging mostly between 4 and 8 µm [15].

Characterization of Finishing Composition for Footwear Made of Natural Leather

Finishing composition (marked FC-1, black, and FC-2, brown) for footwear made of natural leather based on complex metal dyes, ethyl alcohol, nitrocellulose aqueous emulsion, wax emulsion (made from triethanolamine monostearate and paraffin oil), used to obtain glossy finish: dry substance – 10-12%, pH (10% solution) – 7.0-8.0. Viscosities (at 25 ±0.1°C) of footwear finishing compositions (FC-1, FC-2) are

11,0986 cSt and 11,4953 cSt. The constant of viscosimeters used to conduct tests is 0,0522.

Characterization of Footwear Uppers Made of Natural Leather by Mechanical Methods

Table 2 presents physical-mechanical characteristics of tested footwear uppers made of natural leather (samples 1 and 2).

Table 2: Physical-mechanical characteristics of footwear uppers made of natural leather

Sample/ Characteristic	1	2	Test method standard
Elongation at a load of 10 N/mm^2, %	25	29	SR EN ISO 3376: 2012
Elongation at break, %	56	67	SR EN ISO 3376: 2012
Tensile strength, N/mm^2	24.70	24.53	SR EN ISO 3376: 2012
Seam tear strength, N/mm	101.80	106.28	SR 5045:2008
Water vapour permeability, mg/cm^2	147.84	238.56	SR EN ISO 3377-1:2012
Resistance to repeated bending, number of flexions	250,000	250,000	SR EN ISO 5402-1:2012
Strength to dry and wet abrasion (1-5 ranking)	5/5; 4/4	5/4; 4/3	SR EN ISO 11640:2002
Dyeing fastness to raindrop, (1-5 ranking)	5	5	STAS 8259/3-82

Values of physico-mechanical characteristics (elongation under load and at break, tensile strength, tear strength, seam strength and water vapor permeability) of the tested natural leather footwear uppers correspond to ST 1619:1994 standard [16]. The physical-mechanical resistances of the footwear uppers finished with the film coating compositions, have values of 5/4-5/5 for dry abrasion, values of 4/3-4/4 for wet abrasion, values of 250,000 flexions, for resistance to repeated bending, and conforms to the norms provided for natural leather finished with film coating. The water drop resistance of the footwear uppers (leather with smooth grain, box-type natural grain, black and brown) finished with finishing compositions (FC), has values of 5, on a scale of 0-5.

Qualitative Assessment of Finished Footwear

As a result of applying the finishing compositions (FC-1 for the black colour and FC-2 for the brown colour), high quality footwear was obtained, with resistant and aesthetic finishes, in black and brown colors. The values of chemical and physical-mechanical characteristics of footwear uppers fall within the limits of standards for finished leathers.

CONCLUSIONS

- The emulsion obtained by emulsifying a mixture of triethanolamine monostearate and paraffin oil stabilized with lauryl alcohol ethoxylated with 7 moles of ethylene oxide has homogenous appearance and particle sizes ranging mostly between 4 and 8 µm.
- High quality footwear was obtained by applying the finishing compositions, with resistant and aesthetic finishes.
- Footwear finishing compositions for film-coated footwear are evenly spread on the surface of natural leather uppers and have the following physical-chemical characteristics: dry substance 10-12%, pH 7.0-8.0, viscosity 11.0986 - 11.4953 cSt.
- The footwear finishing compositions (FC), consisting of complex metal dyes (black, brown), ethyl alcohol, aqueous nitrocellulose emulsion, wax emulsion (TP) and water, gives the leather uppers with natural grain box-type a glossy appearance, and leads to improved

characteristics of natural leather goods regarding the resistance to wet and dry abrasion and to water drop (raindrop).

- The values of chemical characteristics (chromium VI, free formaldehyde) of the natural leather footwear uppers tested are below the detection limit (3 mg/kg).
- The values of physical-mechanical characteristics (elongation under load and at break, tensile strength, tear strength, seam strength and water vapor permeability) of the natural leather footwear uppers tested correspond to ST 1619:1994 standard.
- The physical-mechanical resistances of the footwear uppers finished by film coating, using the finishing compositions, have values of 5/4-5/5 for dry abrasion, values of 4/3-4/4 for wet abrasion, values of 250,000 flexions for resistance to repeated bending, water drop resistance has values of 5, on a scale of 0-5, and comply with the norms provided for natural leather finished with film-coating.

Acknowledgment

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EUROPEAN RESEARCH AREA

COTANCE NEWSLETTERS

Starting with January 2019, the COTANCE Council will issue a monthly ***COTANCE Newsletter*** with the purpose of **promoting an improved image of leather** to relevant decision makers and domestic stakeholders including Members of the European and National Parliament, Governmental authorities, Ministerial officers, Customers of the leather industry, Brands, Retail chains, Relevant NGOs, Designers, etc. The monthly newsletters present topics that tell the truth about a controversial aspect or a fact that is not well known by the general public to bring about a better understanding of leather and the European leather industry, as well as a positive predisposition to legislate in favor of the leather industry. The newsletters are available in seven languages at https://www.euroleather.com/index.php/newsletter. The newsletters were also published in the first, second and third 2019 issues of *Leather and Footwear Journal*. The October and December newsletter are given below.

NEWS 8/2019 - October 2019

Leather Endures: the Case of Durability

No one can have failed to notice the growing concerns about the impact of fast fashion on the environment. In 2017, Greenpeace reported that between 2000 and 2014, global clothing production doubled, while the average amount consumers spent per item and how long they kept it, both declined. Producing this much clothing uses up huge amounts of natural resources and has a massive negative impact on the environment.

The report by the Ellen MacArthur Foundation, 'A New Textiles Economy: Redesigning fashion's future', found that the clothes themselves, increasingly made of polyester, are putting dangerous amounts of microfibers in the oceans - about half a million tonnes per year - and too often wind up in landfills after little wear.

Every second, the equivalent of one garbage truck of textiles is landfilled or burned and less than 1% of material used to make clothing is recycled into new clothing. Throw-away garments contribute more to climate change than air and sea travel and if nothing changes, by 2050 the fashion industry will use up a quarter of the world's carbon budget.

The contrast with leather, undeniably a material for slow fashion, is stark. Regardless of the final application, leather is made to last, often improving with age.

This durability is one of the characteristics that make leather such a wonderful material. A pair of leather shoes might last 20 years, whereas a pair of synthetic shoes is likely to be thrown away after less than one.

Leather products can be repaired, a central requirement to achieving the circular economy. As noted in the Leather Naturally White Paper on the Sustainability of Responsibly Made Leather, 'using resources for the longest time possible could cut some nation's emissions by up to 70%, increase their workforces by 4% (repairing items) and greatly lessen waste'.

It seems that in our ever-faster world, the value of the durability of leather seems to have been forgotten, lost in the quest for cheap, disposable materials now, without any thought for the consequences down the line. In her book, 'Craft of Use', Kate Fletcher describes true materialism as "a switch from an idea of a consumer society where materials matter little, to a truly material society, where materials – and the world they rely on – are cherished." In our fast world, materials have no value and the damage to the world they rely on is increasingly evident. In contrast, leather goods last, improve with age and may see years of use before repair or disposal is required. And this is to say nothing of the renewable and sustainable raw materials from which leather is made.

Leather is a material that is cherished by those still wise enough to see its virtues. Durability is one of them.

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in collaboration with leather UK

NEWS 9/2019 - December 2019

Leather Production: Safety as the top Priority

Leather has become a worldwide-traded commodity due to its beauty and versatility, and generates a global commercial value of more than 82 billion US dollars per year. Leather is produced with the skins and hides of animals that were slaughtered for meat production for human consumption. Without tanneries, this organic waste would present a considerable health risk if it was disposed of improperly.

Europe as a Pioneer of Health & Safety

Almost every country in the world has a tannery industry. However, not everyone is as concerned with suitable social and environmental standards as we are in Europe, which has taken a pioneering role in this regard. Tanneries in Europe are modern and responsible enterprises. European health & safety standards and regulations are among the highest and most comprehensive in the world, and are applied to leather production throughout Europe. The requirements for safe working conditions and occupational safety, safe machines and chemical processing as well as well-trained employees that apply to all European industries, also apply to the manufacture of leather.

The European industry has contributed to the continuous improvement of Health & Safety in the sector, through collaborative actions funded by the European Commission. These include the development of the OiRA tool for tanneries, which was developed together with social partners in order to further raise these standards. This assists tanners with the development of health & safety policy for their factories, through the use of the assessment tool, which can provide specific guidance for the management of tannery processes. Through UNIDO, this tool is also available worldwide for all tanneries to use (https://oiraproject.eu/en/oira-tools?text=tanning&op=Search&sort=date).

Health & Safety in tanneries was also addressed in 2018 in the EU-funded project "Due Diligence for Healthy Workplaces in the Leather Industry", which sought to evaluate and improve various issues including:

- Occupational safety as the main priority of tanneries
- Recognition of industry-specific instruments for evaluating occupational health and safety
- Relevance of leather customers in the global supply chain with regard to further improvement of occupational safety
- Implementation of due diligence for occupational safety at tannery workplaces as a market opportunity

The final report on Due Diligence for Healthy Workplaces in the Leather Industry can be found here http://euroleather.com/index.php/projects/due-diligence

Measures for the Industry beyond Europe

The measures derived to help the industry operate more safely, apply beyond Europe, and could be used at all production sites and establishments, worldwide. We not only want to further improve these issues here in Europe, but also export these practices to the world so that European standards can be applied throughout the entire supply chain. The health and safety of employees in countries without a similarly robust legal framework is just as important as in the EU.

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NATIONAL AND INTERNATIONAL EVENTS

5TH INTERNATIONAL CONGRESS ON BIOMATERIALS AND BIOSENSORS (BIOMATSEN) 23-29APRIL 2020, OLUDENIZ, TURKEY

The "5th International Congress on Biomaterials and Biosensors (BIOMATSEN)" will be held on April 23-29, 2020 in the stunning Convention Centre of one of the largest international resort in Turkey right in the heart of Blue Lagoon (Oludeniz) area.

BIOMATSEN intends to be a global forum for researchers and engineers to present and discuss recent innovations and new techniques in Biomaterials and Biosensors. In addition to scientific seminars, a wide range of social programs including boat cruises and visits to historical places will be available.

The Organizing Committee also encourages companies and institutions to showcase their modern products and equipment in the conference area.

Abstracts should be submitted until **January 27, 2020**.

More information: http://www.biomatsencongress.org/

7TH INTERNATIONAL CONGRESS ON MICROSCOPY AND SPECTROSCOPY (INTERM) 23-29 April 2020, OLUDENIZ, TURKEY

The "7th International Congress on Microscopy & Spectroscopy (INTERM)" will be held on April 23-29, 2020 in the stunning Convention Centre of one of the largest international resort in Turkey right in the heart of Blue Lagoon (Oludeniz) area.

INTERM is traditional annual congress for scientists and expected to collect a wide audience of participants and listeners. The Organizing Committee is planning an outstanding scientific program led by world-renowned invited speakers, that will not only be a platform to showcase exciting new developments in microscopy and spectroscopy, but will also reveal the transformational role of microscopy in supporting a range of physical and life sciences. The Organizing Committee hopes that the scientific program, including a wide array of topics will live to your expectations, and that participation in the congress will offer you an opportunity to meet up with your colleagues, friends and renowned specialists from all over the world.

Abstracts should be submitted until **January 20, 2020**.

More information: http://www.intermcongress.org/

INTERNATIONAL CONFERENCE ON BIOINFORMATICS AND BIOMEDICAL ENGINEERING - IWBBIO-2020 6-8 MAY 2020, GRANADA, SPAIN

The 8th International Work-Conference on Bioinformatics and Biomedical Engineering (IWBBIO 2020) will take place in Granada (Spain) in May, 2020. Details and instructions for the conference can be found at the conference web site. The conference will be devoted to current researches in Bioinformatics, Computational Biology, Biomedicine and Bioengineering, including the following topics (but not limited to):

1. Translational Bioinformatics
2. Integrative Bioinformatics
3. Next generation sequencing and sequence analysis.
4. High performance in Bioinformatics.
5. Computational proteomics.
6. Biomedicine.
7. Biomedical Engineering
8. Computational systems for modeling biological processes.
9. Healthcare and diseases.
10. E-Health
11. Personalized medicine

Important dates

Submission of abstracts: **December 4th, 2019**.
Submission of papers by authors: **November 24th, 2019**.
Notification of provisional acceptance: **February 8th, 2020**.
Submission of final papers: **February 14th, 2020**.

More information: http://iwbbio.ugr.es

17TH INTERNATIONAL CONFERENCE ON NANOSCIENCES & NANOTECHNOLOGIES (NN20)
7-10 JULY 2020, THESSALONIKI, GREECE

NN International Conference is a world-class event in Nanosciences and Nanotechnologies established in 2004. NN20 focuses on the latest advances on N&N by promoting profound scientific discussions between experts from different disciplines and market leaders. You are encouraged to join NN20 and discuss your R&D&I efforts, network with key Academia, Research and Industry players in the field and advance the creation of innovative concepts and collaboration opportunities.

Abstracts should be submitted until **April 8th 2020**.

More information: https://www.nanotexnology.com/

4TH SOUTH EAST EUROPEAN CONFERENCE ON SUSTAINABLE DEVELOPMENT OF ENERGY, WATER AND ENVIRONMENT SYSTEMS (SDEWES SEE2020 SARAJEVO)
28 JUNE - 2 JULY 2020, SARAJEVO, BOSNIA AND HERZEGOVINA

The main challenge for South East Europe (SEE) economies is to commit to, and sustain the implementation of, long-term reforms aimed at increasing competitiveness and promoting sustainable, inclusive and balanced development, as well as better integration between the EU Member States, candidate and potential candidate countries and neighbouring countries. An adequate response to this challenge will certainly require using the best available scientific knowledge and constant re-evaluation of the development process in light of the scientific findings. Therefore, it will be essential to enhance the scientific understanding, improve the long-term scientific assessments, strengthen the scientific capacities and ensure that the sciences are responsive to the emerging needs.

Along this line, a regional series of biannual Sustainable Development of Energy Water and Environment Systems (SDEWES) conferences have been initiated to provide a venue for the researchers

from the SEE region, but also for world-wide researchers and specialists and those interested in learning about the sustainability of development, to present research progress and to discuss the state of the art, the future directions and priorities in the various areas of sustainable development and regional integration.

Abstract submission deadline: **December 18th, 2019**.

More information: https://www.sarajevo2020.sdewes.org/

4TH GLOBAL SUMMIT ON NANOTECHNOLOGY
27-28 APRIL 2020, PRAGUE, CZECH REPUBLIC

Biocore group proudly announces the 4th Global Summit on Nanotechnology during April 27-28, 2020, Prague, Czech Republic. On behalf of the Organizing Committee, we would like to take this opportunity to sincerely appreciate the Nanotechnology-2019 Keynote Speakers, regular session speakers, specialized session organizers, session chairs and attendees whose contributions and efforts made Nanotechnology-2019 a success one.

Biocore extends a warm welcome to the distinguished speakers, delegates, Nanotechnologists, Materials Science Engineers, and Nanotechnology Engineers from all around the world to attend the 4th Global Summit on Nanotechnology (Nanotechnology Congress) during April 27-28,2020, Prague, Czech Republic.

Nanotechnology Congress is designed in such a way to uncover the basic principles that lead to the drastic emergence and technologies in the field of Materials Science and Nanotechnology. We hope Nanotechnology and Materials Science is the best platform to discuss the basic principles involved in the development of Materials Science and Nanotechnology.

Abstract submission deadline: **March 2nd, 2020**.

More information: https://biocoreconferences.com/nanotech-2020/index.php

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Presentation of Papers

The scientific papers should be presented for publishing in English only. The text of the article should be clear and precise, as short as possible to make it understandable. As a rule, the paper should not exceed fifteen pages, including figures, drawings and tables. The paper should be divided into heads and chapters in a logical sequence. Manuscripts must meet high scientific and technical standards. All manuscripts must be typewritten using MS Office facilities, single spaced on white A4 standard paper (210 x 297 mm) in 11-point Times New Roman (TNR) font.

Paper Format

Title. Title (Centered, 12 pt. TNR font) should be short and informative. It should describe the contents fully but concisely without the use of abbreviations.
Authors. The complete, unabbreviated names should be given (Centered, 10 pt. TNR font), along with the affiliation (institution), city, country and email address (Centered, 9 pt. TNR font). The author to whom the correspondence should be addressed should be indicated, as well as email and full postal address.
Abstract: A short abstract in a single paragraph of no more than 200-250 words must accompany each manuscript (8 pt. TNR font). The abstract should briefly describe the content and results of the paper and should not contain any references.
Keywords. Authors should give 3-5 keywords.

Text

Introduction. Should include the aims of the study and results from previous notable studies.
Materials and Methods. Experimental methods should be described clearly and briefly.
Results and Discussions. This section may be separated into two parts. Unnecessary repetition should be avoided.
Conclusions. The general results of the research are discussed in this section.
Acknowledgements. Should be as short as possible.
References. Must be numbered in the paper, and listed in the order in which they appear.
Diagrams, Figures and Photographs should be constructed so as to be easy to understand and should be named "Figures"; their titles should be given below the Figure itself. The figures should be placed immediately near (after or before) the reference that is being made to them in the text. Figures should be referred to by numbers, and not by the expressions "below" or "above". The number of figures should be kept to minimum (maximum 10 figures per paper).
Tables. Should be numbered consecutively throughout the paper. Their titles must be centered at the top of the tables (12 pt. TNR font). The tables text should be 9 pt. TNR font. Their dimensions should correspond to the format of the Journal page. Tables will hold only the horizontal lines defining the row heading and the final table line. The tables should be placed immediately near (after or before) the reference that is being made to them in the text. Tables should be referred to by numbers, and not by the expressions "below" or "above". The measure units (expressed in International Measuring Systems) must be explicitly presented.
Formulas, Equations and Chemical Reactions should be numbered by Arabic numbers in round brackets, in order of appearance, and should be centered. The literal part of formulas should be in Italics. Formulas should be referred to by Arabic numbers in round brackets.
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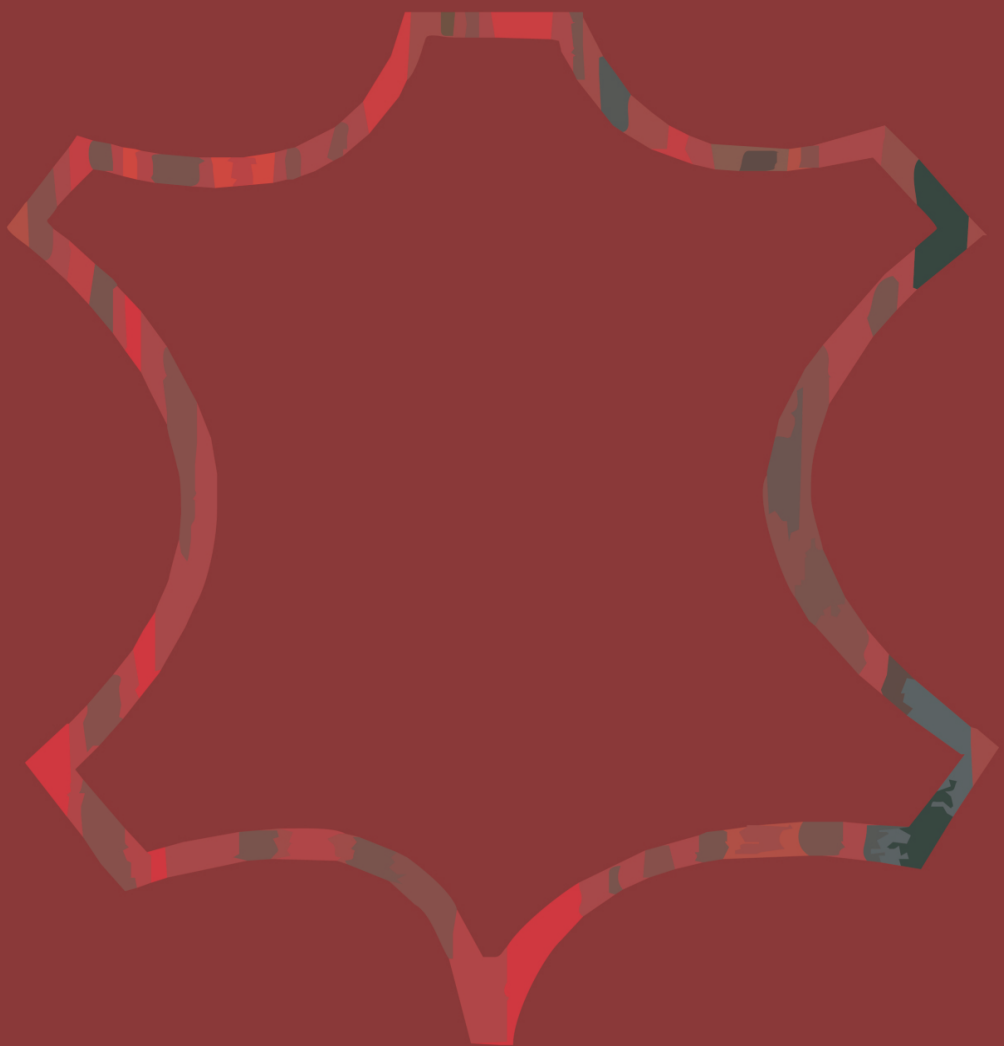

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