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	CONTENTS	***CUPRINS***	***SOMMAIRE***	
Maryna LESHCHYSHYN, Borys ZLOTENKO, Oleg SYNYUK, Svetlana KULESHOVA, Volodymyr ONOFRIICHUK, Yuriy MYKHAILOVSKYI	3D Printing of Pads on Lasts Utilized in the Production of Custom-Made Comfortable Footwear	Imprimarea 3D a inserțiilor pe calapoade utilizate în producția de încălțăminte confortabilă personalizată	Impression 3D d'inserts sur les moules de chaussure utilisés dans la production de chaussures confortables sur mesure	**231**
Guanghua ZHI	Study on the Influence of Biomechanical Characteristics of Functional Insoles on the Foot of Athletes during Running	Studiu privind influența caracteristicilor biomecanice ale branțurilor funcționale asupra piciorului sportivilor în timpul alergării	Etude sur l'influence des caractéristiques biomécaniques des semelles intérieures fonctionnels sur le pied des athlètes pendant la course	**241**
Mihaela NIȚUICĂ, Maria Daniela STELESCU, Maria SÖNMEZ, Mihai GEORGESCU, Laurența ALEXANDRESCU, Dana Florentina GURĂU, Mirela PANTAZI-BĂJENARU, Traian FOIAȘI	Determination of the Immersion Resistance of Polymeric Biocomposites based on TPU (Thermoplastic Polyurethane) / Recycled TPU / Protein and Elastomeric Waste Mixture	Determinarea rezistenței la imersie a biocompozitelor polimerice pe bază de TPU (poliuretan termoplastic) / TPU reciclat / deșeu proteic și elastomeric în amestec	Détermination de la résistance à l'immersion de biocomposites polymères à base de TPU (polyuréthane thermoplastique) / TPU recyclé / déchets protéiques et élastomères en mélange	**247**
Demetra SIMION, Carmen GAIDĂU, Gabriela PĂUN, Daniela BERECHET, Roxana CONSTANTINESCU	Obtaining New Bioemulsions Based on Lavender Extract and Surfactants	Obținerea unor noi bioemulsii pe bază de extract de lavandă și surfactanți	L'obtention de nouvelles bioémulsions à base d'extrait de lavande et de tensioactifs	**257**
Naimah PUTRI, Eka Legya FRANNITA	A Review of Potential Enzymes: Protease and Keratinase for Dehairing Process as Cleaner and Eco-Friendly Leather Processing	O trecere în revistă a potențialelor enzime: proteaza și keratinaza utilizate în procesul de depărare pentru o prelucrare a pieilor mai curată și ecologică	Un examen des enzymes potentielles : protéase et kératinase pour le processus d'épilage comme traitement du cuir plus propre et écologique	**267**
Mihaela-Doina NICULESCU, Brîndușa Georgiana DUMITRIU, Stelica CRISTEA, Lucreția MIU, Magdalena LASOŃ-RYDEL, Joanna SOBCZYK, Cosmin Andrei ALEXE	Eureka Project BIO-PLANT-Protect as Model Knowledge Transfer between Academic, Research and Industry	Proiectul Eureka BIO-PLANT-Protect ca model de transfer de cunoștințe între educație, cercetare și industrie	Le projet Eureka BIO-PLANT-Protect comme modèle de transfert de connaissances entre l'academie, la recherche et l'industrie	**279**
Md. Farhad ALI, Papia HAUQUE, Md. ABDULLA-AL-MAMUN, Tamanna JAMAN	Biodegradable Retanning Material from Tannery Trimming Waste: Extraction, Preparation and Application	Material de retăbăcire biodegradabil din ștuțuitură de la tăbăcirea pieilor: extracție, pregătire și aplicare	Matériau de retannage biodégradable issu des rognures de tannerie : extraction, préparation et application	**287**
Demetra SIMION, Carmen GAIDĂU, Gabriela PĂUN, Daniela BERECHET, Roxana CONSTANTINESCU	Innovative Technologies for Obtaining Structured Emulsions, Based on Sea Buckthorn Extract and Tensides	Tehnologii inovatoare pentru obținerea unor emulsii structurate pe bază de extract de cătină și tenside	Technologies innovantes pour l'obtention d'émulsions structurées à base d'extrait d'argousier et de tensioactifs	**303**
	European Research Area	Spaţiul european al cercetării	Espace Européen de la Recherche	**311**

3D PRINTING OF PADS ON LASTS UTILIZED IN THE PRODUCTION OF CUSTOM-MADE COMFORTABLE FOOTWEAR

Maryna LESHCHYSHYN[1*], Borys ZLOTENKO[2], Oleg SYNYUK[1], Svetlana KULESHOVA[1], Volodymyr ONOFRIICHUK[1], Yuriy MYKHAILOVSKYI[1]

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3D PRINTING OF PADS ON LASTS UTILIZED IN THE PRODUCTION OF CUSTOM-MADE COMFORTABLE FOOTWEAR

ABSTRACT. The study investigated the process of adjusting the shape of the footwear last using solid modeling elements (individual pads) manufactured through 3D printing. Based on a comparative analysis of the results of anthropometric foot studies with the parameters of existing footwear lasts available on the Ukrainian market, the rationale for improving the method of correction lasts using individual pads in mismatched anthropometric zones to achieve consumer foot comfort is substantiated. A schematic diagram of the transverse cross-section of the foot-lasts-pads-footwear system is provided. The study obtained dependencies of the calculated radius of the outer contour of the pad on the thickness of the upper material of the footwear. The anthropometric regions of the foot that most commonly require adjustment in existing lasts to achieve the production of custom-made comfortable footwear have been identified. The method of adjusting the shape of the last has been improved based on the individual parameters of the customer's foot, using pads manufactured using 3D printing technology. The interdependencies between stress and deformation under tension have been established, and the strength limit of polymer material samples for corrective pads obtained through 3D printing has been determined. The rational technological parameters of the 3D printing process using elastane material for corrective pads on lasts have been determined and implemented in the production of custom-made footwear.

KEY WORDS: shoes, materials, modulus of elasticity, shoe last, 3D printing

IMPRIMAREA 3D A INSERȚIILOR PE CALAPOADE UTILIZATE ÎN PRODUCȚIA DE ÎNCĂLȚĂMINTE CONFORTABILĂ PERSONALIZATĂ

REZUMAT. Studiul a investigat procesul de ajustare a formei calapodului pentru încălțăminte folosind elemente de modelare solide (inserții individuale) fabricate prin imprimare 3D. Pe baza unei analize comparative a rezultatelor studiilor antropometrice ale piciorului cu parametrii calapoadelor pentru încălțăminte existente pe piața ucraineană, se justifică raționamentul pentru îmbunătățirea metodei de corecție a calapoadelor pentru încălțăminte cu ajutorul inserțiilor individuale în zonele antropometrice unde este necesar pentru a obține confort la nivelul piciorului consumatorului. Se prezintă o diagramă schematică a secțiunii transversale a sistemului picior-calapod-inserție-încălțăminte. Studiul a condus la determinarea unor variații ale razei calculate a conturului exterior al inserției în funcție de grosimea materialului din care este confecționată fața încălțămintei. S-au identificat regiunile antropometrice ale piciorului care necesită cel mai frecvent ajustări pe calapoadele existente pentru a realiza producția de încălțăminte confortabilă la comandă. Metoda de reglare a formei calapodului a fost îmbunătățită pe baza parametrilor individuali ai piciorului clientului, folosind inserții realizate cu ajutorul tehnologiei de imprimare 3D. S-au stabilit interdependențele dintre tensiune și deformarea sub tensiune și s-a determinat limita de rezistență a probelor de material polimeric pentru inserțiile de corecție obținute prin imprimare 3D. S-au determinat și implementat parametrii tehnologici raționali ai procesului de imprimare 3D care utilizează material elastan pentru inserțiile corectoare de pe calapoadele pentru încălțăminte în cadrul producției de încălțăminte personalizată.

CUVINTE CHEIE: pantofi, materiale, modul de elasticitate, calapod pentru încălțăminte, imprimare 3D

IMPRESSION 3D D'INSERTS SUR LES MOULES DE CHAUSSURE UTILISÉS DANS LA PRODUCTION DE CHAUSSURES CONFORTABLES SUR MESURE

RÉSUMÉ. L'article étudie le processus d'ajustement de la forme du moule de chaussure à l'aide d'éléments de moulage solides (inserts individuels) fabriqués par impression 3D. Sur la base d'une analyse comparative des résultats des études anthropométriques du pied avec les paramètres des moules de chaussures existant sur le marché ukrainien, le raisonnement est justifié pour l'amélioration de la méthode de correction des moules de chaussures à l'aide d'inserts individuels dans les zones anthropométriques où il est nécessaire d'obtenir un confort au niveau du pied du consommateur. Un diagramme schématique de la section transversale du système pied-moule-insert-chaussure est présenté. L'étude a permis de déterminer des variations du rayon calculé du contour extérieur de l'insert en fonction de l'épaisseur du matériau constituant la tige de la chaussure. On a identifié les régions anthropométriques du pied qui nécessitent le plus souvent des ajustements sur les moules existantes pour obtenir une production de chaussures personnalisées confortables. La méthode d'ajustement de la forme de la moule a été améliorée en fonction des paramètres individuels du pied du client, à l'aide d'inserts réalisés par la technologie d'impression 3D. Les interdépendances entre contrainte et déformation sous contrainte ont été établies et la limite d'élasticité des échantillons de matériau polymère a été déterminée pour les inserts de correction obtenus par impression 3D. On a déterminé et mis en œuvre des paramètres technologiques rationnels du processus d'impression 3D utilisant un matériau élasthanne pour les inserts correcteurs sur les moules de chaussures dans la fabrication de chaussures sur mesure.

MOTS CLÉS : chaussures, matériaux, module d'élasticité, moule de chaussure, impression 3D

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INTRODUCTION

Today, it is hard to imagine an industry that has not been touched by 3D printing technology. The application of additive technologies in footwear production is not just a fashionable trend but also a justified modernization of the manufacturing process. Additive technology, or layered synthesis technology, 3D printing — today is one of the most dynamic areas of the digital production [1]. The implementation of additive technologies in modern light industry production enables the manufacturing of polymer products of practically any complexity and configuration [2]. The whole idea of 3D printing is to produce affordable products in an efficient and effective manner, ensuring they are strong, lightweight, and have minimal waste. The primary focus is on high quality, efficiency, and low-volume production. Computer-generated designs will help reduce costs and improve the utilization of energy and resources by aiding in the development and early stages of production of new products in the light industry. They also eliminate the need for storing physical products. Custom-made footwear production offers opportunities for adjusting or creating footwear lasts based on the anthropometric parameters of the customer's foot. This allows for an ideal fit of the footwear to the foot, ensuring maximum comfort during its usage.

EXPERIMENTAL

Materials and Methods

In the study, the three-dimensional graphic environment Delcam Crispin was utilized, employing modules such as ShoeMaker, LastMaker, and PowerShape, which provide a comprehensive cycle of design processes in footwear production. These modules cover tasks ranging from foot scan processing and upper construction modeling to last design. The Ultimaker Cura slicer was used to configure the printing of experimental samples using various polymer materials. The study investigated printed samples made from the following materials: polylactic acid (PLA), high-temperature melting point ABS plastic, Elastan, polycyclohexanedimethylene terephthalate glycol (PCTG), and glycol-modified polyethylene terephthalate (PETG).

For the investigation of footwear last correction using a printed pad, the Fused Deposition Modeling (FDM) method was utilized for 3D printing in the study. The study proposes an improved method for correcting existing lasts using printed pads manufactured through 3D printing technology in anthropometric zones of the foot that require adjustments in volume for individual consumers. The correction of lasts using printed pads made from polymer materials will significantly reduce production time, lower costs, and facilitate the implementation of custom-made footwear lasts.

Analysis of Previous Research and Sources of Investigation

Analysis of theory and practice in footwear production indicates that manufacturing products at a high level of quality is the primary goal of footwear manufacturers. The sportswear industry has long relied on technologies to optimize the characteristics of their products, and thanks to digital workflows, they have numerous opportunities to create limited edition collections [3].

3D printers with 3D printing technology are gradually gaining significance in the footwear design field. Additionally, 3D printing technology allows for the use of multiple different polymer materials in the production of a single product in the lightweight industry [4]. Such an approach allows for addressing issues related to the strength and elasticity of manufactured products. The main applications of additive technologies in the footwear industry include the production of specialized orthopedic models, sports footwear, and designer styles. Prominent global brands such as Nike, Adidas, Reebok, Under Armour, and New Balance are already utilizing 3D technologies in footwear manufacturing.

There are many studies and researches on 3D printing technologies and 3D printers [5-7]. From these studies, it is known that the

primary raw material for manufacturing various parts and products is polymer material [5]. The trends that are driving the footwear industry towards wider adoption of additive manufacturing are primarily associated with the underlying macro trend of increased personalization in consumer goods [8, 9]. Indeed, the widespread adoption of additive manufacturing in the footwear industry is still in its early stages. Brands continue to be valued more than custom-made products. However, younger and future generations are beginning to appreciate the value of customized products, especially when they become more accessible.

3D printing is also an energy-efficient technology that can contribute to the eco-friendliness of the manufacturing process by utilizing up to 90% of the material [10]. In recent years, 3D printing has expanded beyond industrial prototyping and manufacturing processes. The technology has become more accessible to small companies and even individual users. It is now available to a wide audience, and its popularity is growing exponentially every year. There is a growing variety of materials and applications for 3D printing [11, 12].

Adjusting the Pad to the Parameters of the Foot

By analyzing the number of customer requests for custom-made handmade footwear, it can be noted that the areas of the shoe last most commonly not aligned with the anthropometric parameters of customers' feet are the following: the arch area, the instep area, or both the arch and instep areas simultaneously (Figure 1).

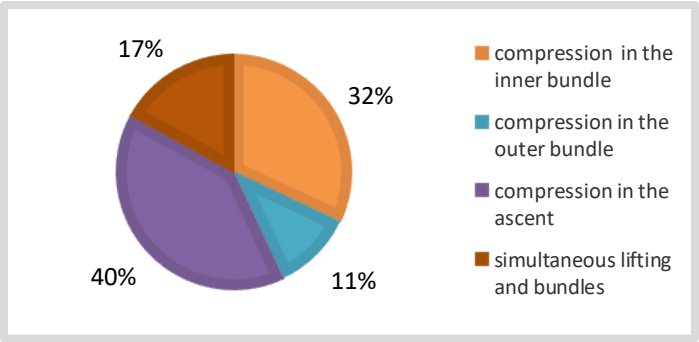

Figure 1. The areas of the foot that most commonly require adjustment in existing shoe lasts

For the purpose of verifying the proposed technology, a custom-made pair of shoes was manufactured for the consumer, whose foot circumference in the instep area exceeded the corresponding size of the shoe lasts. Comparative parameters were obtained based on non-contact measurements using a 3D scanner of the consumer's feet and scanned existing shoe lasts of the appropriate size, matched by the style (Table 1).

Table 1: The comparative analysis of anthropometric parameters of the foot and parameters of the shoe lasts

№	Parameter	Foot Measurement (mm)	Shoe Last Measurement 1, (mm) (Zotti)	Shoe Last Measurement 2, (JB Plast)	Shoe Last Measurement 3, (Lviv Plast)	Deviation of Last 1 from the Foot (1-2)	Deviation of Last 2 from the Foot (1-3)	Deviation of Last 3 from the Foot (1-4)
1	L1- Foot Length	275.0	290.0	292.0	294.0	-15.0	-17.0	-19.0
2	L2 – Length to the end of the 5th toe	243.0	242.0	244.0	243.0	1.0	-1.0	0
3	L3 – Length to the inner beam	190.0	187.0	191.0	189.0	3.0	-1.0	1.0
4	L4 – Length to	181.0	179.5	177.8	182.0	1.5	3.2	-1.0

№	Parameter	Foot Measurement (mm)	Shoe Last Measurement 1, (mm) (Zotti)	Shoe Last Measurement 2, (JB Plast)	Shoe Last Measurement 3, (Lviv Plast)	Deviation of Last 1 from the Foot (1-2)	Deviation of Last 2 from the Foot (1-3)	Deviation of Last 3 from the Foot (1-4)
	the outer beam							
5	C1 – Toe circumference	214.8	215.6	215.0	215.0	-0.8	-.02	-0.2
6	C2 – Bundle circumference,	**289.0**	**275.0**	**274.0**	**278.0**	**14.0**	**15.0**	**11.0**
7	C3 – Girth through the bend and heel	360.0	351.0	350.0	352.0	9.0	10.0	8.0
8	C4 – Lifting circumference	**301.0**	**287.0**	**289.0**	**285.5**	**14.0**	**12.0**	**13.5**
9	H1 – Height of the I toe	25.0	27.0	26.0	27.0	-2	-1	-2

The comparative analysis of the foot measurements and the existing shoe last revealed the need for significant adjustments in the basic shoe last, particularly in the girth parameters. The largest discrepancies were observed in the areas of the forefoot and instep girth (Figure 2).

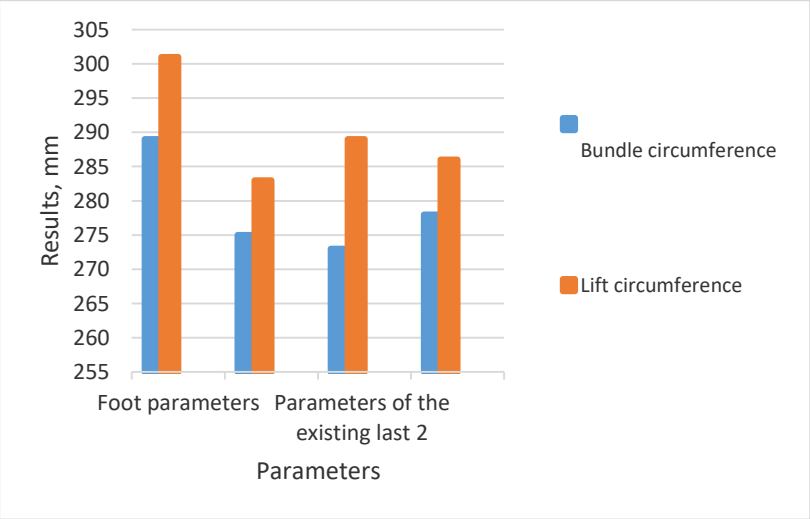

Figure 2. Comparative analysis of deviations in the circumferential parameters of the foot with the parameters of existing shoe lasts

It is advisable to make rational adjustments to the shoe last in areas where it does not correspond to the foot's anthropometric dimensions using overlays. This minimizes the time required to manufacture a new individual shoe last and reduces costs, allowing the same shoe last to be used for different customers by simply changing the individual overlays.

To enhance the performance characteristics of the overlays, it is recommended to manufacture them using 3D printing technology. Modern 3D printers have the capability to create models of various complexities using different types of plastics, at an affordable cost and with a fast turnaround time [13].

For the research purposes, five types of plastic were used for 3D printing, and the printing parameters were selected based on the recommended technical specifications for each material. As a result, samples for investigating the physical and mechanical characteristics were printed using the following materials: PLA (polylactic acid); ABS (acrylonitrile butadiene styrene); Elastan;

PCTG (polycyclohexanedimethylene terephthalate glycol); PETG (modified polyethylene terephthalate glycol).

With the aim of determining the physical and mechanical properties of the polymer materials, experimental investigations of tensile tests were conducted on samples obtained through 3D printing using an upgraded tensile testing machine. From the obtained experimental data on the tensile behavior of the polymer materials, a graph was constructed to illustrate the strength limits of the tested plastics (Figure 3).

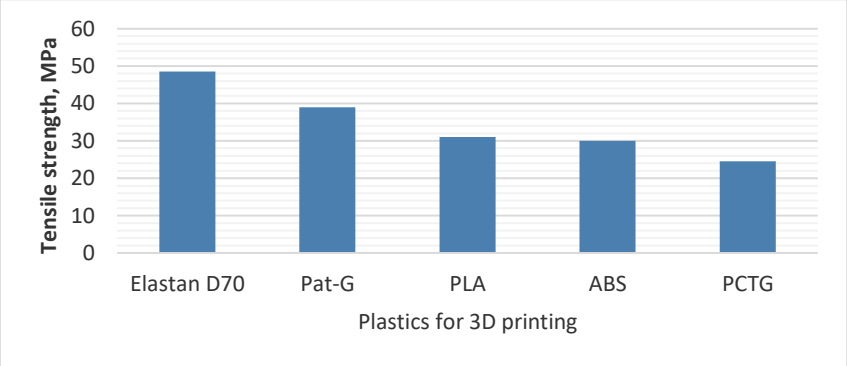

Figure 3. Strength limit of the investigated plastics

Based on the analysis of the research results for 3D printing of overlays, Elastan was chosen as it is an extremely flexible material with a high degree of strength. It is well-suited for producing a range of functional parts using 3D printing. The plastic withstands dynamic loads excellently and can be used in a wide temperature range (from -40°C to +120°C). Elastan is an excellent choice for both technical and decorative purposes. Its melting temperature ranges from 230°C to 260°C.

RESULTS AND DISCUSSIONS

Mathematical Modelling

In custom shoe manufacturing, there are often cases where the customer has a higher arch height, which requires increasing the height of the shoe last to ensure comfortable pressure on the foot from the upper during wear [15]. Increasing the height of the shoe last in the arch area while maintaining the necessary shape and proportion can be achieved by using special inserts made through 3D printing technology. These inserts are designed to fit tightly onto the surface of the shoe last, providing the desired elevation.

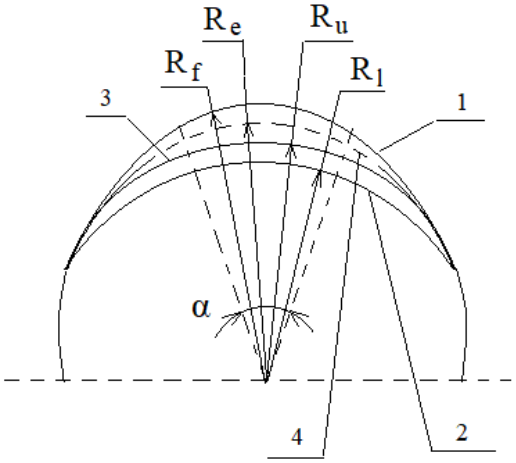

Figure 4. The cross-sectional diagram of the foot - last - pads - footwear system is as follows: 1 - foot contour; 2 - last contour; 3 - pads contour; 4 - contour of the foot-to-upper distribution surface

To determine the thickness of the overlay in the area of the foot arch, we will use the calculation scheme shown in Figure 4.

When manufacturing custom-made footwear, tightening of the upper is primarily done in the toe and heel areas, while in the arch area, the tightening force is almost absent. Therefore, it can be considered that the outer contour of the pads aligns with the contour of the inner surface of the finished footwear. During the wearing process, it is necessary to ensure a comfortable pressure on the surface where the foot and the upper of the footwear come into contact. The magnitude of this pressure, which is 9943 Pa, has been determined in the study [14]. Under the mentioned pressure, there is a slight compression of the foot and stretching of the upper part of the footwear, resulting in the surface where the foot and the upper of the footwear come into contact occupying an intermediate position between the foot surface and the inner surface of the upper part of the finished footwear, which is determined by the radius.

Let's consider a segment of the cross-section of the system: foot - last - pads - footwear, bounded by an angle α. We assume that within this angle, all contours can be approximated as segments of circles drawn from a common center located on the lower surface of the upper part of the footwear. Then, the pressure on the surface where the foot and the upper of the footwear come into contact can be represented based on Hooke's law as follows:

$$P = \frac{R_f - R_e}{R_f} E_f \quad (1)$$

where: P – pressure, (Pa); R_f – radius of the foot contour, (m); R_e – radius of the foot-distribution surface – upper of the footwear contour, (m); E_f – elastic modulus of the foot, (Pa).

From equation (1), we obtain:

$$R_e = R_f\left(1 - \frac{P}{E_f}\right) \quad (2)$$

When the foot is compressed, the upper of the shoe stretches, and the stresses that arise in it can be expressed as circumferential stresses in a cylindrical shell.

$$\sigma = \frac{PR_e}{\delta} \quad (3)$$

where σ – is the tensile stress, (Pa); δ – the thickness of the shoe upper.

Taking into account the small thickness of the upper compared to the radius of its inner surface, the same tensile stresses can be expressed based on Hooke's Law as:

$$\sigma = \frac{R_e - R_u}{R_u} E_u \quad (4)$$

whereR_u – radius of the inner surface of the finished footwear, (m); E_u– modulus of

elasticity of the upper material of the footwear, (Pa).

By equating the right-hand sides of equations (3) and (4) and performing the necessary transformations, we obtain:

$$R_e = \frac{1}{\frac{1}{R_u} - \frac{P}{\delta E_u}} \quad (5)$$

Similarly, by equating the right-hand sides of equations (2) and (5) and performing the necessary transformations, we obtain an expression for determining the radius of the inner surface of the finished footwear or the outer contour of the pad:

$$R_u = \frac{1}{\frac{1}{R_f\left(1-\frac{P}{E_f}\right)} + \frac{P}{\delta E_u}} \quad (6)$$

By substituting equation (6) into equation (5), we obtain an expression for determining the radius of the surface contour between the foot and the upper of the footwear during wear:

$$R_e = \frac{1}{\frac{1}{\frac{1}{R_f\left(1-\frac{P}{E_f}\right)} + \frac{P}{\delta E_u}} - \frac{P}{\delta E_u}} \quad (7)$$

One of the most common materials used for the upper part of footwear is genuine leather, which has a complex internal structure [15]. The magnitude of the elastic modulus of the upper material of footwear depends on the direction of stretching relative to the orientation of fibers for natural leather or the supramolecular structures for synthetic polymer materials [16].

The graphical dependencies of the calculated radius of the external contour of the overlay on the thickness of the upper material of footwear are presented in Figure 2 for different values of its elastic modulus to ensure the desired comfortable pressure on the foot $P = 9943$ Pa, calculated using equation (6), assuming the radius of the foot contour $R_f = 7 \cdot 10^{-2}$m, elastic modulus of the foot $E_f = 616.9 \cdot 10^3$ Pa [14].

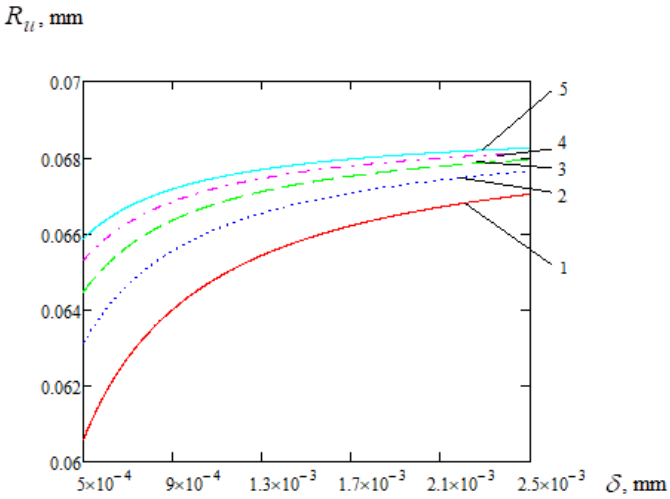

Figure 5. The dependencies of the calculated radius of the outer contour of the overlay from the thickness of the upper material are shown: 1 – $E_u = 10^7$ Pa; 2 – $E_u = 1.5 \cdot 10^7$ Pa; 3 – $E_u = 2 \cdot 10^7$ Pa; 4 – $E_u = 2.5 \cdot 10^7$ Pa; 5 – $E_u = 3 \cdot 10^7$ Pa.

As can be seen from Figure 5, with an increase in the thickness and modulus of elasticity of the upper material, the calculated radius of the outer contour of the overlay increases.

Research Results

Overlays for the lift area were designed for the pre-selected footwear lasts (Figure 6).

The radius of the contour of the outer surface of the overlays is determined using formula (6), where the parameter values are substituted: $P = 9943$ Pa; $R_f = 7 \cdot 10^{-2}$ m; $E_f = 616.9 \cdot 10^3$ Pa; $\delta = 1.5 \cdot 10^{-3}$ m; $E_u = 2 \cdot 10^7$ Pa.

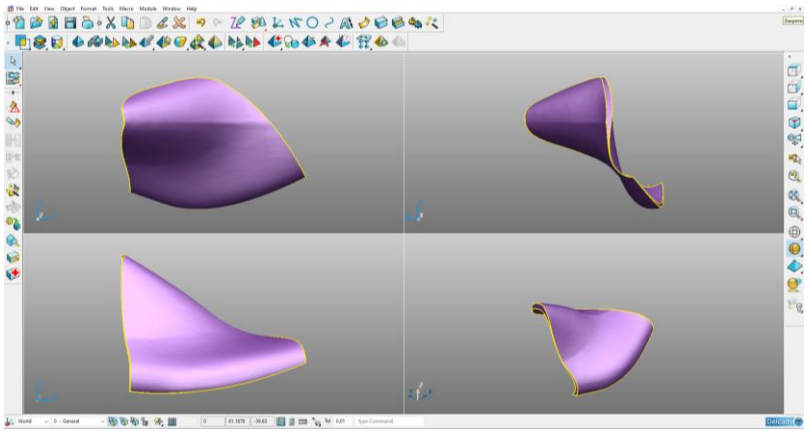

Figure 6. The anthropometric overlay was designed using the Delcam Crispin graphical environment

Below is an image of the tested overlay on the footwear last in Ultimaker Cura slicer, which is necessary to enhance comfort for custom orders. The required settings and estimated print time for the part have been selected (Figure 7, Table 2).

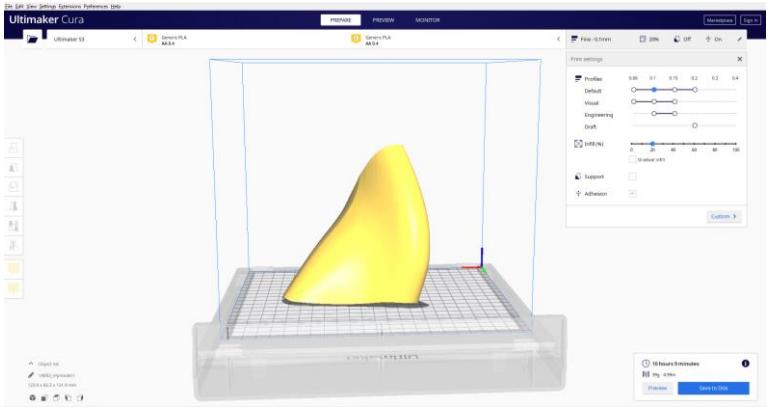

Figure 7. Completed 3D image of the insole in Ultimaker Cura slicer

Table 2: Printing parameters for Elastan D70 plastic insoles

Print settings	Standard values D 70	Settings used for printing the pads D 70
Printing temperature	230-260°C	250°C The optimal printing temperature at which the polymer extrudes uniformly.
Bed temperature	90-110°C	90°C If a lower temperature is chosen, the first layer of the polymer may not adhere firmly to the build platform. On the other hand, a higher temperature, typically by a few tens of degrees, can cause the polymer to not have enough time to cool and solidify, leading to excessive melting and deformations.
Printing direction	Horizontal, Vertical x-y, Vertical z	Horizontal
Line infill	10-100	20
Fan cooling	+	+
Print speed	30 - 80мм/с	50 мм/с The optimal printing speed is the speed at which the polymer consistently and evenly cools and adheres layer by layer.
Printing shrinkage, %	0.7	0.7
Support density, %	20-30	24

Figure 8. a) The custom insole for the shoe was manufactured using 3D printing;
b) The printed insole is attached to the shoe last

The obtained custom insoles were attached to the existing shoe lasts using brackets, which ensure a secure fit and attachment of the insoles to the lasts (Figure 8.b). Using the shoes with the attached insoles, comfortable footwear was made according to the individual anthropometric data of the customer (Figure 9).

Figure 9. The photo of the custom-made pair of comfortable shoes has been taken

The proposed approach to manufacturing customized footwear allows for achieving the desired pressure on the individual's feet, not only in cases where anthropometric parameters differ from the average statistical values but also when each foot has its unique characteristics. In this scenario, individual inserts are used to create each half pair of shoes.

CONCLUSIONS

Based on the experimental study the following conclusions can be drawn:

The method of adjusting the shoe last shape based on the individual parameters of the customer's foot has been improved using inserts manufactured using 3D printing technology. The interdependencies between stress and deformation during stretching have been established, and the strength limit of the polymer material samples for corrective inserts obtained through 3D printing has been determined.

Optimal technological parameters for the 3D printing process of elastane corrective inserts on the shoe last have been identified and implemented in the production of custom-made footwear. An individual pair of men's half shoes has been manufactured using the improved methodology for adjusting the fullness of the shoe last in specific anthropometric areas.

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STUDY ON THE BIOMECHANICAL CHARACTERISTICS OF FUNCTIONAL INSOLES ON THE FOOT OF ATHLETES DURING RUNNING

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STUDY ON THE INFLUENCE OF BIOMECHANICAL CHARACTERISTICS OF FUNCTIONAL INSOLES ON THE FOOT OF ATHLETES DURING RUNNING

ABSTRACT. Functional insoles can reduce foot injuries caused by running. In this paper, ten male volunteers from the Track and Field Department of Guilin University of Electronic Technology were selected as subjects to test the biomechanical characteristics of the foot, such as plantar pressure, impulse, and center line pressure distribution, when using normal insoles and shock-absorbing functional insoles made of latex, ethyl vinyl acetate (EVA), and conventional insoles. The results showed that the plantar pressure and impulse were mainly concentrated on the first toe, the middle of the metatarsal, and the lateral part of the heel. After using the shock-absorbing insoles, the average pressure and impulse of the first toe, second to fifth toe, lateral metatarsal, and lateral heel were significantly reduced, while the average pressure intensity and impulse of the medial metatarsal, middle metatarsal, and medial heel were significantly increased; the center line of pressure became longer and straighter, indicating that the running stability was improved.
KEY WORDS: insole, shock absorption, foot, biomechanics

STUDIU PRIVIND INFLUENȚA CARACTERISTICILOR BIOMECANICE ALE BRANȚURILOR FUNCȚIONALE ASUPRA PICIORULUI SPORTIVILOR ÎN TIMPUL ALERGĂRII

REZUMAT. Branțurile funcționale pot reduce leziunile cauzate de alergare la nivelul picioarelor. În această lucrare, zece voluntari de sex masculin de la Departamentul de atletism al Universității de Tehnologie Electronică din Guilin au fost selectați ca subiecți pentru a testa caracteristicile biomecanice ale piciorului, cum ar fi presiunea plantară, impulsul și distribuția presiunii pe linia centrală, la utilizarea branțurilor normale, a branțurilor funcționale care absorb șocurile, fabricate din latex, etilen-acetat de vinil (EVA) și a branțurilor convenționale. Rezultatele au arătat că a existat o concentrare preponderentă a presiunii plantare și a impulsului în zona halucelui, în zona centrală a metatarsienelor și pe partea laterală a călcâiului. După utilizarea branțurilor care absorb șocurile, presiunea și impulsul medii în zona halucelui, în zona ce cuprinde al doilea până la al cincilea metatarsian, în zona metatarsiană laterală și în cea laterală a călcâiului s-au redus semnificativ, în timp ce intensitatea medie a presiunii și impulsul în zona metatarsiană mediană, în centrul zonei metatarsiene și în zona mediană a călcâiului au crescut semnificativ; linia centrală de presiune a devenit mai lungă și mai dreaptă, ceea ce indică faptul că s-a îmbunătățit stabilitatea în timpul alergării.
CUVINTE CHEIE: branț, absorbția șocurilor, picior, biomecanică

ÉTUDE SUR L'INFLUENCE DES CARACTÉRISTIQUES BIOMÉCANIQUES DES SEMELLES INTÉRIEURES FONCTIONNELS SUR LE PIED DES ATHLÈTES PENDANT LA COURSE

RÉSUMÉ. Les semelles intérieures fonctionnelles peuvent réduire les blessures aux pieds pendant la course. Dans cet article, dix volontaires masculins du département d'athlétisme de l'Université de Technologie Électronique de Guilin ont été sélectionnés comme sujets pour tester les caractéristiques biomécaniques du pied, telles que la pression plantaire, l'impulsion et la répartition de la pression sur l'axe central, lors de l'utilisation de semelles intérieures normales, de semelles intérieures fonctionnelles, en latex et éthylène-acétate de vinyle (EVA), d'absorption des chocs, et de semelles intérieures conventionnelles. Les résultats ont montré qu'il y avait une concentration prédominante de pression plantaire et d'impulsion dans la zone de l'hallux, dans la zone centrale des métatarsiens et sur la face latérale du talon. Après avoir utilisé les semelles intérieures amortissantes, la pression et l'impulsion moyennes dans la zone de l'hallux, la zone du deuxième au cinquième métatarsien, la zone métatarsienne latérale et la zone latérale du talon ont été considérablement réduites, tandis que l'intensité de pression et l'impulsion moyennes dans la zone métatarsienne moyenne, le centre de la zone métatarsienne et la zone médiale du talon ont augmenté de manière significative ; la ligne centrale de pression est devenue plus longue et plus droite, ce qui montre que la stabilité pendant la course s'est améliorée.
MOTS CLÉS : semelle intérieure, absorption des chocs, pied, biomécanique

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INTRODUCTION

In today's fast-paced life, people are paying more and more attention to health issues. As technology advances, more and more health products are being developed, and one of the products that have received much attention is functional insoles [1]. These insoles can provide targeted support and protection according to the biomechanical characteristics of people's feet, thus improving physical conditions and preventing sports injuries. The foot is a very important part of the body [2] and is responsible for supporting the body weight, balancing the body stability and cushioning the ground load and other functions; therefore, during sports, the foot is often subjected to large loads and pressures. During daily walking, the foot is exposed to multiple impacts, not to mention that running exposes the foot to approximately three times the impact of jogging [3]. With such frequent and large impacts, it is difficult for the foot's own shock-absorbing structure (mainly the arch) to fully compensate for the damage caused by the impacts. If the foot is not properly protected and supported, it will cause foot pain and affect human health. The role of insoles is to avoid direct contact between the foot and the sole, and at the same time, by virtue of its own material characteristics, relieve the pressure for the foot and play a role in absorbing sweat, thus improving the comfort of the shoe, and the pattern of the insole surface can also reduce the slippage between the sole and the foot [4]. In addition to the above-mentioned basic functions, functional insoles also have their own features, and shock-absorbing insoles are one of the functional insoles that emphasize shock-absorbing functions. Shock-absorbing functional insoles use the material and structure to improve the shock-absorbing performance, so as to provide sufficient support to the foot [5] and reduce the sports injuries caused during running. For functional insoles, He *et al*. [6] developed a smart insole with real-time monitoring of plantar pressure distribution through wearable sensor technology. The experimental results showed a 44% reduction in heel pressure after using the smart insole. Liu *et al*. [7] investigated the effect of orthotic insoles with medial arch support and heel cushion on postural balance in chronic stroke patients and found that orthotic insoles had a small but significant positive effect on improving postural balance in chronic stroke patients. Han [8] compared the biomechanical and clinical effects of three different insoles on rearfoot motion (RFM) and ankle moment parameters and found that insoles with arch support and cushioning were effective in reducing sports injuries. In this paper, ten male volunteers from the Track and Field Department of Guilin University of Electronic Technology were used to test the biomechanical characteristics of the foot such as plantar pressure intensity, impulse and center line distribution of pressure under normal insoles and shock-absorbing functional insoles.

EXPERIMENTAL

Subjects

In this paper, ten male volunteers were selected from the Track and Field Department of Guilin University of Electronic Technology, and their basic conditions are shown in Table 1. There were no significant differences in age, height and weight among the ten volunteers, and they were also in good health, with no serious sports injuries to the lower limbs, especially the feet, in the past six months. The shoe sizes worn by the volunteers were all 41. The volunteers were awake during the experiment and all gave informed consent.

Table 1: Basic information of male volunteers

	Age/years	Height/cm	Body weight/kg
Average value	20±1.1	170.3±1.1	62.1±1.1
P value	0.114	0.123	0.145

Equipment and Materials

The experimental equipment and materials included the Novel Pedar-X plantar pressure insole testing system [9] (Novel, Germany) used to test the biomechanics of the foot, stopwatch, treadmill (Yijian brand, model ELF, 0.3~4 m/s speed adjustable range),

size 41 sports shoes of common brand, white board paper, marker, glue, carving knife, latex, and ethyl vinyl acetate (EVA) [10]. Among them, the plantar pressure insole testing system mainly consisted of insoles with 99 capacitive pressure sensors and a signal transmission box. The signal transmission box transmitted the collected plantar pressure data to the computer via wireless signals, and each insole then used 99 pressure sensors [11] to collect the distribution of plantar pressure. The sampling frequency of the pressure sensors was 50 Hz. The sampling positions constituted by the pressure sensors and their corresponding foot regions are shown in Figure 1. Area ① is the 1st toe region; area ② is the 2nd to 5th toe region; area ③ is the medial metatarsal region; area ④ is the middle metatarsal region; area ⑤ is the lateral metatarsal region; area ⑥ is the midfoot region; area ⑦ is the medial heel region; area ⑧ is the lateral heel region [12].

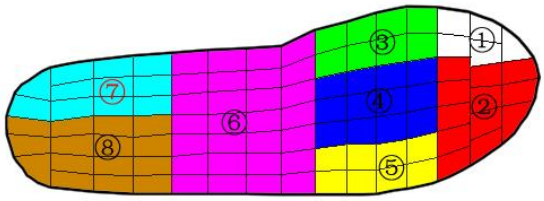

Figure 1. Schematic diagram of the sampling position of the pressure sensors and the corresponding plantar regions

The shock-absorbing functional insoles used in the experiments were all prepared independently, and the preparation process is as follows.

① A size 41 ordinary sports shoes insole with a hardness of 35 °ShA was selected.

② Structural design of shock-absorbing functional insoles: The design principle of the shock-absorbing functional insoles was to bond different materials of insoles at specific areas to achieve the shock-absorbing function. Its basic structure is shown in Figure 2. The light blue A area corresponded to the forefoot metatarsal area, which required a certain amount of rebound to improve the efficiency of movement; the yellow B area and the pink C area corresponded to the lateral and medial heel areas, respectively, which required a certain amount of shock absorption to reduce the impact of landing. The parameters of the material used in areas A, B, and C are shown in Table 2.

Table 2: Material-related parameters of the three regions

Area code	Materials	Hardness/°ShA	Thickness/mm
A	Latex	18	2
B	Latex	22	3
C	EVA	40	3

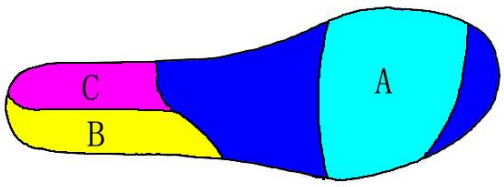

Figure 2. Basic structure of shock-absorbing functional insoles

③ Making the shock-absorbing functional insole: first, the structure shown in Figure 2 was drawn on the white board paper. Then, areas A, B and C were cut out as samples. Then, the same shapes were cut from the materials according to the samples and glued to the corresponding areas using glue. Air bubbles were avoided when gluing the functional insoles. After the glue had set, the glued edges were sanded with sandpaper [13].

Methods

Blank Experiment

First, the pressure insole of the plantar pressure testing system was placed into the

corresponding sports shoes. The pressure insole was kept as close as possible to the sports shoe sole without sliding. After the volunteer put on the sports shoes, the pressure insole and the signal transmission box were connected using the connection cable (note the difference between left and right), and then the signal transmission box was fixed at the waist [14].

The volunteers warmed up before wearing the test system. After wearing, they ran on the treadmill at a speed of 3 m/s for 5 s, and the change in plantar pressure was recorded during the process. The test was conducted three times with a 6-minute interval between each test to ensure that the volunteers were rested.

Comparison Experiments

The volunteers also warmed up before the test and then replaced the original insoles in the shoes with the prepared shock-absorbing functional insoles. After that, the volunteers also ran on the treadmill at a speed of 3 m/s for 5 s to record the change in plantar pressure. The test was conducted three times, with each test interval of 6 minutes.

Statistical Analysis

SPSS software [15] was used to statistically analyze the collected data. The measurement data were expressed as mean ± standard deviation (X ± SD). Independent T-test was used to compare the two insoles. $P < 0.05$ indicates a significant difference, and $p < 0.01$ indicates a highly significant difference.

RESULTS AND DISCUSSIONS

As the right and left feet are symmetrical and the space of this paper is limited, only the right foot was used as an example. Table 3 shows the average pressure intensity of each area of the sole of the subject's right foot under the action of the two insoles. It was seen from Table 3 that the average pressure intensity distribution in the foot was greater in the 1st toe, the middle metatarsal and the lateral heel, especially in the middle metatarsal and the lateral heel. Due to the arch-shaped structure of the human foot arch, the pressure intensity borne by the foot is mainly concentrated in the upper and lower ends of the foot, i.e., the toes, metatarsals and heel area. The midfoot is located in the center of the foot arch, so the pressure intensity borne by it is small.

Table 3: Average pressure in each region of the right foot under the action of the two insoles

Plantar area number	Area name	General sports insoles/kPa	Shock-absorbing functional insoles/kPa	P value
①	1st toe	101.3±10.2	92.4±12.4	0.004**
②	2nd to 5th toe	42.2±11.4	38.6±12.6	0.001**
③	Medial metatarsal	66.5±11.3	75.4±11.2	0.000**
④	Mid-metatarsal	167.3±32.1	192.4±42.6	0.001**
⑤	Lateral metatarsal	61.35±12.8	44.7±12.4	0.002**
⑥	Midfoot	0.2±0.1	0.1±0.1	0.215
⑦	Medial heel	71.3±22.6	93.6±27.7	0.002**
⑧	Lateral heel	125.9±19.7	105.6±25.8	0.001**

In addition, except for the midfoot region, all other regions of the foot showed significant changes in average plantar pressure after using the shock-absorbing insoles. The average pressure intensity of the 1st toe, 2nd to 5th toe, lateral metatarsal and lateral heel showed a significant decrease, while the average pressure intensity of the medial metatarsal, mid-metatarsal and medial heel showed a significant increase. This indicated that the pressure on the toes and the medial and lateral metatarsals was directed to the mid-metatarsal and the pressure on the lateral heel was directed to the medial heel after the use of the shock-absorbing insoles. The overall distribution of pressure intensity was closer to the midline of the foot and relatively more balanced.

Table 4: Impulse of different areas of the right foot under the action of the two insoles

Plantar area number	Area name	General sports insoles/Ns	Shock-absorbing functional insoles/Ns	P value
①	1st toe	10.5±1.1	9.4±2.5	0.012*
②	2nd to 5th toe	7.9±2.3	6.8±2.7	0.001**
③	Medial metatarsal	12.1±2.2	16.9±2.8	0.001**
④	Mid-metatarsal	52.2±14.8	69.1±15.5	0.000**
⑤	Lateral metatarsal	10.6±2.9	9.6±2.1	0.025*
⑥	Midfoot	0.1±0.1	0.0±0.0	0.236
⑦	Medial heel	16.7±11.4	22.2±10.2	0.002**
⑧	Lateral heel	41.6±15.7	35.6±15.8	0.000*

Also taking the right foot as an example, Table 4 shows the impulse of different areas of the foot during the running process under the action of two kinds of insoles, i.e., the impact received by the foot during the running process. It was seen from Table 4 that the distribution of the impulse on the 1st toe, middle metatarsal and lateral heel were large, especially the middle metatarsal and lateral heel, and the distribution of the impulse was almost the same as the distribution of the average pressure intensity. The intensity of pressure is the pressure per unit area, and the impulse is the product of the applied force and the action time. In the same running time period, the amount of impulse on the sole of the same person is proportional to the pressure, so the distribution of the impulse on the sole of the foot was nearly consistent with the average pressure intensity.

As a result, the impulse of the 1st toe, 2nd to 5th toe, lateral metatarsal and lateral heel were significantly reduced, while the impulse of the medial metatarsal, mid-metatarsal and medial heel were significantly increased after the use of shock-absorbing insoles. The reason for this is also the guiding effect of the shock-absorbing insole on the plantar pressure, which makes the pressure intensity closer to the midline of the foot, i.e., the distribution of the pressure intensity is more balanced, so the distribution of the impulse, which is proportional to the pressure intensity, is more balanced.

In addition to the above two measures, the center line of pressure is also a measure of the distribution of plantar pressure. The center line of pressure is a trajectory curve formed by the movement of the center of pressure on the bottom of the foot over time, and its shape can reflect the stability of the foot during running. When running is stable, there will not be multiple pressure peaks at the same moment, and the center line becomes longer as time goes on; when running is unstable, the center line of pressure will be shifted and shortened.

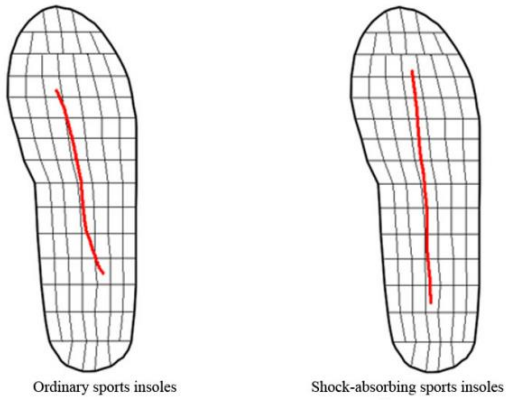

Figure 3. Distribution of the center line of pressure on the bottom of the foot after using the two kinds of insoles

In addition, the more balanced the pressure distribution on the foot during running, the flatter the center of pressure line will be along the direction of movement. Figure 3 shows the distribution of the center line of pressure after using the two types of insoles in one of the subjects during running. It was seen from Figure 3 that the center of the pressure line in the normal sport insole was shorter and had more lateral offset bending than the shock-absorbing sport insole, indicating that the subject was more stable during running with the shock-absorbing insole, and the pressure distribution in the foot was balanced.

CONCLUSION

In this paper, ten male volunteers from the Track and Field Department of Guilin University of Electronic Technology were selected as subjects to

test the biomechanical characteristics of the foot such as plantar pressure, impulse and pressure center line distribution after using ordinary insoles and shock-absorbing functional insoles. The shock-absorbing functional insoles were prepared independently by latex, EVA, conventional insoles, etc. The experimental results obtained are summarized as follows. (1) The average pressure intensity and impulse of the 1st toe, mid-metatarsal and lateral heel were relatively greater. (2) The average pressure intensity and impulse of the 1st toe, 2nd to 5th toe, lateral metatarsal and lateral heel were significantly reduced, while the average pressure intensity and impulse of the medial metatarsal, middle metatarsal and medial heel were significantly increased after using shock absorbing insoles. (3) The center line of pressure on the bottom of the foot after using the shock-absorbing sports insole was longer and straighter along the direction of motion, indicating more stable running.

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DETERMINATION OF THE IMMERSION RESISTANCE OF POLYMERIC BIOCOMPOSITES BASED ON TPU (THERMOPLASTIC POLYURETHANE) / RECYCLED TPU / PROTEIN AND ELASTOMERIC WASTE MIXTURE

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DETERMINATION OF THE IMMERSION RESISTANCE OF POLYMERIC BIOCOMPOSITES BASED ON TPU (THERMOPLASTIC POLYURETHANE) / RECYCLED TPU / PROTEIN AND ELASTOMERIC WASTE MIXTURE

ABSTRACT. Collection and recycling of waste from the footwear industry (elastomeric waste) and leather goods (protein waste), as well as other related fields, in order to use it to obtain new products, also easy to recycle and environmentally friendly, is increasingly emphasized. Both elastomeric and protein waste mixed with current elastomers, thanks to new technologies, lead to obtaining new polymer structures / composites (biocomposites) with high-performance properties. This article describes the obtaining of polymeric biocomposites based on thermoplastic polyurethane/recycled thermoplastic polyurethane/mixed protein and elastomeric waste, and also the determination of their immersion resistance in different immersion environments. Recycled thermoplastic polyurethane waste, but also mixed protein and elastomeric waste (SBR rubber) were modified in the first phase by cryogenic grinding. Subsequently only the mixed leather and SBR rubber waste was modified with 5% polydimethylsiloxane (PDMS). The polymer biocomposite specimens were characterized from the point of view of immersion in liquids in various immersion environments, after being conditioned at room temperature for 22-24 hours. The characterization is done according to the ISO 1817:2015 standard, following the variation in volume (ΔV) and mass (ΔM). The immersion was carried out in brown and tightly closed containers. The immersion time was 22 hours, at ambient temperature.
KEY WORDS: resistance to immersion, polymeric biocomposites, TPU, protein and elastomeric waste, recycled TPU

DETERMINAREA REZISTENȚEI LA IMERSIE A BIOCOMPOZITELOR POLIMERICE PE BAZĂ DE TPU (POLIURETAN TERMOPLASTIC) / TPU RECICLAT / DEȘEU PROTEIC ȘI ELASTOMERIC ÎN AMESTEC

REZUMAT. Colectarea și reciclarea deșeurilor provenite din industria de încălțăminte (deșeu elastomeric) și din domeniul marochinăriei (deșeu proteic), dar și alte domenii conexe, în vederea utilizării acestora pentru a obține noi produse și, de asemenea, ușor de reciclat și prietenoase cu mediul, este din ce în ce mai accentuată. Atât deșeurile elastomerice, cât și cele proteice în amestec cu elastomeri actuali, datorită noilor tehnologii, duc la obținerea de noi structuri / compozite polimerice (biocompozite) cu proprietăți performante. Prezenta lucrare descrie obținerea, dar și determinarea rezistenței la imersie în diferite medii de imersare a biocompozitelor polimerice pe bază de poliuretan termoplastic/poliuretan termoplastic reciclat/deșeu proteic și elastomeric în amestec. Deșeurile de poliuretan termoplastic reciclat, dar și deșeul proteic și elastomeric (cauciuc SBR) în amestec au fost modificate în primă fază prin măcinare criogenică. Ulterior doar deșeul de piele și cauciuc SBR în amestec a fost modificat cu 5% polidimetilsiloxan (PDMS). Epruvetele de biocompozite polimerice au fost caracterizate din punctul de vedere al imersării în lichide în medii de imersare diverse, după ce au fost condiționate la temperatura camerei timp de 22-24 de ore. Caracterizarea se face conform standard ISO 1817:2015 urmărind variația de volum (ΔV) și de masă (ΔM). Imersarea s-a realizat în recipiente de culoare brună și închise etanș. Timpul de imersie a fost de 22 de ore, la temperatură ambiantă.
CUVINTE CHEIE: rezistență la imersie, biocompozite polimerice, TPU, deșeu proteic și elastomeric, TPU reciclat

DÉTERMINATION DE LA RÉSISTANCE À L'IMMERSION DE BIOCOMPOSITES POLYMÈRES À BASE DE TPU (POLYURÉTHANE THERMOPLASTIQUE) / TPU RECYCLÉ / DÉCHETS PROTÉIQUES ET ÉLASTOMÈRES EN MÉLANGE

RÉSUMÉ. La collecte et le recyclage des déchets de l'industrie de la chaussure (déchets élastomères) et de la maroquinerie (déchets protéiques), ainsi que d'autres domaines connexes, afin de les utiliser pour obtenir de nouveaux produits, également faciles à recycler et respectueux de l'environnement, sont de plus en plus soulignés. Les déchets élastomères et protéiques mélangés aux élastomères actuels, grâce aux nouvelles technologies, conduisent à l'obtention de nouvelles structures polymères/composites (biocomposites) aux propriétés performantes. Le présent article décrit l'obtention, ainsi que la détermination de la résistance à l'immersion dans différents milieux d'immersion, de biocomposites polymères à base de polyuréthane thermoplastique/polyuréthane thermoplastique recyclé/déchets de protéines et d'élastomères en mélange. Les déchets de polyuréthane thermoplastique recyclé, mais également les déchets protéiques et élastomères (caoutchouc SBR) présents dans le mélange ont été modifiés dans une première phase par broyage cryogénique. Par la suite, seuls les déchets de cuir et de caoutchouc SBR présents dans le mélange ont été modifiés avec 5 % de polydiméthylsiloxane (PDMS). Les échantillons de biocomposites polymères ont été caractérisés du point de vue de l'immersion dans des liquides dans divers environnements d'immersion, après avoir été conditionnés à température ambiante pendant 22 à 24 heures. La caractérisation se fait selon la norme ISO 1817 : 2015 suivant la variation de volume (ΔV) et de masse (ΔM). L'immersion a été réalisée dans des récipients marron et bien fermés. La durée d'immersion est de 22 heures, à température ambiante.
MOTS-CLÉS : résistance à l'immersion, biocomposites polymères, TPU, déchets protéiques et élastomères, TPU recyclé

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INTRODUCTION

Thanks to advances in science and production, the development of new innovative materials, as well as techniques capable of eliminating waste and at the same time recycling and reintroducing it into the production process, are of topical interest. The increasing concern about the elimination of waste from the environment has led to the issuance of laws and regulations in this regard [1-4]. Innovative, high-performance materials have determined the emergence of new polymer structures based on elastomers (thermoplastics) and different types of wastes. Waste can come from various fields – footwear, leather goods, textiles, agriculture, etc. – and it can be: elastomeric, protein-based, textile fibers, and so on [5, 6]. By recycling and reusing it, we can also reduce the environmental impact and, of course, protect human health, through a less toxic working environment.

The reintroduction of a waste into a new composite requires certain modifications such as grinding, putting it in contact with various precursors [7, 8]. These precursors can be silanes (polydimethylsiloxane – PDMS) and are used to improve the properties of new composites [9-11]. In mixtures based on thermoplastic elastomers (TPU) [12, 13] and not only, natural protein, cellulosic and other types of waste can successfully replace inorganic fillers such as silicon or carbon black, etc., also leading to formation of biocomposites [8-11]. Thermoplastic polyurethane is resistant to abrasion, low temperatures, aggressive working environments, it has adhesion to the surface and is resistant to slipping, it returns to its original shape when it is deformed, and the working temperature is low: 80°C. However, these properties can be improved by adding compatibilizers such as PE-g-MA [7, 8, 14, 15].

In this work, polymer biocomposites based on TPU, TPUW (recycled), protein and elastomeric waste (SBR) in a modified/unmodified mixture with PDMS (5%) and PP-g-MA (compatibilizer) were obtained using the mixing technique on a Plasti-Corder Brabender mixer with a capacity of 350 cm^3, according to the working recipe [16-20]. Polymeric biocomposites were tested in terms of solvent behavior by appropriate techniques. The solutions used for immersion were oil, HCl 30%, NaOH 10% [21].

EXPERIMENTAL

Materials

The following materials were used in making the polymer biocomposites [11]:

- TPU – Thermoplastic Polyurethane: specific gravity - 1.03 g/cc, hardness – 65-85 Sh°A, tensile strength - >20 N/mm^2, colour – black, melt temperature of 170°-190°C, from MD Graphene SL, Spain;
- PP-g-AM – polypropylene-graft-maleic anhydride: density – 0.91 g/cm^3, hardness – 45 Sh°D, melting point – 117°C, MFI – 2 g/10 min (190°C/2.16 kg), viscosity 330000 cps, colour – honey yellow, from PolyRam Group;
- TPUW – recycled thermoplastic polyurethane waste, from the footwear industry, cryogenically ground to sizes of approximately 0.3-0.5 mm;
- Mixed leather and butadiene-styrene rubber (SBR) waste: from the footwear industry, cryogenically ground to micrometric sizes of 0.35 mm;
- PDMS – Polydimethylsiloxane fluid, from Sigma-Aldrich, Inc., USA.

Preparation of Polymeric Composite

Polymeric biocomposites based on TPU/recycled TPUW/mixed protein and elastomeric waste/PP-g-MA were obtained on a Brabender mixer (Brabender GmbH&Co KG, Duinsburg, Germany). Stages for obtaining polymeric biocomposites are the following [11], Figure 1: collection of recycled TPU waste, but also of mixed leather and SBR rubber waste; cryogenic grinding of waste to sizes of 0.3-0.5 mm using a cryogenic mill at 12.000 rpm (Retsch ZM 200, Verder Scientific, Germany), and using dry ice as a cooling agent, in the form of 3-6 cm pellets; waste modification; dosage of raw materials that are

used to obtain polymer biocomposites – Table 1; obtaining polymeric biocomposites through the mixing technique using the Plasti-Corder Brabender mixer; obtaining dumbbell-type specimens to standard size on an electric laboratory press (Fortune Press, TP/600 model, Fontijine Grotness Vlaardingen, the Netherlands); tests according to the standards in force.

Table 1: Formulation of biopolymeric composite based on TPU, TPUW waste, mixed leather and SBR rubber waste and PE-g-MA [11]

Ingredients	UM	Sample								
	%	MM	T20	T60	T80	TBB1	TBB2	TBB11	TBB12	TBB13
TPU	%	100	80	40	20	80	80	80	80	80
Recycled TPU	%	0	20	60	80	-	-	20	-	-
Leather and SBR rubber waste	%	-	-	-	-	20	-	-	20	-
Leather and SBR rubber waste modified with 5% PDMS	%	-	-	-	-	-	20	-	-	20
PE-g-MA 5%	%	-	-	-	-	-		5	5	5

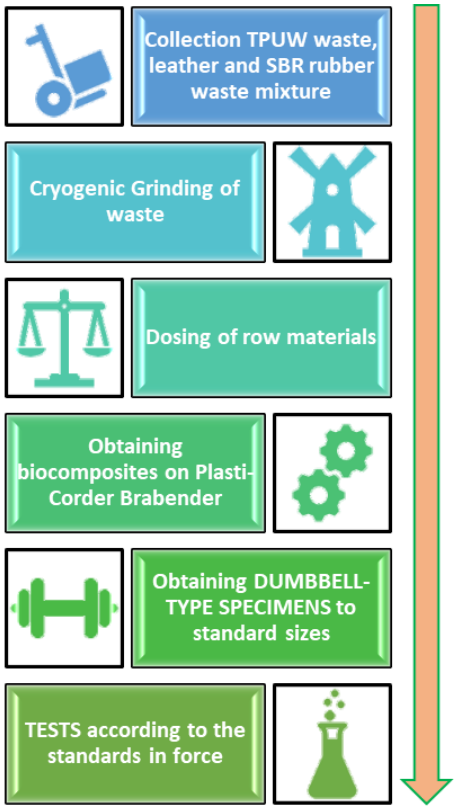


Figure 1. The stages of obtaining polymer biocomposites based on TPU/recycled TPUW/elastomer and protein waste in mixture/PE-g-MA

The working method and parameters for obtaining polymer biocomposites based on TPU/recycled TPUW/mixed protein and elastomeric waste/PE-g-MA is shown in Table 2 [11].

Table 2: Working method using the Brabender Plasti-Corder mixer [11]

The order of introducing the ingredients	Time (minutes)	Working speed, rpm	Working temperature, °C
TPU	2’ (TPU plasticization)	30 rpm	160°C
Recycled TPUW (in the proportion of 20, 60, 80%) - and ingredients according to the working recipe	4’	30 rpm	160°C
Leather and SBR rubber waste in mixture, modified with PDMS - and ingredients according to the working recipe	4’	30 rpm	160°C
Mixture homogenization	5’	80 rpm	160°C

The specimens for testing were obtained in the laboratory-scale electric press by pressing between its plates, in forming molds, by the compression method according to the following parameters, Table 3.

Table 3: Vulcanization parameters for making specimens in the electric press for mixtures based on TPR/TPUW/mixed leather and SBR rubber waste/PE-g-MA [11]

Vulcanization parameters (All the samples were carried out at the same parameters)	
Vulcanization temperature	160°C
Pressing force	300 kN
Preheating time	3’
Press time	3’
Cooling time	10’
Cooling temperature	45°C
The samples are conditioned for 24 h at ambient temperature and then subjected to testing	

The waste was modified by cryogenic grinding, a process in which the chemical bonds of the polymer chains of the vulcanized elastomer, and those of the leather waste, respectively, were broken under the action of mechanical forces. The process of modifying this waste continued by adding 5% PDMS under temperature conditions (70°C) and mixing every 15-20 minutes for 3-4 hours, with the aim of forming intermolecular or even chemical bonds between the waste and PDMS, to eliminate the tendency of waste particles to agglomerate. At the same time, this procedure ensures an improved dispersion of the waste particles in the polymer matrix. PDMS has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein and rubber waste in the polymer matrix.

Characterization of Polymer Biocomposites

Polymer biocomposites were characterized in terms of immersion in various liquid environments. The characterization was performed according to the ISO 1817:2015 standard [21, 22], following the volume and mass variation. The two methods used according to the mentioned standard are: volumetric method and gravimetric method. Immersion is done in a liquid medium, in dark and sealed vessels, for 22 hours. The immersion mediums were oil, sodium hydroxide 10% and sulfuric acid 30%. For each sample, three discs were used. The specimens that are subjected to the immersion have a thickness of 2±0.2 mm and a volume of 1-3 cm^3. After the 22 h period, the specimens are removed from the test liquids, the excess

liquid is removed by gently dabbing with a filter paper. Then the samples are weighed, and the calculated results are expressed as the percentage difference compared to the initial value.

The calculation for determining immersion in liquids is done according to equation 1 for mass variation and equation 2 for volume variation from the standard [22]:

$$\Delta m_{100} = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where:
m_0 = initial mass of the specimen,
m_1 = mass of the specimen after immersion,
and the result is expressed as the average value for the three weighed samples.

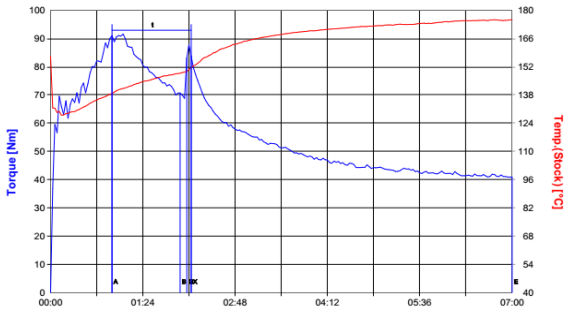
$$\Delta v_{100} = \left[\left(\frac{m_i - m_{i,w} + m_{s,w}}{m_0 - m_{0,w} + m_{s,w}} - 1\right) x\ 100\right] \quad (2)$$

where:
m_0 = initial mass of the specimen,
m_i = mass of the specimen after immersion,
$m_{0,w}$ = initial mass of the specimen in water,
$m_{i,w}$ = mass of the specimen after immersion in water,
$m_{s,w}$ = mass of sinker, if used, in water.
The final result is expressed as the average value for the three tested specimens.

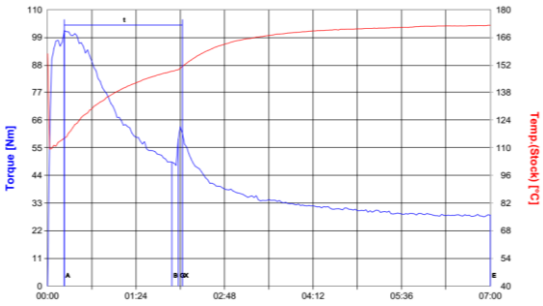
RESULTS AND DISCUSSIONS

Characteristics of Plastograms (Obtained from Brabender Plasti-Corder)

The polymer biocomposites were made using the mixing technique on a Brabender mixer with a capacity of 350 cm^3, which records the variation of torque and temperature versus time. For each mixture, the variation of torque and temperature was recorded as a function of time, and the diagrams obtained are shown in Figures 2-6.

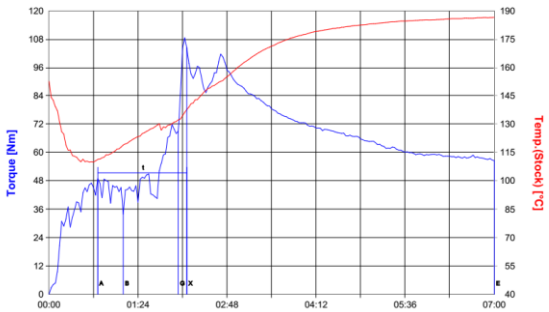


Sample MM

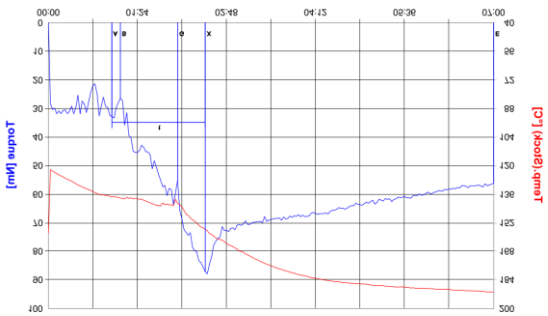


Sample T60

Figure 2. The torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining the MM (control) and T60 samples



Sample TBB1



Sample TBB2

Figure 3. The torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining samples (TBB1 and TBB2)

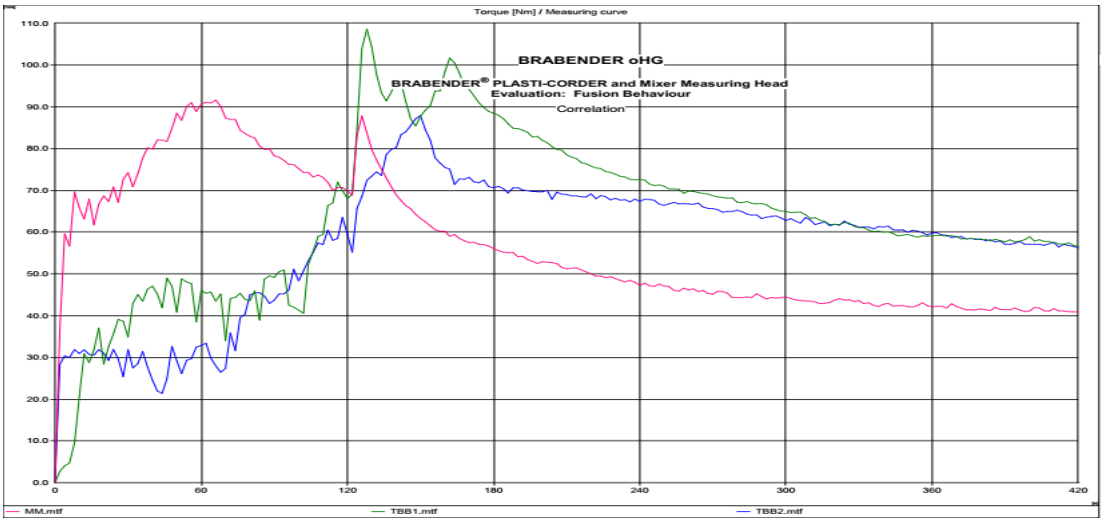


Figure 4. The torque variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining the polymer biocomposite mixtures, samples MM (control), TBB1 and TBB2

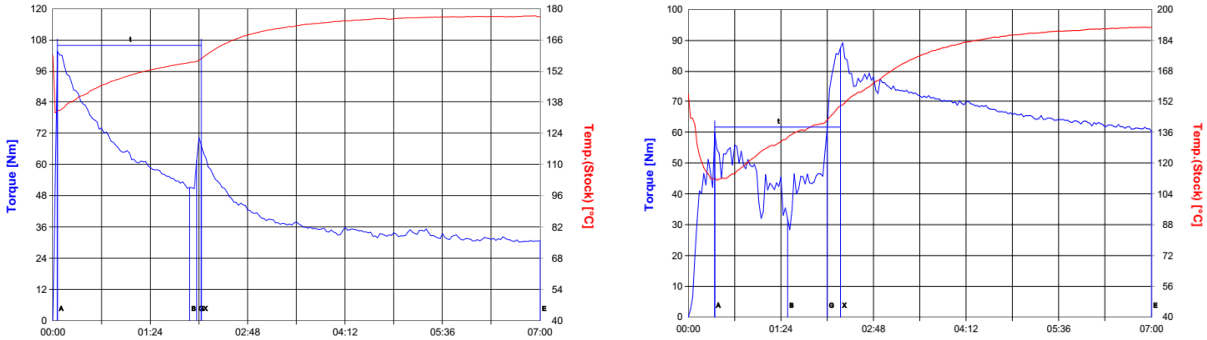


Figure 5. The torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining samples TBB11 and TBB13

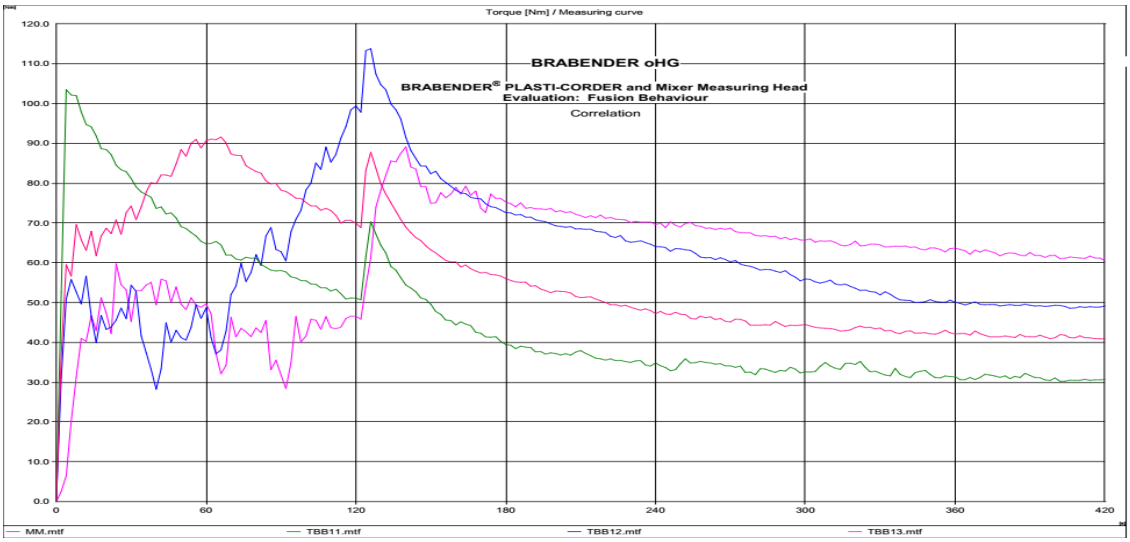


Figure 6. The torque variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining the polymeric biocomposite mixtures, samples MM (control) and the TBB11-TBB13 series

From the torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer during the preparation of the recipes (MM, T20, T60, T80, TBB1, TBB2 and TBB11-TBB13 series), presented in Figures 2-6, it can be noted that for each series of tests carried out, the working method is respected according to the established work parameters. In A-B part, which represents the plasticization of the thermoplastic polyurethane for 2 minutes at 30 rpm, the torque increases. As the torque increases, the temperature in the working chamber (mixing chamber) also increases due to the friction of the screws of the Brabender mixer. As the thermoplastic polyurethane plasticizes and its homogenization takes place, the torque decreases in the A-B part. After the TPU plasticizes, the rest of the ingredients are introduced, following the order specified in the working recipe (see Table 1) in 4', at 30 rpm, during which the mixer is open, so that the torque shows variations between points B and X. Mixing continues for 5' at 80 rpm, at a temperature of 160°C, until homogenization, so that the torque, due to the homogenization of the mixture, has a maximum value.

Determination of Resistance to Immersion

Immersion was carried out in dark-brown containers (tightly closed). The immersion time was 22 hours, at ambient temperature. The mixtures were analyzed from the point of view of behavior after immersion in the established liquids (oil, NaOH 10%, HCl 30%), and the values calculated according to the standard for mass and volume variation are shown in Table 4 [10, 23-26].

Table 4: Immersions of polymer biocomposites based on TPR/TPUW/mixed leather and SBR rubber waste/PP-g-MA

Sample		Immersion environment		
		Oil (ASTM)	Hydrochloric acid 30%	Sodium hydroxide 10%
MM	ΔM	1.22	0.36	-0.22
	ΔV	1.36	0.77	-0.40
T20	ΔM	0.54	1.036	-0.24
	ΔV	1.04	1.28	-0.51
T60	ΔM	-0.28	0.60	0.18
	ΔV	-0.74	1.07	0.51
T80	ΔM	0.34	0.40	0.04
	ΔV	0.77	0.76	0.24
TBB1	ΔM	1.01	0.66	0.42
	ΔV	1.08	0.71	0.65
TBB2	ΔM	1.47	1.7	-3.02
	ΔV	1.72	2.08	-3.60
TBB11	ΔM	0.51	0.73	-0.28
	ΔV	0.72	0.85	-0.57
TBB12	ΔM	1.61	1.17	-0.57
	ΔV	1.82	1.36	-0.66
TBB13	ΔM	1.68	1.10	-4.72
	ΔV	1.18	1.30	-5.34

Following the immersion in ASTM oil solutions, sodium hydroxide 10% and hydro-chloric acid 30%, as well as the values calculated for the mass variation (ΔM) and the volumetric variation (ΔV), the following are found:

- For polymer composites based on TPU/TPUW (recycled thermoplastic polyurethane), the mass and volumetric variations depend on the concentration of TPUW introduced into the mixture, concentration between 20 and 80% (samples T20-20%, T60-60%, T80-80%);
- For polymer biocomposites based on TPU/recycled TPU, mixed leather and SBR rubber waste, unmodified or

modified with 5% PDMS and compatibilized with PE-g-MA, both mass and volumetric variation are influenced by the compatibilizer used and the modification of leather and SBR waste mixed with 5% PDMS. The values are approximately close, which demonstrates a good compatibility, as well as a good homogenization of the waste in the polymer biocomposite mass;

- After immersing the samples in the relevant solutions, they do not undergo changes in the appearance of the surface through color change or swelling through liquid absorption. This indicates that both the working (processing) parameters, the established production technologies, and the waste modification method are the optimal ones, demonstrating at the same time a good mixing of the ingredients.

CONCLUSION

The polymer biocomposites based on TPU, TPUW, protein and elastomeric waste in a mixture modified/unmodified with PDMS and compatibilized with PP-g-MA were obtained by the mixing technique on a Plasti-Corder Brabender mixer with a capacity of 350 cm^3, according to the working recipe. Using the mixer, the variation of torque and temperature versus time is recorded for each mixture, and it can be observed that for each series of tests carried out, the working method is respected according to the established working parameters.

The thermoplastic polyurethane waste and protein and SBR rubber waste used in the mixture underwent changes both by cryogenic grinding and by the use of PDMS, which has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein and rubber waste in the polymer matrix.

Determination of the resistance to immersion of polymer biocomposites was tested by immersion in different environments (ASTM oil, NaOH 10%, HCl 30%) and the mass and volume variation was calculated according to the standard. After immersion in the solutions, it is found that the samples do not undergo changes in the appearance of the surface due to color change or swelling due to liquid absorption, thus demonstrating a good homogenization of the ingredients (a good compatibility, as well as a good homogenization of the waste in the polymer biocomposite mass).

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OBTAINING NEW BIOEMULSIONS BASED ON LAVENDER EXTRACT AND SURFACTANTS

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OBTAINING NEW BIOEMULSIONS BASED ON LAVENDER EXTRACT AND SURFACTANTS

ABSTRACT. New bioemulsions were created using biotechnologies based on lavender extract (oil) and two surfactants: Tween® 20 and Tween® 80 mixture: E1 – lavender oil/Tween® 20/water; E2 – lavender oil/ Tween® 80/water; E3 – lavender oil/ Tween® 20 and Tween® 80 (ratio 1:1)/water, for different concentrations (28.56%, 7.14%) of lavender oil, in order to improve surface properties with applications in leather industry. More concentrated emulsions with oil lavender (28.56%) were marked E1c, E2c, E3c. In the process of finishing the leathers by spraying with six types of emulsions obtained compared to an untreated leather, the aim was to improve the antifungal, antimicrobial properties as well as the softness, appearance of the leathers. The order of introducing components in the developed biotechnologies, the working conditions, and especially the choice of the concentration of surfactants >CMC, are essential in the solubilization of vegetable oils and obtaining the desired bioemulsions. Comparatively, bioemulsions were made for the version with two surfactants, but instead of lavender, immortelle was introduced, resulting in emulsions: Lemulsion, Iemulsion. The bioemulsions and leathers processed with them were analyzed by FTIR-ATR spectroscopy, DLS and microbiological tests. It can be seen that the leather with the largest amount of lavender after processing with concentrated emulsions is E3c (having the highest intensity over the entire spectral range) and the maximum absorption specific to lavender oil was found. The lavender oil is fixed better on the leathers than the immortelle oil, with the new bioemulsions created.

KEYWORDS: new bioemulsions, biotechnologies based on lavender extract and surfactants, immortelle, leathers processed

OBȚINEREA UNOR NOI BIOEMULSII PE BAZĂ DE EXTRACT DE LAVANDĂ ȘI SURFACTANȚI

REZUMAT. S-au creat noi bioemulsii utilizând biotehnologii bazate pe extract de lavandă (ulei) și doi agenți tensioactivi: amestec Tween® 20 și Tween® 80: E1 – ulei de lavandă/Tween® 20/apă; E2 – ulei de lavandă/Tween® 80/apă; E3 – ulei de lavandă/Tween® 20 și Tween® 80 (raport 1:1)/apă, pentru diferite concentrații (28,56%, 7,14%) de ulei de lavandă, pentru a îmbunătăți proprietățile suprafeței cu aplicații în industria de pielărie. Emulsiile mai concentrate cu ulei de lavandă (28,56%) s-au notat cu E1c, E2c, E3c. În procesul de finisare a pieilor prin pulverizare cu șase tipuri de emulsii obținute comparativ cu o piele netratată, s-a urmărit îmbunătățirea proprietăților antifungice, antimicrobiene precum și moliciunea, aspectul pieilor. Ordinea introducerii componentelor în biotehnologiile dezvoltate, condițiile de lucru și mai ales alegerea concentrației de surfactanți >CMC sunt esențiale în solubilizarea uleiurilor vegetale și obținerea bioemulsiilor dorite. Comparativ, s-au realizat bioemulsii pentru varianta cu doi surfactanți, dar în loc de lavandă s-a introdus imortelă, rezultând emulsiile: Lemulsion, Iemulsion. Bioemulsiile și pieile prelucrate cu acestea au fost analizate prin spectroscopie FTIR-ATR, DLS și teste microbiologice. Se poate observa că pielea cu cea mai mare cantitate de lavandă după prelucrare cu emulsii concentrate este E3c (având cea mai mare intensitate pe întregul interval spectral) și s-a determinat absorbția maximă specifică uleiului de lavandă. Uleiul de lavandă se fixează mai bine decât cel de imortelă pe piei, cu noile bioemulsii create.

CUVINTE CHEIE: noi bioemulsii, biotehnologii bazate pe extract de lavandă și agenți tensioactivi, imortelă, piei prelucrate

L'OBTENTION DE NOUVELLES BIOÉMULSIONS À BASE D'EXTRAIT DE LAVANDE ET DE TENSIOACTIFS

RÉSUMÉ. De nouvelles bioémulsions ont été créées par les biotechnologies à base d'extrait (huile) de lavande et de deux tensioactifs : Tween® 20 et Tween® 80 mélange : E1 – huile de lavande/Tween® 20/eau ; E2 – huile de lavande/Tween® 80/eau ; E3 – huile de lavande/Tween® 20 et Tween® 80 (rapport 1:1)/eau, pour différentes concentrations (28,56%, 7,14%) d'huile de lavande, afin d'améliorer les propriétés de surface avec des applications dans l'industrie du cuir. Les émulsions plus concentrées en huile de lavande (28,56%) ont été notées : E1c, E2c, E3c. Dans le processus de finition des cuirs par pulvérisation de six types d'émulsions obtenues par rapport à un cuir non traité, le but était d'améliorer les propriétés antifongiques, antimicrobiennes ainsi que la douceur, l'aspect des cuirs. L'ordre d'introduction des composants dans les biotechnologies développées, les conditions de travail et surtout le choix de la concentration en tensioactifs >CMC, sont essentiels à la solubilisation des huiles végétales et à l'obtention des bioémulsions souhaitées. Comparativement, des bioémulsions ont été réalisées pour la version avec deux tensioactifs, mais à la place de la lavande, de l'immortelle a été introduite, ce qui a donné des émulsions : Lemulsion, Iemulsion. Les bioémulsions et les cuirs traités avec celles-ci ont été analysés par spectroscopie FTIR-ATR, DLS et tests microbiologiques. On constate que le cuir qui contient la plus grande quantité de lavande après traitement avec des émulsions concentrées est le E3c (ayant l'intensité la plus élevée sur toute la gamme spectrale) et on a déterminé l'absorption maximale propre à l'huile de lavande. L'huile de lavande se fixe mieux que l'huile d'immortelle sur les cuirs, grâce aux nouvelles bioémulsions créées.

MOTS CLÉS : nouvelles bioémulsions, biotechnologies à base d'extrait de lavande et de tensioactifs, immortelle, cuirs traités

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INTRODUCTION

This paper presents biotechnologies to create new bioemulsions, based on lavender extract (oil) for different concentrations (28.56%, 7.14%) and two surfactants: Tween® 20 and/or Tween® 80 [1], in order to improve surface properties with applications in leather industry.

Lavender oil is an essential oil obtained by distillation from the flower spikes of certain species of lavender. There are over 400 types of lavender worldwide with different scents and qualities. Two forms of lavender oil are distinguished, lavender flower oil, a colorless oil, insoluble in water, having a density of 0.885 g/mL; and lavender spike oil, a distillate from the herb *Lavandula latifolia* (Figure 1), having a density of 0.905 g/mL. Like all essential oils, it is not a pure compound; it is a complex mixture of phytochemicals, including linalool and linalyl acetate.

Figure 1. Image of *Lavandula latifolia*

The phytochemical composition of lavender oil varies from species to species, consisting primarily of monoterpeneoid and sesquiterpeneoid alcohols [2-6]. Linalool (20-35%) and linalyl acetate (30-55%) dominate, with moderate levels of lavandulyl acetate, terpinen-4-ol and lavandulol, 1,8-cineole, camphor, limonene and tannins. Lavender oil typically contains more than 100 compounds, although many of these are at negligible concentrations. Lavender oil has been used for perfume, aromatherapy and skincare applications, but these uses have no clinical benefit. Lavender oil is used in massage therapy as a way of inducing relaxation through direct skin contact.

Tween 80 and Tween 20 are biocompatible surfactants [1-6]. Tween 80 is a polyethylene sorbitol ester, also known as Polysorbate 80, PEG (80) sorbitan monooleate, polyoxyethylenesorbitan monooleate. Tween 20 is a polyoxyethylene sorbitol esteris, a frequently used member of the polysorbate family. These have been used as emulsifying agents for the preparation of stable oil-in-water emulsions. Tween is a group of non-volatile surfactant derivatives derived from glycerol esters. Tween-20 and Tween-80 vary in chemical and physical properties very much but are usually solubilized or suspended in water. Tween-20 is mainly used as an effective binding agent in the production of foam and other polymers by means of its high solubility and low boiling point. Tween also has other important uses like as a thermosetting agent in the process of manufacturing thermosetting plastics and as an adhesive for repairing paper materials. It also helps in the manufacture of plastic parts and even metal parts.

The most important usage of Tween is its application as an oil absorber and emulsifier. It is also used in the manufacturing of water-based and oil-based goods like shampoos, facial masks, hair gels, ointments, soaps, and cleansers. These goods are usually produced using emulsifying waxes.

In this research the new bioemulsions created and leathers processed with them were analyzed by FTIR-ATR spectroscopy, DLS and microbiological tests.

EXPERIMENTAL

Materials and Methods

In order to obtain new bioemulsions the following materials have been used: Tween 20 and Tween 80 from Sigma-Aldrich; lavender oil from “VIORICA” company.

The experimental techniques used in this paper consist in:

- “MALVERN” zetasizer-nano equipment, with measuring range between 0.3 nm-60.0 microns and zeta potential determination with an accuracy of +/-2%;
- JASCO FTIR-ATR spectrophotometer.

A number of four samples of bioemulsions were prepared in the following working conditions: Tween 20 or/and Tween 80 at 1:1 ratio, temperature=45°C for 60

minutes with lavender or immortelle oil – c=7.14%, Figure 2. More concentrated emulsions with oil lavender (28.56%) were created and marked: E1c, E2c, E3c. Comparatively, bioemulsions were made for the version with two surfactants, but instead of lavender, immortelle was introduced, resulting in emulsions: Lemulsion, Iemulsion.

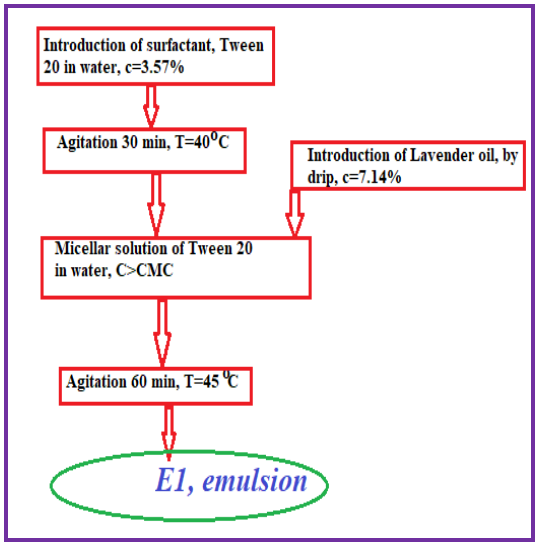
a) b) c) d)

Figure 2. Image of bioemulsions: a) 1 – E1 – lavender oil/Tween® 20/water; 2 – E2 – lavender oil/Tween® 80/water; 3 – E3 – lavender oil/ Tween® 20 and Tween® 80 (ratio 1:1)/water; 4 – Iemulsion – immortelle oil/ Tween® 20 and Tween® 80 (ratio 1:1)/water; b) Lavender oil; c) Tween 20; d) Tween 80

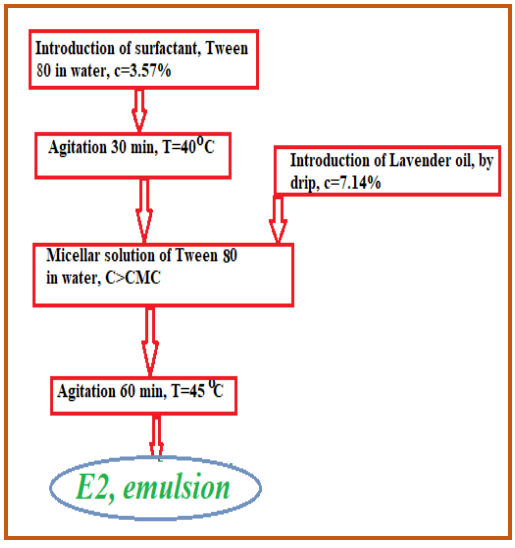
RESULTS AND DISCUSSIONS

Obtaining New Bioemulsions Based on Lavender or Immortelle Oil and Surfactants

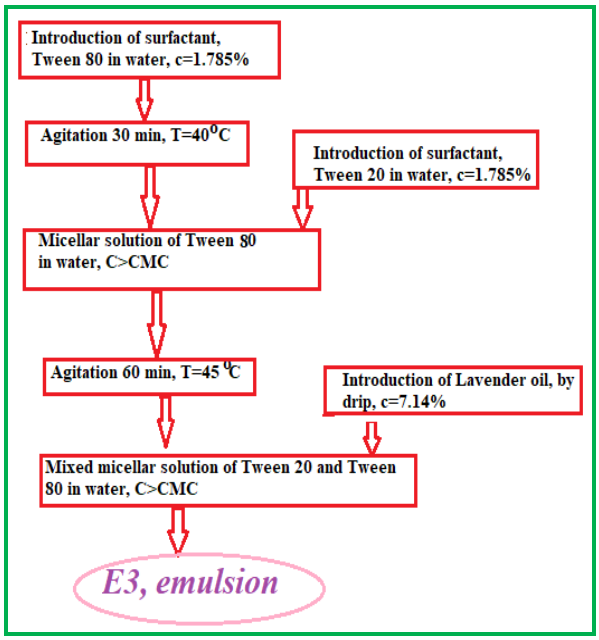
Aqueous emulsions were obtained using two surfactants with different hydrophobic chains, Tween 20 and Tween 80, in which oil plant extracts (lavender or immortelle oil) were introduced. According to original innovative biotechnologies in Figure 3, three types of lavender-based bioemulsions were made: E1, E2, E3. The preparation biotechnologies of bioemulsions were optimized, introducing a larger amount of lavender, c=28.56%, four times higher than c=7.14%. The new emulsions were marked: E1c, E2c, E3c and the leathers processed with them: E1l, E2l, E3l. The antimicrobial and antifungal effect was increased with the increase in the amount of lavender.



a)



b)



c)

Figure 3. Biotechnologies for obtaining three types of bioemulsions with lavender oil: a) E1; b) E2; c) E3

For immortele oil, the method of obtaining emulsions is similar to the one in Figure 3, but the lavender oil is replaced with the immortele oil. Only the E3 emulsion was made for comparison, in which the lavender oil was introduced once and then the immortelle oil, obtaining the emulsions marked: Lemulsion, Iemulsion. The E3 emulsion variant with the two surfactants, Tween 20 and Tween 80, in a 1:1 ratio was selected because it is the most stable over time (1 month). The way of introducing surfactants and vegetable oil in obtaining emulsions is very important. The surfactant micellar solution is always made in water at a concentration above the micellar critical concentration – CMC, and then the vegetable oil is added drop by drop and mixed. The chosen temperature is 40-45°C for a good solubilization of the vegetable oil in the surfactant micelles. When there are two surfactants, micellar solutions in water are made separately for them, then the two solutions are mixed and mixed micelles in water are obtained. In the solution of mixed micelles, the vegetable oil is introduced drop by drop, stirring at the appropriate temperature. In the end, the emulsion is obtained with lavender oil solubilized in the mixed micelles. The yield of multiple drop formation decreases rapidly as the homogenization time increases. Bioemulsions are formed and the properties derive from the surfactants used, as well as the conditions and working parameters. This phenomenon is controlled by the concentration of lavender or immortelle oil, surfactants**,** temperature, pH=4.

Mechanism of Lavender Oil Solubilization in Surfactant Micelles

In order to solubilize the lavender oil, many media are adopted, among which surfactant solubilization is important. In this research, the interaction of lavender oil with two nonionic tween surfactants, Tween 20 and Tween 80, was investigated. A mechanism for the solubilization of lavender oil in surfactant micelles was proposed, Figure 4.

The effect of the length of the carbon chain on the interaction was analyzed by FTIR-ATR spectroscopy. The experimental results suggested that Tween 80 was most efficient out of the two surfactants taken for the study. The order of stability is given as Lavender oil – Tween 80 > Lavender oil – Tween 20.

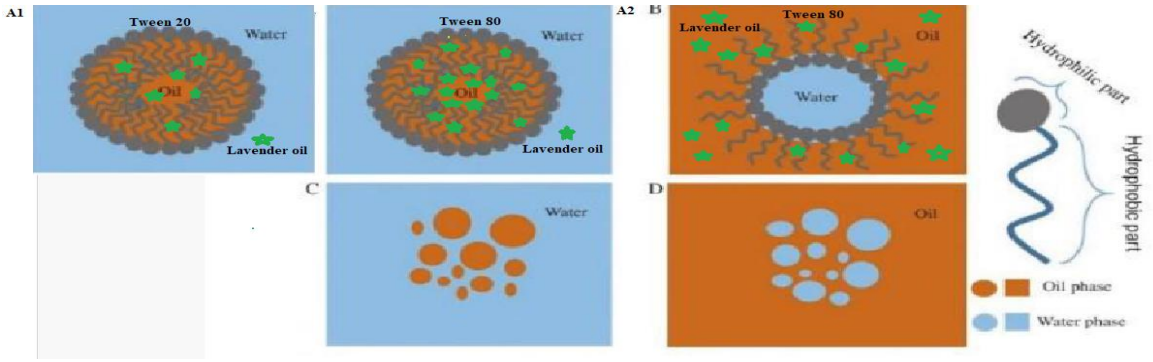


Figure 4. Proposed mechanism for solubilization of lavender oil in Tween 20 or Tween 80 surfactants. Schematic representation of oil-in-water (O/W)-A1-A2; water-in-oil (W/O)-B; emulsions, oil droplets in water-C; and water droplets in oil-D

Lavender oil is hydrophobic and gets stuck in the core of the micelles but also on the alkyl ends of the hydrophobic chains. For Tween 80, the amount of solubilized lavender oil is higher than in the case of Tween 20, because it has a larger hydrophobic chain. Interaction forces are responsible. The mechanism is similar for immortelle oil.

Characterization of the Emulsions Obtained and the Leathers Processed with Them

Characterization by FTIR-ATR Spectroscopy

The FTIR-ATR spectroscopy is part of the nondestructive analytical methods whose objective is to determine the functional groups of the analyzed sample by absorbing IR radiation at characteristic frequencies, thus obtaining an individual spectrum. FTIR-ATR spectrometers being coupled to computers equipped with specialized software can process the spectra and also store databases with a rich content of IR spectra of known substances that can be used in the automatic identification of a new, unknown substance. Emulsions obtained based on surfactants and lavender or immortele oils were used in the processing of leathers in different variants. The emulsions and leathers processed with them were analyzed spectrophotometrically by FTIR-ATR. Lavender oil has the following characteristic absorption maxima at the wavenumbers: 2966 cm^{-1}, 2927 cm^{-1}, 1735 cm^{-1}, 1450 cm^{-1}, 1370 cm^{-1}, 1240 cm^{-1}. The spectrum of immortelle oil is also shown in Figure 5.

The overlap of the FTIR-ATR spectra for the obtained emulsions E1, E2, E3 and lavender oil are illustrated in Figure 6.

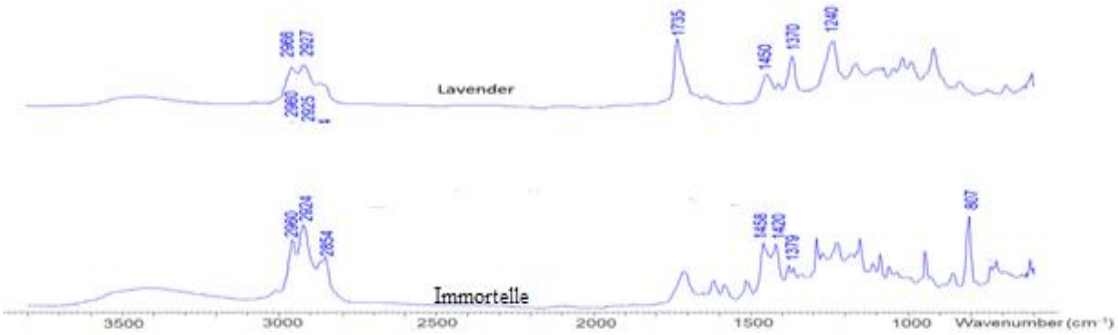


Figure 5. FTIR-ATR spectra for lavender and immortelle oils

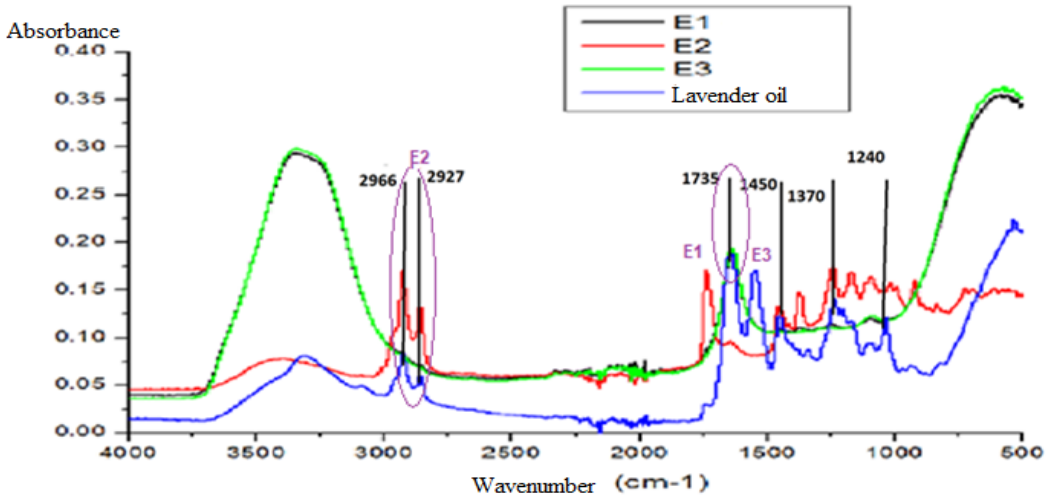
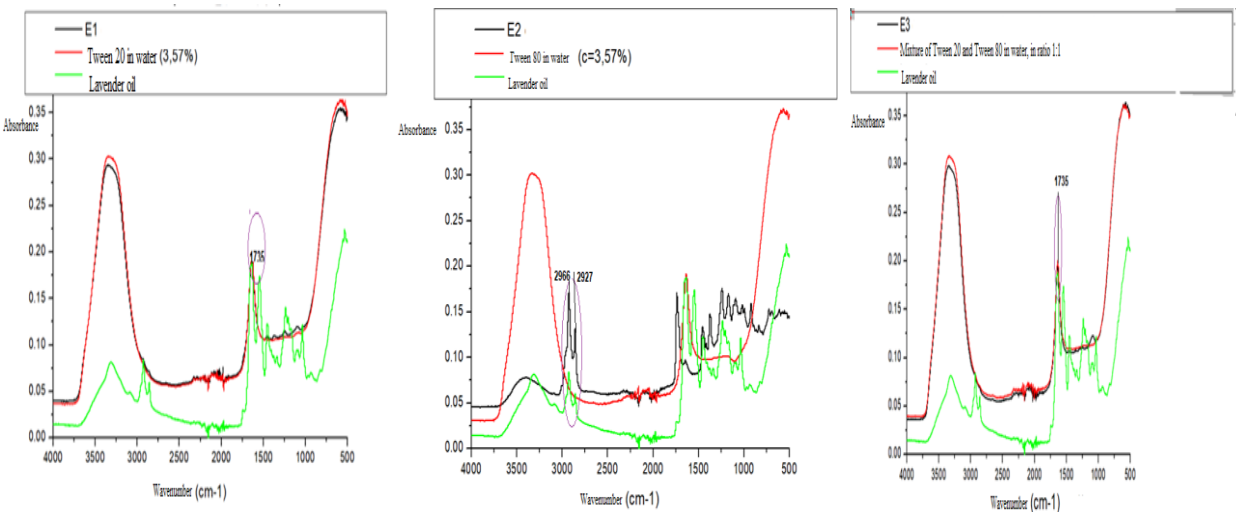


Figure 6. The overlap of the FTIR-ATR spectra for the obtained emulsions E1, E2, E3 and lavender oil

For the FTIR-ATR spectrum of lavender oil the absorption maxima corresponding to the range of wavenumbers ~1375-1450 cm^{-1} are due to the functional group $=CH_2$, originating from a plane deformation at 1420 cm^{-1}. The presence of the $=CH_2$ grouping increases the intensity of the absorption maxima in the range of wavenumbers: 1330–1410 cm^{-1} specific to the existence of terpenes. The absorption maximum at the wavenumber ~1450 cm^{-1} is the result of the overlap of the CH_2 deformation with the asymmetric CH_3 deformation (the intensity of the absorption maximum being proportional to the number of CH_2 and CH_3 groups present). The range of wavenumbers: 3400–3500 cm^{-1} is specific to oil extracts from the *Lamiaceae* family that have a high content of phenolic compounds and flavonoids. The absorption maximum at the wavenumber: 842 cm^{-1} represents a weak skeletal vibration of isopropyl ($R_1R_2C=CHR_3$), the deformation being out of plane for undeformed, weakly strained systems, i.e. for cyclohexene derivatives. The range of wavenumbers: 1635–1650 cm^{-1} is characteristic of low intensity maxima respectively for $RHC=CH_2$ i.e. linalool and linalool acetate. The absorption maximum specific to the wavenumber: 1745 cm^{-1} is given by the carbonyl group. It can be seen from Figure 6 that the shape of the spectra of E1 and E3 emulsions is similar with higher intensity for E3 emulsion because it contains two surfactants, Tween 20 and Tween 80, compared to E1 which contains only Tween 20. It is found that the spectrophotometric imprint is stronger for Tween 20 than for Tween 80 because the spectrum for E3 which has two surfactants is almost identical to that for E1 which only has Tween 20. For E1 and E3 emulsions the presence of Tween 20 surfactant is given by two characteristic absorption maxima in the range of wavenumbers: 3250-3500 cm^{-1} (given by the phenolic groups) and 2000-2250 cm^{-1} (from the CH_2 and CH_3 groups present), Figure 7. The presence of lavender oil in the two emulsions E1-E3 is given by the significant absorption maximum at 1735 cm^{-1} specific to the carbonyl group but also by the identical spectral allure in the range of wavenumbers: 1450-1240 cm^{-1}. Emulsion E3 is more stable over time (1 month) than E1 (7 days). The presence of two surfactants gives greater stability to the E3 emulsion. Emulsion E2 (compared to E1 and E3) solubilizes lavender oil best, the allure of their spectra being very similar. The Tween 80 surfactant present in E2 emulsion solubilizes lavender oil better than Tween 20. Tween 80 has characteristic absorption maxima at wavenumbers: 3500 and 1750 cm^{-1}. Emulsion E2 has good stability for five days.



a) *b)* *c)*

Figure 7. The overlap of the FTIR-ATR spectra for the samples: a) E1, Tween 20 in water, lavender oil; b) E2, Tween 80 in water, lavender oil; c) E3, mixture of Tween 20 and Tween 80 in water, in ratio 1:1, lavender oil

The leathers were processed by spraying with the three obtained emulsions, E1, E2, E3 and were marked E1l, E2l, E3l (Figure 8) and then analyzed spectrophotometrically using FTIR-ATR.

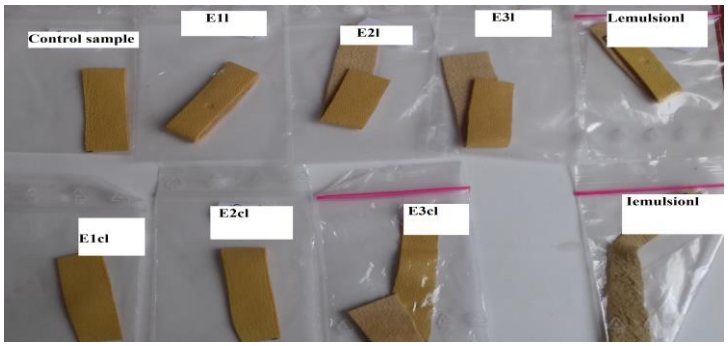


Figure 8. Image of the leathers processed with the three emulsions and oils (lavender and immortelle) and a control sample

To increase the antimicrobial and antifungal effect, the amount of lavender was increased four times in the emulsions. Emulsions marked with E1c, E2c and E3c were made and the leathers processed with these were marked E1cl, E2cl, E3cl. From Figure 9 it can be seen that the largest amount of lavender is found in the leather treated with the E2 emulsion (the spectrum intensity is the highest in the entire spectral range). The order of the lavender on the leather for the three emulsions is as follows: E2>E1>E3.

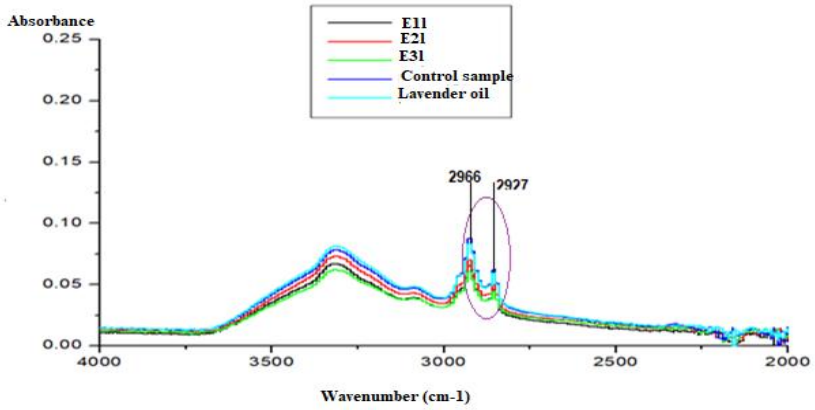


Figure 9. Overlay of FTIR-ATR spectra for leathers processed with emulsions E1, E2, E3, control sample, lavender oil

It can be seen from Figure 9 that all three leathers treated with emulsions contain lavender, the allure of the spectra of the leathers and lavender oil being similar. It can be seen from Figure 10 that the leather with the largest amount of lavender after processing with concentrated emulsions is E3c (having the highest intensity over the entire spectral range) and finding the maximum absorption specific to lavender oil. The order with the amount of lavender fixed on the leathers after processing with concentrated emulsions is E3c>E1c>E2c. The concentrated E3c emulsion is also the most stable >1 month.

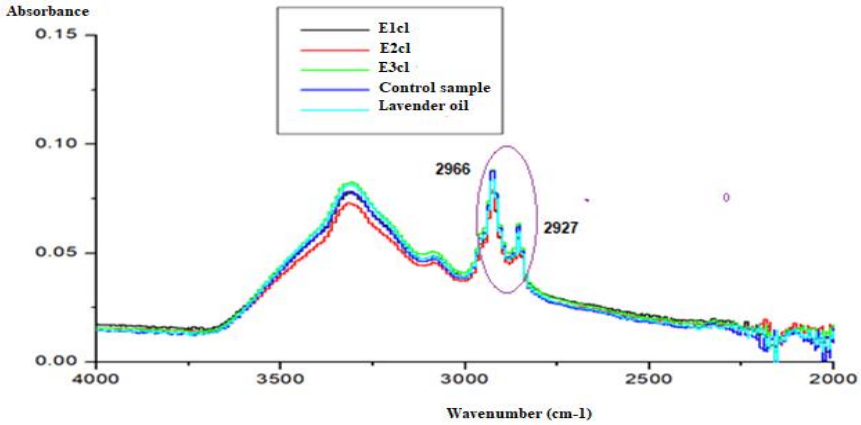


Figure 10. Overlay of FTIR-ATR spectra for leathers processed with emulsions E1cl, E2cl, E3cl, control sample, lavender oil

Characterization by DLS

The three types of emulsions were analysed by dynamic light scattering (DLS), Table 1.

Microbiological Tests of Leathers Processed with Emulsions

The microbiological tests of leathers processed with three emulsions against the attack of *Staphylococcus aureus* ATCC 6538 are presented in Table 2.

Table 1: Results of DLS for three emulsions: E1, E2, E3

Sample at room temperature	Average diameter (nm)	% Intensity	Zeta Potential (mV)
Multiple emulsion based on Tween 20 & Tween 80 mix, E3	27	76.3	-33
	195	19.1	
	351	4.6	
Multiple emulsion based on Tween 20, E1	657	91.7	-52
	22	8.39	
Multiple emulsion based on Tween 80, E2	102	100	-39

Table 2: Results of microbiological tests of leathers processed with three emulsions: E1, E2, E3

Sample	Results	R%	Log_{10}red
Inoculum concentration	T_0=1.5x10^{6}UFC/mL		
Control sample	T_0=1.5x10^{6}UFC/mL T_{24}=6.58x10^{3}UFC/mL	41	1.1
Multiple emulsion based on Tween 20 & Tween 80 mix, E3	T_0=1.5x10^{6}UFC/mL T_{24}=4x10^{3}UFC/mL	87.3	1.3
Multiple emulsion based on Tween 20, E1	T_0=1.5x10^{6}UFC/mL T_{24}=3.89x10^{3}UFC/mL	82.1	1.4
Multiple emulsion based on Tween 80, E2	T_0=1.5x10^{6}UFC/mL T_{24}=3.80x10^{3}UFC/mL	93	1.45

CONCLUSIONS

The conducted research has led to the following results:

1. The innovation consists in biotechnologies for obtaining new bioemulsions based on: lavender/(and/or) Tween® 20, Tween® 80/water and their use in leather finishing.

2. The order with the amount of lavender fixed on the leathers after processing with concentrated emulsions is: E3c>E1c>E2c. The lavender oil is fixed better than the immortelle oil on the leathers, in the created bioemulsions, as shown by the spectral allure and the higher intensity in the case of the leather with lavender compared to the one with immortelle.

3. Tween 20 and Tween 80 are non-ionic surfactants that play a critical role in emulsion preparations, especially in forming stable water/water emulsions and solubilizing hydrophobic substances in aqueous solutions. Their versatility, compatibility and stability-enhancing properties make them valuable ingredients in a variety of industries including the leather industry.

4. A mechanism of solubilization of lavender oil in surfactant micelles was proposed. Lavender oil is hydrophobic and gets stuck in the core of the micelles but also on the alkyl ends of the hydrophobic chains. For Tween 80, the amount of solubilized lavender oil is higher than in the case of Tween 20, because it has a larger hydrophobic chain. Van der Waals interaction forces are responsible for this.

5. The changes in the aggregation process were observed for each type of emulsion (E1, E2, E3), the solubilization of lavender oil by dynamic light scattering.

6. In the process of finishing the leathers by spraying with three types of emulsions obtained compared to an untreated leather, the antifungal and antimicrobial properties, as well as the softness and appearance of the leathers were improved.

Acknowledgments

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A REVIEW OF POTENTIAL ENZYMES: PROTEASE AND KERATINASE FOR DEHAIRING PROCESS AS CLEANER AND ECO-FRIENDLY LEATHER PROCESSING

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A REVIEW OF POTENTIAL ENZYMES: PROTEASE AND KERATINASE FOR DEHAIRING PROCESS AS CLEANER AND ECO-FRIENDLY LEATHER PROCESSING

ABSTRACT. In recent decades, there has been growing concern and negativity from the environmental impact of industrial development, which produces lots of technological changes. The significant contribution of the leather industry has a good impact on the economic sector; however, it is faced with challenges caused by pollution to the environment. Special attention is required for disposal of solid wastes because of the large amounts that are generated and legal restrictions. Environmental problems are caused by the large amount of wastes originating from chemicals during processing, especially in dehairing process. Conventional dehairing by lime sulfide process causes high chemical oxygen demand emission, biological oxygen demand, and total suspended solids. The dehairing mechanism is vaguely understood at present from the point of view of the enzyme specificity, which is needed for consistent and satisfactory hair removal without deleterious effect on the leather quality. It is known that the use of enzymes has potential as an alternative that can be used to reduce the harm caused by toxic chemicals including for waste management. Recently, there has been increasing research on application of enzymes in various leather production processes. The use of protease and keratinase enzymes in leather processing industry has the most promising potential to improve the surrounding environment. Therefore, this study aimed to review relevant literature in terms of dehairing processes without adverse effects in order to make good quality leather. Further scientific discussion is needed for understanding the gap of these critical issues in this area.

KEY WORDS: dehairing, protease, keratinase, eco-friendly, leather processing

O TRECERE ÎN REVISTĂ A POTENȚIALELOR ENZIME: PROTEAZA ȘI KERATINAZA UTILIZATE ÎN PROCESUL DE DEPĂRARE PENTRU O PRELUCRARE A PIEILOR MAI CURATĂ ȘI ECOLOGICĂ

REZUMAT. În ultimele decenii au existat preocupări și efecte adverse tot mai mari din cauza impactului asupra mediului a dezvoltării industriale, care generează o mulțime de schimbări tehnologice. Industria de pielărie contribuie favorabil în mod semnificativ la dezvoltarea sectorului economic, însă se confruntă cu provocări cauzate de poluarea mediului. O atenție deosebită este necesară pentru eliminarea deșeurilor solide din cauza cantităților mari care sunt generate și a restricțiilor legale. Problemele de mediu sunt cauzate de cantitatea mare de deșeuri provenite din substanțele chimice utilizate în timpul prelucrării, în special în procesul de îndepărtare a părului. Depărarea convențională cu soluție de var generează valori mari ale consumului chimic de oxigen, consumului biochimic de oxigen și solidelor în suspensie totale. Mecanismul de îndepărtare a părului este vag înțeles în prezent din punctul de vedere al specificității enzimatice, necesară pentru o îndepărtare uniformă și satisfăcătoare a părului, fără efecte dăunătoare asupra calității pielii. Se știe că utilizarea enzimelor poate reprezenta o alternativă în vederea reducerii daunelor cauzate de substanțele chimice toxice, cu efecte inclusiv în gestionarea deșeurilor. Recent, s-au realizat tot mai multe cercetări privind aplicarea enzimelor în diferite procese de producție a pielii. Utilizarea enzimelor protează și keratinază în industria de prelucrare a pielii are cel mai promițător potențial de a îmbunătăți mediul înconjurător. Prin urmare, acest studiu și-a propus să treacă în revistă literatura de specialitate relevantă referitoare la procesele de îndepărtare a părului pentru a obține piele de bună calitate, fără efecte adverse asupra pielii finite. Sunt necesare discuții științifice suplimentare pentru a înțelege decalajul creat de problemele critice din acest domeniu.

CUVINTE CHEIE: depărare, protează, keratinază, ecologic, prelucrarea pielii

UN EXAMEN DES ENZYMES POTENTIELLES : PROTÉASE ET KÉRATINASE POUR LE PROCESSUS D'ÉPILAGE COMME TRAITEMENT DU CUIR PLUS PROPRE ET ÉCOLOGIQUE

RÉSUMÉ. Au cours des dernières décennies, l'impact environnemental du développement industriel, qui entraîne de nombreux changements technologiques, a suscité de préoccupations croissantes et effets négatifs de plus en plus grands. La contribution significative de l'industrie du cuir a un impact positif sur le secteur économique, mais elle est confrontée aux défis causés par la pollution de l'environnement. Une attention particulière est requise pour l'élimination des déchets solides en raison des grandes quantités générées et des restrictions légales. Les problèmes environnementaux sont causés par la grande quantité de déchets provenant de produits chimiques lors du traitement, en particulier lors du processus d'épilation. L'épilation conventionnelle par le procédé au sulfure de chaux provoque des valeurs élevées pour la demande chimique en oxygène, la demande biologique en oxygène et les matières en suspension totales. Le mécanisme d'épilation est vaguement compris à l'heure actuelle du point de vue de la spécificité enzymatique, qui est nécessaire pour une épilation cohérente et satisfaisante sans effet délétère sur la qualité du cuir. Il est connu que l'utilisation d'enzymes constitue une alternative potentielle pour réduire les dommages causés par les produits chimiques toxiques, notamment pour la gestion des déchets. Récemment, de plus en plus de recherches ont été menées sur l'application d'enzymes dans divers processus de production du cuir.

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L'utilisation d'enzymes protéases et kératinases dans l'industrie du cuir est la plus prometteuse pour améliorer l'environnement. Par conséquent, cette étude fait un examen de la littérature pertinente qui fait référence au processus d'épilation pour l'obtention du cuir de bonne qualité sans effet négatif. Des discussions scientifiques plus approfondies sont nécessaires pour comprendre les lacunes de ces questions critiques dans ce domaine.
MOTS CLÉS : épilation, protéase, kératinase, éco-responsable, traitement du cuir

INTRODUCTION

Biotechnology is the utilization of biological-based materials and nature's production processes [1], which can be an alternative technology that replaced conventional technology that leads to eco-friendly production processes [2]. Among biotechnologies, the enzymatic process is an alternative that can be developed from conventional and promising processes [3]. Bacteria and fungi that grow in submerged or solid fermentation are capable of producing enzymes that can be used for industry. Fermentation process on enzyme production is further followed by filtration and cell disruption. Downstream processing of the crude enzyme collectively by precipitation followed by centrifugation and vacuum drying or lyophilization [4].

Enzymes have high specificity, are easily biodegradable, have lower toxicity than chemicals [1]. Producers can benefit by developing products that are of equal or even better quality using less raw material, chemical, water and consumption and with less problematic waste generation than traditional processes by the properties of enzymes [1, 3]. Industries use enzymes for various production processes such as leather production [5, 6], textile production [7], food production [8], and animal feed production [2].

In several articles, books, and reports during last decade, we have discussed and agree the impact of using enzymes on the environment compared to conventional processes [9-15]. However, a concrete assessment is needed that the production of enzymes and auxiliary materials for enzyme processes require more energy and raw material besides being based only based on qualitative assessments. Therefore, to assess the true environmental benefits of enzymatic processing, a qualitative environmental impact assessment is required [4].

Recently, enzyme technology has been used as a substitute for polluting chemicals in stages of leather processing. The use of enzymes in soaking, degreasing, and application of protease for dehairing in the last two decades has increased. The action of enzymes is one of the methods that the leather technologist used just to accelerate soaking and minimize the use of harmful dehairing chemicals [16, 17]. Enzymatic dehairing is part of the efforts for greener leather.

Therefore, this paper aims to update and discuss the available data on the main use of enzymes, considered as one of the most promising methods for improving environmental conditions related to leather processing. The study was conducted through a survey of scientific articles. Thus, this appears as providing an accurate database for an environmental leather guide in dehairing processes and the development of cleaner leather production.

METHODOLOGY

Mechanism of Conventional Dehairing and Enzymatic Dehairing

Good quality leather is obtained by removing the hair from the skin. In conventional leather making, the skins are treated by soaking in liquor containing lime for long duration depending on the thickness of the skin. Later, to accelerate the process, sulfides can be an alternative which results in the quick loosening of the hairs. Keratin is abundant in the main outer layer of the skin, epidermis and hair or wool. The high content of sulfur-rich amino acid and cystine causes the keratin helices to be stabilized by intra-molecular disulfide bonds. The reduction process cleaves these disulfide links by removing the keratinous substances.

Sulfide treatment affects the integrity of all layers of the skin. Sulfides are in continuous contact with the hair side of the

skin so that the outer root sheath of the hair and the cortex of the hair shaft are also dissolved in the hair burning process [18]. However, the use of these sulfides leaves residual hair root or short hair in the follicle that have to removed so they are not visible in the finished leather. This short hair removal is carried out by a bating process using proteases. There is deionization of basic amino acids in collagen due to high alkaline conditions resulting in high fiber opening through an osmotic process [19]. Making the leather soft and durable depends on opening the fiber bundles [18].

The mechanism of the chemical dehairing process is much better understood, while the dehairing process using proteases lacks clear comprehension (Figure 1). The keratinolytic activity is still debated by researchers, while all researchers highly appreciate the activity of non-collagenolytic enzymes. Epidermal barrier containing keratin should be dislodged by enzymes in order to reach the hair bulb and remove the hair. In fact, proteases have been shown to have hair removal abilities even in the absence of keratinolytic activity [20, 21]. The outer root sheath which contains keratin is shed with the base membrane with an ideal protease without keratin specificity.

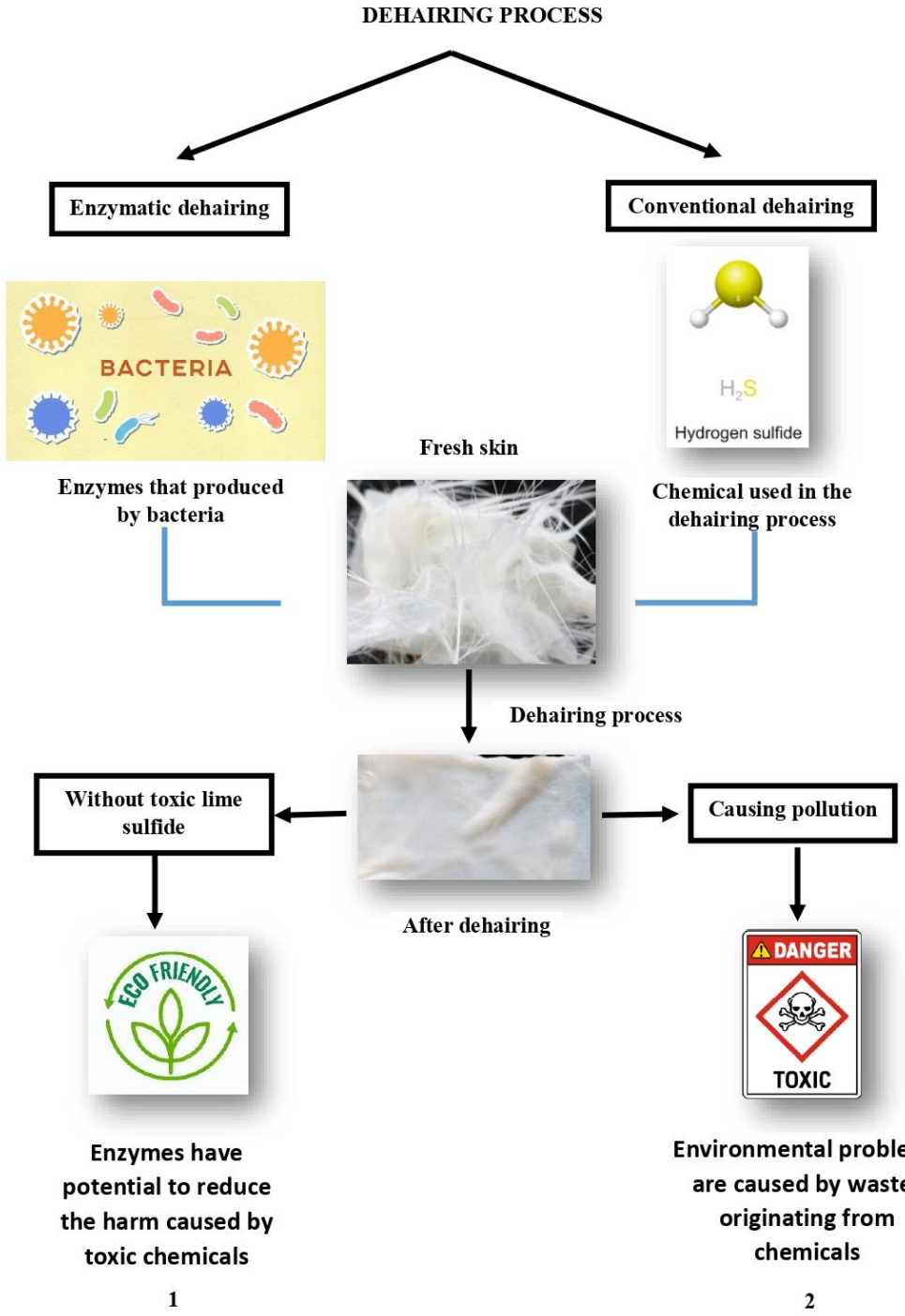

Figure 1. Schematic representation in animal hide during the dehairing process. **1** - Schematic diagram of dehairing process by enzymatic. **2** - Schematic of conventional dehairing process using chemicals

The inner root sheath can be degraded easily by protease because it contains low cysteine. The high amount of cystine due to the keratin structure affects the next layer, the cuticle is resistant to non-keratinolytic proteases. This also occurs in the cortex because some mammals share the same chemical composition. The hair bulb can be a site of attack in the process of hair removal because the hair bulb contains dermal papilla

which is primarily composed of non-structural proteins. Above the hair bulb where disulfide bonds form is a zone of pre-keratinization, which has so few characteristics of keratin that it can be a point of attack in protease-mediated dehairing [22]. To loosen the hair follicle by targeting the surrounding area, a protease with the right specificity can be used.

RESULTS AND DISCUSSIONS

Enzymes

Enzymes are generally proteins, organic substances and known as biocatalysts for chemical reaction and have been used in various applications including detergent, food, pharmaceutical, diagnostic, chemical industries, agriculture, paper, and leather. According to some authors, the use of enzymes is an important component of sustainable industry [23]. Pollutants that harm the environment have to be removed, changed, or detoxified to make them less toxic through natural processes and bioremediation techniques with biological agents such as microbes that can produce enzymes [24].

The advantage of using enzymes in dehairing process, besides reducing chemicals, is also shortening the time needed, and resulting in cleaner grain layer because the enzymes attack the connection between the hair and the derma, thereby facilitating the shedding of hair without damaging it.

Proteolytic Enzymes

Protease

Protease are enzymes that hydrolyze proteins and peptides. Proteases act to break protein peptide bonds through catalytic hydrolysis and are used to remove non-fibrillar proteins [25]. Animal skin is composed of hair, unwanted protein and fat. Unnecessary fat and protein have to be removed before being processed into leather. Mechanical treatment, called soaking followed by liming process so that the hair is digested by the action of sulfides, is a conventional method to remove unnecessary parts. According to Li *et al*. [26], protein and fat can be degraded by using protease as a supplement so that it can be used in soaking and liming processes.

Pseudomonas bacteria from visceral wastes utilize protease to dehair goatskins and indicate that dehairing using enzymes generate similar or improved characteristics [5]. According to Briki *et al*. [27], protease from *Bacillus* sp. SB12 can be used for dehairing process in goat skin processing in industry. Simillar results were reported [28-30] using *Bacillus* strain for hide unhairing to replace the chemical process, which uses toxic sulfides and lime.

Conventional dehairing by lime sulfide process causes high chemical oxygen demand (COD) emissions, biological oxygen demand (BOD), and total suspended solids (TSS) [31]. One of the main contaminants of wastewater is ammonium salt which is usually added when using lime during unhairing process [32]. A reliable absorption of sulfide, nitrogen, COD, and sludge load to the environment is a good dehairing effect from the use of low sulfide and lime [33]. The Table 1 shows various enzymes that can be used for dehairing process from bacteria. From the above it can be stated that the conventional process is not friendly to the environment compared to the enzymatic dehairing process.

Table 1: Compilation of dehairing by protease from 2003-2018

Bacterial strain	Sample	Type of skin/hide	Author
Bacillus subtilis S14	Bovine hair, skins wastes and oil samples	Bovine hide	[34]
Bacillus subtilis P13	Vajreshwari hot spring (45-50°C)	Goat hide	[35]
Bacillus subtilis MTCC 6537	Tannery	Goat skin	[20]
Bacillus subtilis IH-72	Soil from tannery area	Goat skin	[36]
Bacillus subtilis P	Soil	Goat skin	[37]
Bacillus subtilis AP	Goat skin	Goat skin	[38]
Bacillus subtilis Blbc	Tannery sludge	Hide	[29]
Bacillus subtilis Strain VV, AP	Sediments from river	Goat skin	[39]

Bacterial strain	Sample	Type of skin/hide	Author
Bacillus subtilis Strain AKRS3, AP	Waste soil	Goat and sheep skin	[40]
Bacillus subtilis, P		Buffalo hide	[41]
Bacillus subtilis, AP	Soil	Goat skin	[42]
Bacillus subtilis KT004404, P		Goat skin	[43]
Bacillus subtilis AKAL7, AP	Poultry waste mixed soil	Cow hide	[44]
Bacillus subtilis R82, P		Goat skin	[45]
Bacillus pumilus UN-31-C-42	Living waste	Skin	[46]
Bacillus pumilus BA 06, AP		Pig skin	[47]
Bacillus pumilus TMS55, ASP	Marine sediment	Goat skin	[30]
Bacillus pumilus MCAS8, ASP	Lake sediment	Goat skin	[48]
Bacillus pumilus MTCC 7514, AP	Marine soil	Goat skin	[49-50]
Bacillus pumilus, AP	Soil, fish market, waste water	Goat skin	[51]
Bacillus licheniformis, AP	Soil	Bovine hide	[52]
Bacillus licheniformis ER-15, K	Soil	Bovine hide	[53]
Bacillus licheniformis RP1, AP	Water	Goat skin	[54]
Bacillus licheniformis MZK05M9, P	Laboratorium	Goat skin	[55]
Bacillus cereus MCM B-326, P	Slaughterhouse	Buffalo hide	[56-57]
Bacillus cereus IZ-06b and IZ 06r, K	Wool and skin	Sheep skin	[58]
Bacillus cereus VITSN04, AP	Soil	Goat skin	[59]
Bacillus megaterium RRM2, P		Goat skin	[60]
Bacillus megaterium DSM319, P		Cow hide	[61]
Bacillus velesensis, K	Aquatic environments	Bovine skin	[62]
Bacillus circulans, P		Goat skin	[63]
Bacillus altitudinis GVC11, ASP	Soil from slaughter	Goat skin	[64]
Bacillus halodurans JB 99, AP		Buffalo hide and goat skin	[65]
Bacillus safensis LAU 13, K	Soil	Goat skin	[66]
Bacillus sp kr10,	Feather waste	Bovine skin	[67]
Bacillus sp., AP	Lake	Cow hide	[68]
Bacillus JB 99, AP	Laboratorium	Goat skin	[69]
Bacillus sp. AMUa38, AP	Soil	Goat skin	[70]

Keratinase

Keratin can be found in hair, wools, nail, feathers and is a main structural protein of hides. The protein content of feather keratin is 91%, while water and lipids are 8% and 1%. Keratinase is included in the protease group that can be applied in cosmetics, textile, and leather industries [49]. According to Kalaikumari *et al*. [71], the use of keratinase to remove sheepskin from *Bacillus paralicheniformis* MKU3 has an efficiency up to 100%. *Bacillus cereus* and *Pseudomonas* sp. derived from poultry feathers containing keratinase showed effectiveness compared to chemicals without any damage to leather. Replacing conventional methods of dehairing with enzymatic methods will help reduce environmental pollution [57]. The use of keratinase enzyme as a substitute for sodium sulfide can be an environmentally-friendly tanning agent. The Table 2 shows various keratinase enzymes that can be used for dehairing process.

Table 2: Compilation of dehairing by keratinase from 2001-2020

Bacterial strain	Sample	Type of skin/hide	Author
Pseudomonas aeruginosa PD100, P		Cow and sheep skin	[72]
Pseudomonas aeruginosa MCM B-327, P		Hides	[73]
Pseudomonas aeruginosa MTCC 10501, AP	Slaughter soil	Goat skin	[74]
Alcaligenesfaecalis, AP	Soil	Goat skin	[75]
Lysobacter NCIMB 9497, K			[76]
Proteus vulgaris, P			[77]
Paenibacillus woosongensis TKB2, P	Poultry processing plant	Goat skin	[78]
Brevibacillus brevis US575, K	Soil	Rabbit, goat, sheep	[79]

Bacterial strain	Sample	Type of skin/hide	Author
		and bovine hides	
Vibrio metschnikovii NG155, P	Soil and water from leather and meat industry	Goat skin	[80]
Stenotrophomonas maltophilia K279	Feather	Goat skin	[81]
Brevibacterium luteolum, MTCC 5982	Laboratorium	Goat skin	[82]
Idiomarina sp. C9-1, P	Lake	Cattle hide and Goat skin	[7]

Environmental Impact of Dehairing Process

The conventional method in dehairing process causes a large amount of sulfides concentration in wastewater around 3 % w/w of skin as well as the release of high total solids in wastewater. This conventional method raises pollutants to 50–60% in which those numbers are evaluated based on several essential parameters used to evaluate the quality of wastewater, such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS) and total suspended solids (TSS). The imbalance of these parameters causes environmental damage. An example of using sulfide for the dehairing process is illustrated in the use of hazardous sulfide (such as H_2S resulting from the dehairing process), which impacts environmental stability. It also decreases the effectiveness of the effluent treatment plants. Even in low concentrations, sulfide has been proven to lead to a serious impact. The use of H_2S in the dehairing process is fatal, causing lethal effects even at concentrations as low as 200 ppm. The increase in concentration and toxicity causes a decrease in various human perceptions [83-84].

Experiments conducted by [19] illustrated the environmental impact of the use of enzymes in the dehairing process by comparing the performance of the conventional and enzyme-assisted methods in the dehairing process on goatskins and cowhides. According to the experiments carried out, it has been proved that the enzymatic process offered a significant contribution to the dehairing process and was more effective than employing lime and sulfide. It was evident from the reduction of total dissolved solids (TDS) and total suspended solids (TSS) by about 85% in both types of skins. Those experiments also reported that the value of pollutants in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) also decreased by more than 78% in both types of skins. Those achievements proved that the enzymatic method was more effective for the dehairing process in terms of environmental protection. Not only giving significant advantages, enzymatic process was also effective for reducing toxicity during the dehairing process.

However, despite the significant advantages of employing the enzymatic method, some hurdles still remain in the enzyme-assisted process. One of the important hurdles was in how much alkalinity could be generated using the enzymatic method. It could be noticed that pH during the dehairing process would be near neutral to reduce toxicity. This condition can be reached if the dehairing process can generate high alkalinity. However, the dehairing process using an enzyme cannot generate an alkaline pH as much as lime or sulfide does. Hence, it would be an advanced challenge for the next research to produce a more effective and efficient dehairing method.

Briki *et al*. [26] showed the environmental impact of using alkaline protease from *Bacillus* sp. SB12. This research illustrated that the leather tanning process produced at least 75% organic waste in which hair contributed 70% of them. Conducting chemical procedures in this process would affect the stabilization since the chemical procedure would increase the level of BOD and COD. Briki's research successfully proved that employing enzymes was one of the suitable solutions in the dehairing process. It reduced BOD and COD levels by 40% and 50%, respectively. According to the research mentioned earlier, the enzymatic method was suitable as an alternative method in the dehairing process. It significantly reduced the toxicity in order to prevent the sustainability of the environment.

Potential Use of Enzymes in Several Leather Processes

The conventional dehairing method in leather processing causes a large amount of sulfides with concentrations of around 3 % w/w of skin. Regarding to those facts, the use of sulfides which cause emissions into liquid waste can be replaced by enzymatic processes. Enzymatic processes proved to be beneficial to decrease total dissolved and suspended solids. Table 3 shows that enzymes can be used for various leather processes.

Table 3: The use of enzymes in leather processing

Stage	Traditional technology	Enzymatic alternatives
Soaking	Neutral salts, acids, bacteria	Proteolytic and lipolytic
Dehairing	Calcium hydroxide and sulfides	Enzymes with proteolytic on collagen and keratin
Bating		Alkaline active protease of alkaliphile
Pickling	Acids, particularly sulfuric acid and formic acid	Proteolytic enzymes to enhance exhaustion of vegetable tanning agents
Dyeing	Dyes and some auxiliaries, acids to fix dyes	Collagenase

CONCLUSIONS

There are three main stages (beamhouse, tanning and post-tanning) in leather processing. The dehairing process is an important stage to prepare for the next step, which is beamhouse. Beamhouse operations in leather processing which have been carried out so far cause more than 70% pollution of the total pollution generated. Sodium sulfide and lime are chemicals that play an important role during the liming and dehairing steps. Several treatments using biological or physical means have been proposed but the treatment methods have not been able to fully produce toxin-free by-products.

Social and economic sustainability are the two pillars of sustainability which are highly prioritized, but it is necessary to pay attention to environmental sustainability. In this review, various bacteria produced by protease and keratinase enzymes can be used in dehairing process. In addition, enzymatic dehairing can help reduce dependence on the use of hazardous chemicals commonly used in leather processing such as sulfide, lime and amines as well as maintain a balance between human health, wildlife, reducing water, soil and environmental pollution. Therefore, the use of enzymes can be a good alternative to conventional processes.

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EUREKA PROJECT BIO-PLANT-PROTECT AS MODEL KNOWLEDGE TRANSFER BETWEEN ACADEMIC, RESEARCH AND INDUSTRY

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EUREKA PROJECT BIO-PLANT-PROTECT AS MODEL KNOWLEDGE TRANSFER BETWEEN ACADEMIC, RESEARCH AND INDUSTRY

ABSTRACT. This paper presents an example of interdisciplinary cooperation between scientific research, education and industry to develop innovative products. Through its complex, inter-related activities, the project generates innovation in bioeconomy, in the agrifood system, developing a double action product (protection for plants and stimulation of agricultural production), as well as treatment schemes adapted to pest control and amplification of germination, specifically designed for their applicability domain (e.g. apple orchards, tomato seeds).

KEY WORDS: knowledge transfer, bio-fungicide, protection, nutrition, bioeconomy

PROIECTUL EUREKA BIO-PLANT-PROTECT CA MODEL DE TRANSFER DE CUNOȘTINȚE ÎNTRE EDUCAȚIE, CERCETARE ȘI INDUSTRIE

REZUMAT. Această lucrare prezintă un exemplu de cooperare interdisciplinară între cercetarea științifică, educație și industrie pentru a dezvolta produse inovatoare. Prin activitățile sale complexe, interconectate, proiectul generează inovație în bioeconomie, în sistemul agroalimentar, dezvoltând un produs cu dublă acțiune (protecția plantelor și stimularea producției agricole), precum și scheme de tratare adaptate combaterii dăunătorilor și amplificării germinației, special concepute pentru domeniul lor de aplicabilitate (ex. livezi de meri, semințe de roșii).

CUVINTE CHEIE: transfer de cunoștințe, bio-fungicid, protecție, nutriție, bioeconomie

LE PROJET EUREKA BIO-PLANT-PROTECT COMME MODÈLE DE TRANSFERT DE CONNAISSANCES ENTRE L'ACADÉMIE, LA RECHERCHE ET L'INDUSTRIE

RÉSUMÉ. Cet article présente un exemple de coopération interdisciplinaire entre la recherche scientifique, l'éducation et l'industrie pour développer des produits innovants. A travers ses activités complexes et interdépendantes, le projet génère de l'innovation dans la bioéconomie et dans le système agroalimentaire, en développant un produit à double action (protection des plantes et stimulation de la production agricole), ainsi que des schémas de traitement adaptés à la lutte antiparasitaire et à l'amplification de la germination, spécifiquement conçus pour leur domaine d'application (par exemple vergers de pommiers, graines de tomates).

MOTS CLÉS : transfert de connaissances, bio-fongicide, protection, nutrition, bioéconomie

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INTRODUCTION

The BIO-PLANT-Protect project is a European cooperation between research, education and industry from Romania and Poland to capitalize animal and vegetal waste in circular agriculture and to develop new bio-fungicides compositions with bivalent activity: protection against pathogens and bio-stimulation of germination and growth of plants.

The general objective of BIO-PLANT-Protect project is achieved through appropriate capitalization of vegetal waste from *Solanaceae* family and leather industry by-products – fertilizers resulting from protein extracts (collagen, keratin), associated with *Camelina sativa* oil and bio-active compounds from *Asteraceae* / *Fabaceae* family.

The innovative character is anchored in scientific priorities and European Union requirements (Directive 782/2019), regarding the minimization of harmful substances in agriculture. The concept of this project brings concrete and feasible innovative solutions by: (i) exploiting the bioactive potential of indigenous natural compounds; (ii) optimized technologies – cost-effectiveness and significant performances improvement; (iii) new prototype-amplified fungicide efficacy due to active compounds profile and ratio, for a complex spectrum of pathogens; (iv) new treatment schemes for two stages of plants' development, vegetation and seeds.

The feasibility is supported by the interdisciplinarity between partners: SC BIOTEHNOS SA Romania – research for isolation and characterization of actives, *in vitro* studies, formulation and field testing; National Research and Development Institute for Textiles and Leather, Division: Leather and Footwear Research Institute, Romania – research in capitalisation of proteinic nutrients extracts, with the involvement of doctoral young researchers and doctoral students in research activity; University of Agronomic Science and Veterinary Medicine, Bucharest, Romania – excellence in phytopathology, with the involvement of students and master's students in research activities; Łukasiewicz Research Network – Institute of Leather Industry, Łódź, Poland – recovery of collagen hydrolysates in phyto-treatments and specific analysis; Pestila II, Wolborz, Poland – pesticide production and marketing capacity at European level.

The complementary experience and expertise of the research-education-industry consortium [1] ensure a complete cycle of innovative products development and validation. Also, the work in consortium ensures the conditions for an important scientific production for dissemination and increasing the visibility of project partners.

The project generates the knowledge transfer between academic, research and industry, career development of future graduates and young graduates through involvement in applied research and the innovation capacity extension oriented to products and technologies, as well as large scale dissemination of results. Through its complex, inter-related activities, the project generates innovation in bioeconomy, in the agrifood system, developing a double action product (protection for plants and stimulation of agricultural production), as well as treatment schemes adapted to pest control and amplification of germination, specifically designed for their applicability domain (apple orchards, tomato seeds).

The main object of research in this project is to create an innovative, ambivalent bio-pesticide, using plant extracts of marigolds and fenugreek with antifungal effects [2, 3] and protein extracts of collagen and keratin recovered from animal skin by-products [4-6], with properties to stimulate seed germination and nutrition of horticultural plants in vegetation.

Previous research has demonstrated both the ability of plant extracts to prevent and combat fungal infestations in agricultural crops [7, 8], as well as the properties of animal protein extracts for biostimulation and plant nutrition [9, 10].

EXPERIMENTAL

Materials and Methods

Materials

- Residual semi-processed bovine leather for collagen extraction was collected from the leather processing pilot station of INCDTP – Division: Leather and Footwear Research Institute, chopped, and preserved by freezing.

- Wool for keratin extraction was purchased from sheep farmers and degreased at the INCDTP Division: Leather and Footwear Research Institute.

- Hydrated calcium oxide (CaO CaOH, MW = 81.371 g/mol) was purchased from Cristal R Chim SRL (Bucharest, Romania).

- Analytical grade chemical reagents, such as ammonia potassium hydroxide and oxalic acid, were purchased from Chimreactiv SRL (Bucharest, Romania).

- Alcalase 2.4 L (protease from *Bacillus licheniformis* with 2.4 U/g activity) and propionic acid were purchased from Sigma-Aldrich (Bucharest, Romania).

- Protamex® (an endo-protease from *Bacillus* spp. with 1.5 U/g activity) was purchased from Novozymes (Atasehir, Turkey).

Methods

- The methods of extracting protein hydrolysates are: thermal hydrolysis at pH=5.5-6.0 for gelatin, enzymatic hydrolysis at pH=8.0-8.5 for collagen hydrolysate, and alkaline-enzymatic hydrolysis with calcium and potassium hydroxides, at pH=8.0-9.0 for keratin hydrolysate, then settling, filtering and conditioning by drying at 60°C, cooling and grinding.

- The method of extracting antifungal compounds from plants: by stirring of the crushed vegetables at ambient temperature in a hydroalcoholic solution of ethanol 70% v/v, filtration and concentration under vacuum at 170-70 mbar at a temperature of 60°C, conditioning in butylene glycol, centrifugation for 20 min. at ambient temperature with 8000 rpm.

- Methods of characterizing protein and vegetable extracts: texture properties of gelatin (strength, consistency, elasticity, adhesion strength) were analysed according to GMIA standard methods for the testing of edible gelatin (Official Procedure of the Gelatin Manufacturers Institute of America, Inc.), using a TEX'AN TOUCH Texture Analyser, equipped with Bloom cylinder and special cylinder for CRT (Compression-Relaxation-Traction); the nanometric particle size and distribution were analysed by Dynamic Light Scattering (DLS) using a ZetaSizer Nano ZS (Malvern, UK). The determinations were made using solutions containing 1% protein; The amino acid composition of gelatin, collagen, and keratin hydrolysates was analysed by HPLC using an Amino Acid Analyzer LC 3000 (Sykam GmbH, Eresig, Germany), equipped with a polymeric cation exchanger column, post-column ninhydrin derivatization at 125°C, and photometric measurement at 570 nm. The results were monitored by Chromatography-Software ChromStar 6.0 (SCPA GmbH, Bremen, Germany) and were reported as a means of triplicate determinations.

- The method of studying germination is based on calculation of the mean standard deviation (±) and the relative standard deviation (RSD). The statistical analysis was carried out with the help of Microsoft Excel 2019. The results were interpreted by applying the Paired Two Sample for Means test to compare the phytostimulation activity of the studied protein hydrolysates. A value of $p < 0.05$ was considered to be statistically significant.

- The method of testing the fungicidal action of the extracts was the diffusion method with filter paper discs impregnated in the test substance and placed on the PDA medium (potato-dextrose-agar from Carl Roth GmbH +Co), solidified by cooling at 45°C. The effectiveness of the solution was assessed by manually measuring the growth of the inoculum around the discs.

RESULTS AND DISCUSSIONS

So far, models and technologies have been developed and experimented for the

extraction of proteins from leather by-products and the extraction of active plant principles with antifungal properties. Protein extracts, conditioned and characterized, were made at the laboratory and pilot scales: gelatin, collagen hydrolysate, keratin hydrolysate and their combinations; vegetable extracts with content strictly determined by active principles: flavones and α-terthiophene in the marigold extract; diosgenin in fenugreek extract. The effectiveness of combinations of protein extracts was evaluated through germination tests of bell pepper and tomato seeds treated with protein extracts. The evaluation of plant extracts was carried out from the point of view of the cytotoxic effect on human cells. Formulas of biopesticides with antifungal and fertilization activity have been created, which are being evaluated through tests in real conditions. The results were disseminated through the publication of articles in journals with international visibility and presentation in international conferences.

Figure 1 shows the experimental protein extracts in a conditioned form: gelatin extracted from hide byproducts, collagen hydrolysate extracted from residues from the gelatin extraction process and keratin hydrolysate extracted from sheep wool, after it has been degreased.

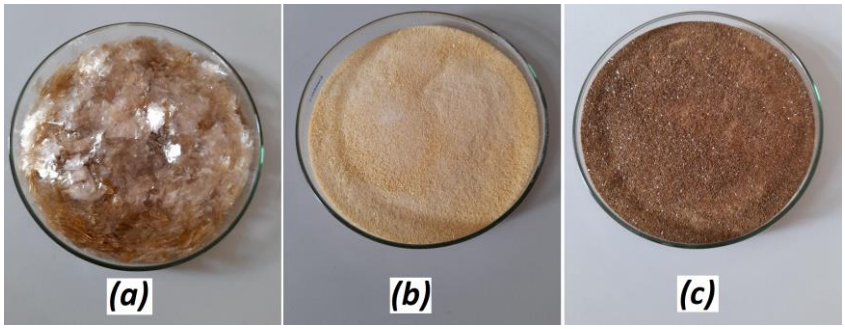

Figure 1. Protein extracts: (a) gelatin; (b) collagen hydrolysate; (c) keratin hydrolysate

The protein extracts were analysed to determine the most important properties.

Figure 2 shows the texture parameters of the gelatin, determined according to the GMIA standard methods for testing edible gelatin (Official Procedure of the Gelatin Manufacturers Institute of America, Inc.), and gelatin hardness, respectively, by Bloom test and consistency, elasticity and adhesive strength by CRT test (Compression-Relaxation-Traction).

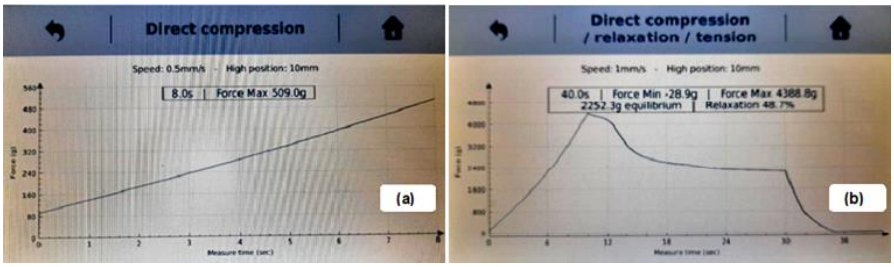

Figure 2. Gelatin texture: (a) Bloom test; (b) CRT test

Analytical data according to the Bloom test indicate that the gelatin has a high strength, expressed by the maximum force of 509 g. The consistency evaluated by the CRT (contraction-relaxation-tension) test is defined by the maximum force of 4388.8 g, elasticity is inversely proportional to the relaxation of 48.7% and the adhesion force is defined by the minimum force of -28.9 g.

As a top-level gelatin (strength over 300 g in the Bloom test), there is no risk of coagulation at low temperatures, when preparing mixtures of protein additives, or at low dilutions, but it ensures a high content of

large polypeptides to induce a good adhesion for surface applications and the delayed release of protein components with low molecular masses, amino acids and oligopeptides, respectively.

The amino acid content of collagen and keratin hydrolysates was analysed, and synthesized in the graphs in Figure 3, while the nanometric particle size distribution is presented in the histograms in Figure 4.

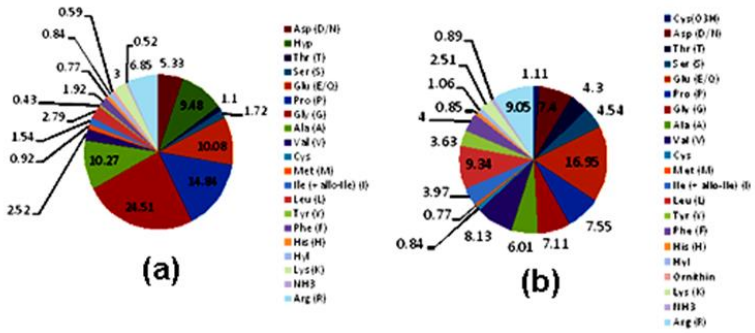

Figure 3. Amino acid content in: (a) collagen hydrolysate (b) and keratin hydrolysate

It is obvious that there are significant differences between the collagen hydrolysate and the keratin one, from simple to double or even triple, such as the case of proline, glycine, alanine more abundant in collagen hydrolysate, or the case of threonine, serine, valine, leucine, tyrosine, more abundant in keratin hydrolysate. Collagen is characterized by the presence of hydroxyproline, and in the case of keratin, it is the presence of cysteine that brings sulfur, a phytonutrient that can significantly improve the crop yield and quality.

The presence of nanometric particles and their distribution in the hydrolysates is highlighted by the dynamic measurement technique of the reflected light that crosses the diluted solutions, as shown in Figure 4. For the protein extracts, nanometric particles are associated with the presence of free amino acids and oligopeptides especially in hydrolysates, the only ones capable of penetrating cell membranes and stimulating biological processes in seeds and plants.

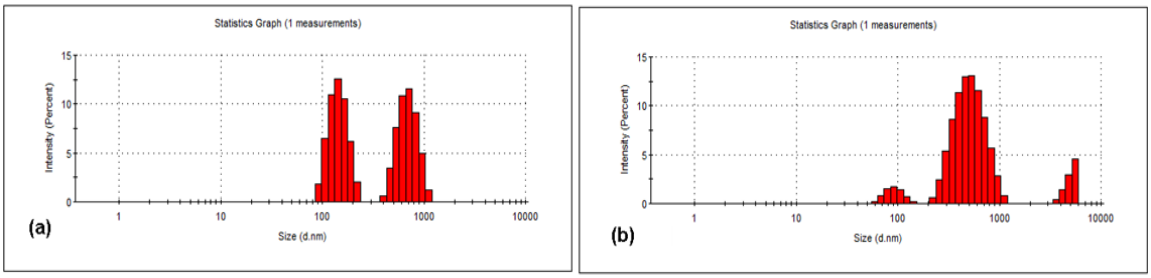

Figure 4. Particle size distribution in: (a) collagen hydrolysate; (b) and keratin hydrolysate

The light intensity measurements reflected in the hydrolysate samples indicate both small and medium particle populations, in the 100-1000 nm range, as well as particle populations with sizes smaller than 100 nm and larger than 1000 nm, especially in the keratin hydrolysate. In the composition of collagen hydrolysate, we find a population of 1.8% particles of 10-100 nm, a predominant population of 97% particles of 100-1000 nm and a population of 1.2% particles of 1000-6000 nm. In the composition of keratin hydrolysate, we find a population of 4.2% particles of 10-100 nm, a population of 85.6% particles of 100-1000 nm and a population of 10.2% particles of 1000-6000 nm.

The protein extracts made were associated with each other to potentiate the nutritional and systemic protection effects of plants in various periods of vegetation and

two types of protein combinations were made: (I) collagen-keratin protein combination, with gelatin, collagen hydrolysate and keratin hydrolysate; (II) collagenic combinations, with gelatin and collagen hydrolysate, in two variants, with which bell pepper and tomato seeds were treated at concentrations of 1%, 3% and 10%, which were subjected to a germination test, as shown in Figure 5.

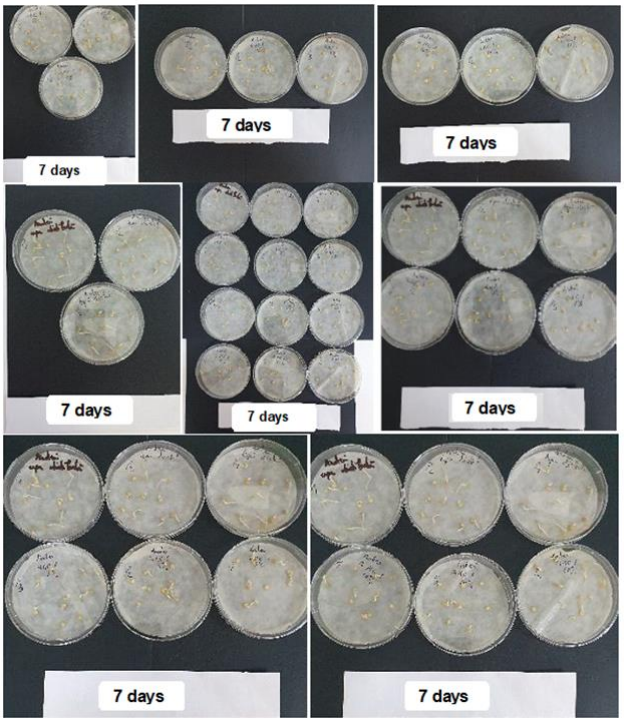

Figure 5. Testing the germination of bell pepper seeds treated with collagen and keratin combinations

The results were analysed by determining the following indicators: germination percentage, relative seed germination index (RSG), relative root growth index (RRG) and germination index (Gi). The protein combinations tested showed a phytostimulating effect on tomato seeds, when applied at a concentration of 1%, the best values being obtained for the combination with keratin content. The pepper seeds proved to be more sensitive to the phytochemical substances in the protein combinations, this being observed after the delayed germination process of the seeds, inhibiting the growth and development of the roots at the same time.

The plant extracts of French marigold and fenugreek were tested for their antifungal activity against the pathogenic fungi of the species *Botrytis cinerea*, *Monilinia* spp., *Fusarium* spp. and *Alternaria* spp.

Figure 6 shows the fungicidal action of vegetable extracts on the growth of *Monilinia* spp. pathogens at 3, 6, 9 and 12 days after incubation.

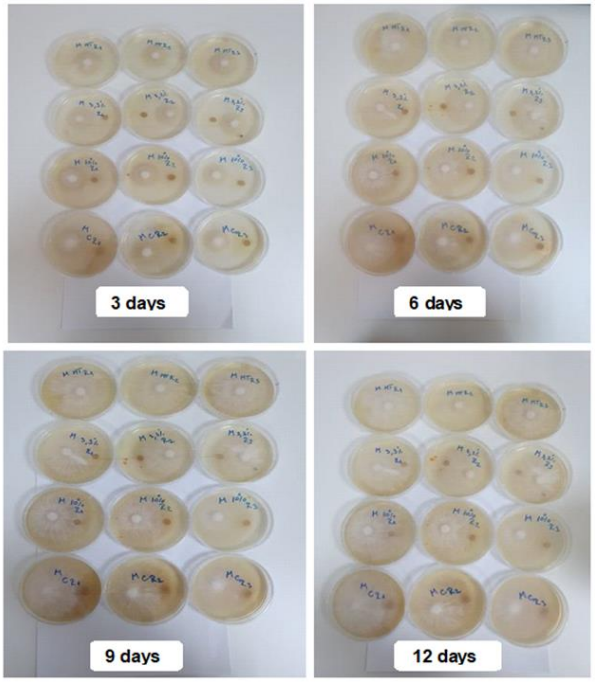

Figure 6. The fungicidal action of vegetable extracts on the growth of *Monilinia* spp. Pathogens

The highest value of the effectiveness of the French marigold extract conditioned in butylene glycol was recorded against *Botrytis cinerea* with E=66.9%, 6 days after incubation. However, with 10% aqueous extract solutions, the highest efficacies were recorded against *Botrytis cinerea* at 6 and 9 days, with close values E=73% and E=72.9%, followed by *Fusarium* spp. with E=72.6% after 6 days and E=66.4 9 days after incubation. Compared to *Alternaria* spp. and *Monilinia* spp., the highest inhibition percentage values were recorded after 9 days of incubation with E=65.7% for *Monilinia* spp. and E=63.2% for the pathogen *Alternaria* spp.

The highest values of the effectiveness of the fenugreek extract were E=81.16% for *Botrytis cinerea* and E=71.51% for *Monilinia* spp., while for the pathogens *Fusarium* spp. and *Alternaria* spp. the effectiveness was over 68% and 64%, respectively.

Two of the variants of biopesticide formulas with antifungal activity and plant nutrition, made for testing in real orchard and field culture conditions, are presented in Figure 7.

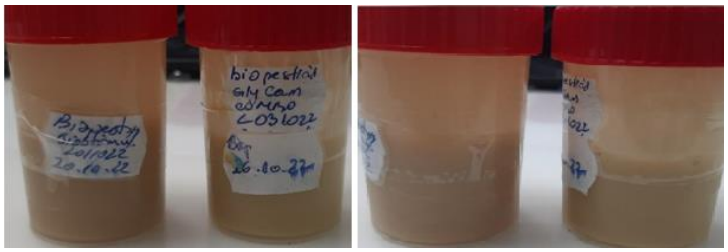

Figure 7. Variants of biofungicide for testing in real conditions of horticultural crops

One of the variants represents the association between the protein combination based on collagen and keratin, hydrolysed extract from fenugreek seeds conditioned in butylene glycol, camelina oil and extract from *Solanum lycopersicum*, and the second variant represents the association between extract from French marigold flowers conditioned in butylene glycol, protein combination based on collagen, camelina oil and *Solanum lycopersicum* extract.

The results of the application tests of the biofungicide test variants in real conditions of horticultural crops will be available for presentation in a future article, dedicated exclusively to biofungicide

applications with protective and nutritional effects in horticultural crops.

CONCLUSIONS

The project has achieved the scientific and technical objectives up to the present moment.

The complementary experience and expertise of the research-education-industry consortium ensure a complete cycle of innovative products development and validation.

The BIO PLANT Protect project created the conditions for the launch on the market of a new biopesticide with additional properties for biostimulation and nutrition in horticulture.

The visibility of the research consortium increased by disseminating the results (joint publications and presentations).

Acknowledgements

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BIODEGRADABLE RETANNING MATERIAL FROM TANNERY TRIMMING WASTE: EXTRACTION, PREPARATION AND APPLICATION

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ABSTRACT. The leather industry has long grappled with environmental challenges associated with waste disposal. One ton of wet-salted hides or skins generates approximately 650 kg of solid waste. The majority of trims and hair waste remain underutilized, with hair often discarded or used inefficiently. We initiated the creation of a retanning agent devoid of formaldehyde by utilizing discarded tannery trimmings, with the goal of promoting a circular economy approach in the leather processing industry in our sustainability efforts. Optimal hydrolysis conditions were determined, involving an alkaline (3.75% w/w NaOH) pre-treatment followed by thermal hydrolysis at 100 °C for 5 hours, effectively maximizing the use of trimmings. Similar treatments were applied to hair waste, particularly red sheep hair, yielding successful hydrolysis. Keratin hydrolysate-g-methacrylic acid (KH-g-MA) copolymers were synthesized through in situ polymerization, employing hydrolysates in a redox system. Characterization was carried out using dynamic light scattering and Fourier transform infrared spectroscopy. These newly developed copolymers were applied as retanning agents in the leather industry, enhancing leather qualities such as fullness, grain tightness, and color brightness. Moreover, they improved leather mechanical strength and reduced the need for post-tanning chemicals. This innovative approach not only addresses solid waste issues but also contributes to greener leather processing, thereby fostering a more sustainable environmental landscape.

KEY WORDS: retanning material, trimming waste, retanning application

MATERIAL DE RETĂBĂCIRE BIODEGRADABIL DIN ȘTUȚUITURĂ DE LA TĂBĂCIREA PIEILOR: EXTRACȚIE, PREGĂTIRE ȘI APLICARE

REZUMAT. Industria de pielărie se confruntă de mult timp cu provocările de mediu asociate cu eliminarea deșeurilor. O tonă de piei sărate umede generează aproximativ 650 kg de deșeuri solide. Majoritatea deșeurilor cum ar fi ștuțuitura și părul rămân neutilizate, părul fiind adesea aruncat sau folosit ineficient. S-a realizat un agent de retăbăcire fără formaldehidă utilizând ștuțuitură, cu scopul de a promova o abordare a economiei circulare în industria de prelucrare a pieilor în vederea dezvoltării sustenabilității. S-au determinat condițiile optime de hidroliză, ceea ce a presupus o pretratare alcalină (3,75% g/g NaOH) urmată de hidroliză termică la 100°C timp de 5 ore, maximizând în mod eficient utilizarea ștuțuiturii. S-au aplicat tratamente similare deșeurilor de păr, în special blana de oaie roșie, realizând cu succes procesul de hidroliză. S-au sintetizat copolimeri de tip hidrolizat de cheratină-g-acid metacrilic (KH-g-MA) prin polimerizare in situ, folosind hidrolizatele într-un sistem redox. Caracterizarea a fost efectuată utilizând difuzia dinamică a luminii și spectroscopia în infraroșu cu transformată Fourier. Copolimerii dezvoltați au fost aplicați ca agenți de retăbăcire în industria de pielărie, îmbunătățind calitățile pielii, cum ar fi plinătate, compactizare și strălucirea culorii. Mai mult, au îmbunătățit rezistența mecanică a pielii și au redus necesarul de substanțe chimice post-tăbăcire. Această abordare inovatoare nu numai că rezolvă problemele legate de deșeurile solide, ci contribuie și la o prelucrare mai ecologică a pielii, încurajând astfel un peisaj ecologic mai durabil.

CUVINTE CHEIE: material de retăbăcire, ștuțuitură, aplicare la retăbăcire

MATÉRIAU DE RETANNAGE BIODÉGRADABLE ISSU DES ROGNURES DE TANNERIE : EXTRACTION, PRÉPARATION ET APPLICATION

RESUME. L'industrie du cuir est depuis longtemps confrontée aux défis environnementaux liés à l'élimination des déchets. Une tonne de peaux salés humides génère environ 650 kg de déchets solides. La majorité des rognures et des poils restent sous-utilisées, les poils étant souvent jetés ou utilisés de manière inefficace. Nous avons lancé la création d'un agent de retannage sans formaldéhyde en utilisant des rognures de tannerie, dans le but de promouvoir une approche d'économie circulaire dans l'industrie du cuir dans nos efforts vers le développement durable. Les conditions optimales d'hydrolyse ont été déterminées, impliquant un prétraitement alcalin (3,75 % p/p de NaOH) suivi d'une hydrolyse thermique à 100 °C pendant 5 heures, maximisant efficacement l'utilisation des rognures. Des traitements similaires ont été appliqués aux poils, en particulier aux poils de mouton roux, réalisant avec succès le processus d'hydrolyse. Des copolymères d'hydrolysat de kératine-g-acide méthacrylique (KH-g-MA) ont été synthétisés par polymérisation in situ, en utilisant des hydrolysats dans un système redox. La caractérisation a été réalisée par diffusion dynamique de la lumière et spectroscopie infrarouge à transformée de Fourier. Ces copolymères nouvellement développés ont été utilisés comme agents de retannage dans l'industrie du cuir, améliorant les qualités du cuir telles que la fermeté, l'adhérence de fleur et la luminosité des couleurs. De plus, ils ont amélioré la résistance mécanique du cuir et réduit le besoin de produits chimiques de post-tannage. Cette approche innovante résout non seulement les problèmes de déchets solides, mais contribue également à un traitement du cuir plus écologique, favorisant ainsi un paysage environnemental plus durable.

MOTS CLÉS : matériau de retannage, rognures, application de retannage

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INTRODUCTION

The leather industry plays a pivotal role in the modern economy, employing various chemical and mechanical processes to transform animal hides and skins into a chemically and physically stable material. This transformation facilitates the production of a wide range of goods that cater to diverse human needs. Typically, the primary raw materials for the leather industry are hides and skins, which are byproducts of the meat and meat product industry. It is worth noting that the leather sector could be recognized as environmentally friendly to some extent due to its utilization of waste products derived from the cattle processing business [1].

Traditional leather production methods are notorious for causing significant pollution, characterized by noxious odors, organic waste discharge, and excessive water consumption [2]. These methods generate waste products comprising solids and release offensive odors due to the degradation of the proteinaceous material found in hides and skins. Additionally, the process emits gases such as NH3, H2S, and CO2. The conversion of raw animal skins and hides into finished leather results in the creation of various waste materials, some of which pose environmental hazards [3].

Annually, the leather industry discards approximately 850 kg of raw hides, a stark contrast to the 150 kg of hides needed to produce one tonne of leather. Within the tanning industry, common operations contribute to a solid waste output ranging from 2% to 5%. These operations include shaving (50%-60%), chrome shaving (35%-40%), chrome splits, and buffing dust (35%-40%), as well as skin trimming (7%). Notably, eighty percent of this waste originates from the beam house, nineteen percent from the tanning process, and the remaining one percent from the finishing process [4].

Within the tannery industry, only 25% to 55% of the produced materials are deemed usable, leaving a substantial amount as waste [5]. The consumption of disposable goods plays a significant role in contributing to pollution. To address this issue, organic and fermentative compounds have been explored for the hydrolysis of protein-containing waste, resulting in the production of bioactive peptides [6]. The chemical composition of goatskins primarily comprises water (60-70%), proteins (25-30%), fat (2%), and miscellaneous elements (1%) [7]. Notably, collagen protein, a vital component derived from this solid waste, constitutes a substantial portion, accounting for 25–30% of animal protein [8].

Slaughterhouses, meat processing plants, poultry processing plants, and the wool textile industry generate substantial amounts of waste materials containing fibrous proteins such as collagen, elastin, and keratin. These wastes encompass viscera, skin remnants, meat trimmings, bones, blood, bristle, horns, hooves, animal hair, feathers, and low-quality raw wool unsuitable for spinning [9, 10]. The degradation processes of keratin-rich waste materials from diverse industries stand to gain significant advantages from the incorporation of keratinolytic enzymes [11].

Alpha- and beta-keratins, characterized by dominant motifs of alpha helices and beta sheets, respectively, exhibit dense packing and stability owing to a high degree of inter- and intra-molecular disulfide bonds, non-covalent hydrogen bonds, and hydrophobic interactions [12]. Alpha-keratins, with molecular weights ranging from 60 to 80 kDa and low sulfur content, constitute 50–60% of wool fiber, primarily located in the cortex. Meanwhile, beta-keratins, which predominantly compose the protective cuticle, are present in smaller quantities. Gamma-keratins, making up 20–30% of wool fiber and having molecular weights ranging from 11 to 28 kDa, boast a high sulfur concentration, facilitated by their abundant cysteine and tyrosine content, serving as disulfide crosslinkers and aiding in maintaining cortical superstructures [13].

Keratin structures are water-insoluble, enzyme-resistant (pepsin, trypsin, and papain), and mechanically stable [14]. However, waste materials rich in keratin do not accumulate in nature due to the presence of keratinolytic bacteria capable of breaking down keratin. In environments where keratinous materials accumulate, keratinolytic bacteria are frequently identified [15].

Notably, a defining feature distinguishing keratin from other structural proteins like elastin and collagen is its high cysteine concentration at the protein's N- and C-terminal regions. Based on cysteine content and, consequently, disulfide linkages, keratins can be categorized into soft and hard keratins. Epidermal keratins, classified as soft keratins, possess a cysteine concentration of less than 2%. On the other hand, hard keratins include feathers (with a cysteine concentration of 4–8%) and hair and wool (with a cysteine level of 10–17%) [16].

MATERIALS AND METHODS

Materials

Wet-salted goat raw trimmings and sheep hair waste were collected from the Tipara tannery in Hemayetpur, Savar, Dhaka. Various chemicals, including sulfuric acid, sodium hydroxide, hydrogen peroxide, methacrylic acid (MAA), potassium persulfate ($K_2S_2O_8$), and sodium metabisulfite ($Na_2S_2O_5$), were purchased from Hatkhola scientific store in Dhaka. The leather preparation process exclusively utilized industrial-grade chemicals. To determine the required chemical proportions for the leather-making process, wet blue leather from a goat was first weighed after being shaved.

Pretreatment of Wastes

To remove any salts or other contaminants that had settled on the surface of the hair and trimmings, we conducted a thorough washing with distilled water. Subsequently, we air-dried the hair, and the purified trimmings were soaked in water until they reached a moisture content of approximately 65% by weight. These two raw materials were then utilized to create a retanning agent.

Optimizing the Hydrolysis of Raw Trimmings

After rehydration, the initial step involved subjecting the raw trimmings to a pre-treatment procedure, which included the application of either acid, alkali, or alkali-hydrogen peroxide, followed by thermal hydrolysis. To carry out this process, the rehydrated trimmings, maintaining a dry weight to water ratio of 1:10, were broken down into smaller segments and immersed in water along with one of the designated pre-treatment agents for a period of 6 hours. Trimmings that had not been pretreated were hydrolyzed at 100°C for five hours. In Fig. 1 we see the entire experimental procedure carried out. The hydrolysis process required a quantity of chemicals equal to the dry weight of the raw trimmings.

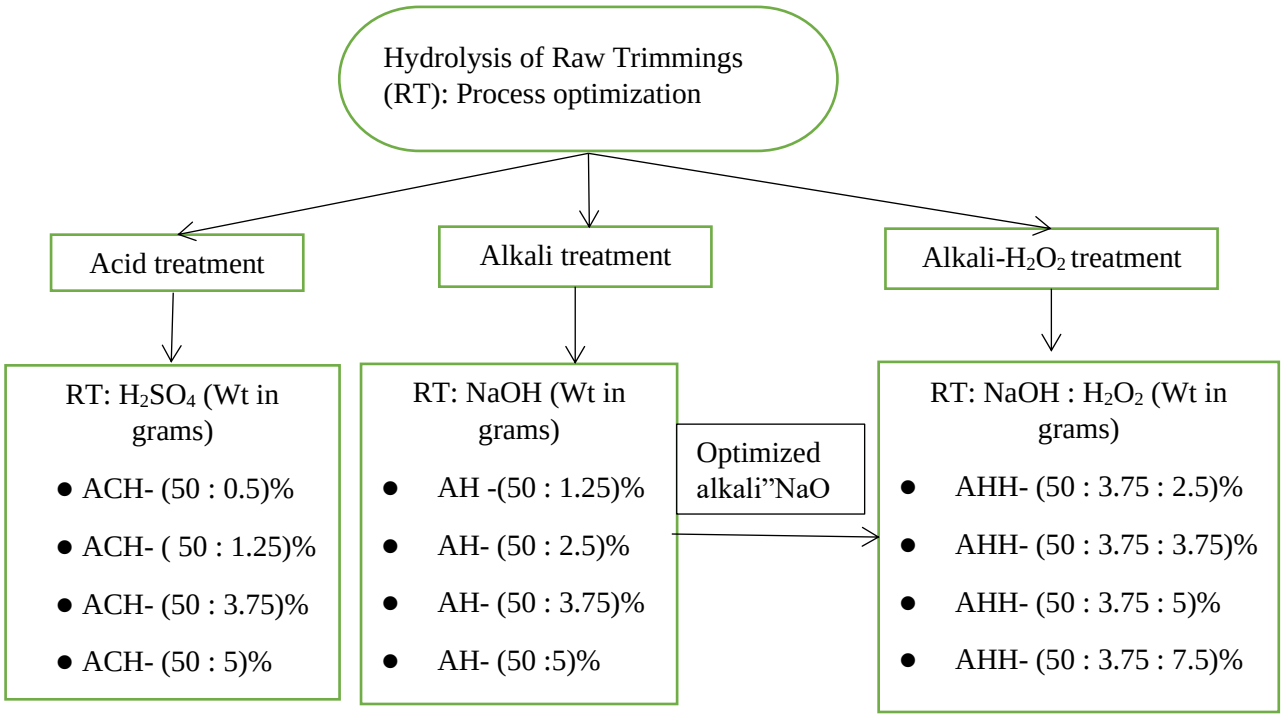

Figure 1. Complete experimental procedure for optimizing hydrolysis of trimmings

We used Eq. (1) to determine the hydrolysis efficiency, often known as the degree of hydrolysis.

$$DH\ (\%) = \frac{W_{RT} - W_{IT}}{W_{RT}} \times 100 \quad (1)$$

In this context, DH represents the degree of hydrolysis, while W_{RT} stands for the initial weight of unprocessed trimmings, and W_{IT} signifies the weight of trimmings that remain insoluble after the hydrolysis process.

Table 1: Efficiency of the Process Optimization for Hydrolyzing Raw Trimmings

Acid hydrolysis		Alkali hydrolysis		Optimized alkali-H_2O_2 hydrolysis	
Sample ID	DH (%)	Sample ID	DH (%)	Sample ID	DH (%)
$ACH_{0.5}$	47	$AH_{1.25}$	71	$AHH_{2.5}$	84
$ACH_{1.25}$	54	$AH_{2.5}$	74	$AHH_{3.75}$	89
$ACH_{3.75}$	61	$AH_{3.75}$	76	AHH_{5}	93
ACH_{5}	69	AH_{5}	81	$AHH_{7.5}$	93

* Note: Acid hydrolysis (ACH), alkali hydrolysis (AH), and alkali hydrogen peroxide hydrolysis (AHH), respectively.

Production of Retanning Agent from Unprocessed Trimmings

50 grams of goat raw trimmings were rehydrated (moisture content: 65% w/w) in 250 milliliters of water that contained 2.5 milliliters of hydrogen peroxide and 1.9 grams of sodium hydroxide. Following that, the mixture was mechanically stirred for a total of 6 hours. The trimmings turned sticky and swelled after being treated with hydrogen peroxide and alkali. The swelled scraps were subjected to hydrolysis at 100 °C for 5 hours. Hydrolysis was followed by cooling and centrifugation to remove the insoluble components. Just before the freeze-drying process, the pH of the supernatant was adjusted with acetic acid to a more controllable 8.5. The freeze-dried material served as a

retanning agent in the leather production process (Fig. 3).

Preparation of Keratin Hydrolysate: Process Optimization

The dried sample was crushed using a crushing machine. After adding 20 g of NaOH to 500 ml of water, 100 g of crushed hair were included in the mixture (weight of hair: volume of NaOH solution ratio 1:5). The substance was heated to 90 °C and stirred magnetically for 4 hours. After hydrolysate the hair was cooled at room temperature and it was centrifuged for 5 minutes at 5000 rpm to separate out the insoluble components. The solution was then performed on keratin hydrolysate.

The following formula was used to calculate the degree of hydrolysis of hair:

$$\text{Degree of hydrolysis \%} = \frac{W_{RH} - W_{UH}}{W_{RH}} \times 100 \quad (2)$$

where, W_{RH} = Raw hair weight, W_{UH} = Undigested hair weight.

Table 2: Enhancing the Hair Hydrolysis Process and Alkali Percentage Optimization

Sample ID	DH%
AH (10: 1)	50%
AH (10: 1.25)	62.5%
AH (10: 1.5)	82%
AH (10: 2)	91%

*Note: Alkali hydrolysis (AH), Degree of hydrolysis (DH). Percentage of alkali = 1, 1.25, 1.5, 2. Weight of hair = 10 gm)

Development of Retanning Agent from Keratin (Graft Polymerization Process)

In a 100 ml reactor vessel equipped with three necks, an extra funnel, a water reflux condenser, a thermometer, and a stirrer were installed. Subsequently, 10 ml of keratin hydrolysate was introduced into the reactor. The reactor should be filled with 10 ml of the redox initiators $K_2S_2O_8$ (18.49 x 10^{-3} moles/liter) and stirred for 30 minutes at room temperature. Simultaneously, the monomer MAA was gradually introduced at a concentration of 1.3887 mol/L into the designated inlet, with continuous stirring maintained for a duration of 30 minutes at a speed of 350 rpm. Following this initial 30-minute period, the mixture underwent an additional hour of stirring at a temperature of 85°C. The reaction was then continued for 1 hour after the addition of 5 ml of the reducing agent $Na_2S_2O_5$ (0.00350 mol/L). To get the pH of the finished product to 5.0, 40 percent of sodium hydroxide was then added. The viscous polymer was formed, the reactor's temperature was lowered to room temperature, and it was transferred to a plastic container and kept there. Keratin hydrolysate and the copolymer formed by grafting keratin hydrolysate with g-methacrylic acid, referred to as KH and KRA respectively, are both designated as "KH" and "KRA" (grafted keratin retanning agent). KRA displayed complete water solubility. To assess the grafting percentage, methanol was introduced into the graft copolymer solution to separate the loosely attached (non-covalently bound) free homopolymer. After a period of a few hours, a precipitate formed and was separated from the solution. Subsequently, the sample was weighed, measured, and placed in an evaporating dish. Employing established procedures involving weight variations, the grafting percentage and grafting efficiency were determined.

Physical and Chemical Testing Analysis

Moisture and Ash Content Analysis

Hydrolysate powder, samples of the powder were first weighed and put in an oven at 105°C for 30 min to determine the moisture content of the protein. After 30 minutes, the sample was weighed and recorded.

Ash content of protein hydrolysate powder: The oven-dried sample was taken in a silica crucible, weighing about 1 g. On the hot plate, the sample-containing crucible was fired and burned until it was scorched. The crucible and sample were then held in a muffle furnace and heated for four hours at 80°C. The ash that developed after it had been allowed to cool

was weighed. The percent of ash was found out using the following formula:

$$\% \text{ Ash} = \frac{\text{Weight of ash (g)}}{\text{Weight of sample taken (g)}} \text{ x } 100\ \% \quad (3)$$

Analysis of Particle Size

The particle size distribution of hydrolyzed protein powder (HPP) and KRA was assessed utilizing the Dynamic Light Scattering (DLS) zeta sizer 3000HS at a temperature of 25°C.

FTIR Analysis

FTIR (Fourier-Transform Infrared Spectroscopy) was employed to capture the spectra of the substances in the 4000-400 cm^{-1} range. This was accomplished using potassium bromide (KBr) pellets that had been compressed before analysis.

Thermal Gravimetric Analysis (TGA)

A thermo-gravimetric analyzer (TGA 8000) was employed for this test. Temperature Program: In a nitrogen atmosphere, heat at a rate of 10 °C per minute from 50 to 600 °C while purging at a rate of 20 ml per minute.

X-Ray Diffraction Analysis (XRD)

For the XRD analysis, a Japan Science 2200PC X-ray diffractometer was employed. Diffractograms were recorded at 2 using a Cu-K beam (=0.1543 nm) mono chromated by a nickel filter, and the wavelength range was 20–100. The final form of the product was examined using the H-600 transmission electron microscope under settings that replicated its initial manufacture, such as a 20mA X-ray tube, a scanning speed of 10/min, and a current rating of 40KV.

Evaluation of the Post-tanning Phase, Involving a Comparison of the Effectiveness of KRA against a Commercially Available Retanning Agent

We conducted four leather retanning experiments to assess the effectiveness of the newly developed retanning agent in the post-tanning process, comparing the outcomes with those achieved using a commercial retanning agent. The raw material for this study was four wet blue goat skins that had been shaved down to a diameter of 1.1 mm. The skins were then split down the middle along the neck, with the left halves serving as the control (IL) and the right halves serving as the experimental (EE) samples (IR, 2R, 3R, 4R, 5R, 6R). Three right sides were processed with 2%, 4%, and 8% protein hydrolysate powder, while three left sides were processed with 4%, 8%, and 12% KRA. The left half was treated with a technical polypeptide-based retanning agent at a concentration of 6%. The compactness and density of the fibers would be different for each species. Everything else about the retanning process, including the chemicals, coloring material, and fat liquor, was the same for both the standard and observational runs.

Conducting Assessments of Leather's Physical Properties

Employing the INSTRON universal testing machine following the IUP methods to measure various physical properties of leather, including tensile strength, percentage of elongation at break (STM 566), stitch tear strength (DIN 53331), grain crack load (SATRA STM 463), and distention at the grain crack. These measurements were taken from matched pairs of leather samples extracted from symmetrical locations for both the control and experimental groups. The leather sample was chosen for additional research due to its exceptional mechanical properties [17].

Post-tanning Liquor Assessment

Liquor that was not used during the observational and standard procedures (4% KRA, protein-based and traditional retanning agent) was gathered and analyzed for impurity metrics like chemical oxygen demand (COD), total solids (TS), biochemical oxygen demand (BOD), total dissolved solids (TDS), and total suspended solids (TSS) [18].

RESULTS AND DISCUSSION

Raw Trimmings Hydrolysis: Process Optimization

Type-1 collagen makes for 26% of the dry weight of rehydrated goat trimmings (moisture: 65% w/w), while keratin (hair) accounts for 8% of the dry weight [19]. Collagen and keratin differ greatly in their structural makeup and amino acid composition. With a molecular weight of 300 kDa, type-1 collagen is a protein made up of three left-handed polypeptide chains coiled-coil-helical in the right direction. However, keratin has a molecular weight of between 44 and 66 kDa [20] and an α-helix structure. While keratin is maintained via disulfide bond/hydrophobic contact and colored via melanin, collagen relies mostly on non-covalent interactions and is conjugated with polysaccharide. Therefore, collagen hydrolysis conditions may vary from keratin hydrolysis conditions. Three alternative pre-treatment techniques were used to optimize the hydrolysis conditions, and their impact on the effectiveness of the hydrolysis process was researched. Table 1 displays the results of several tests assessing the efficiency of hydrolysis. Table 1 makes it clear that only around 69% of the raw trimmings are hydrolyzed by the acid treatment, which is ineffective for achieving complete hydrolysis. Perhaps the extensive compound of keratin and the presence of a slippery surface account for the protein's exceptional resistance to acid treatment. When sodium hydroxide was used in place of sulfuric acid, hydrolysis efficiency increased significantly; the highest efficiency was 81% when sodium hydroxide was used at a concentration of 5%. Table 1 further shows that 7.5% sodium hydroxide ($AH_{3.75}$) has a comparable hydrolysis efficiency to that of 5% sodium hydroxide (AH_5). As a result, the hydrogen peroxide in subsequent experiments ranged from 2.5 to 7.5% w/w while the sodium hydroxide concentration was maintained at 3.75%. Table 1 shows that the hydrolysis efficiency has increased with the addition of hydrogen peroxide, reaching a high of 93% for 5% hydrogen peroxide. When it was raised by more than 5%, no improvement was seen. As a result, the best way for efficient hydrolysis is to pre-treat raw trimmings with 3.75% NaOH and 5% H_2O_2.

Retanning Chemical Production from Raw Trimmings

Preliminary hydrolysis data shows that the raw trimmings can be fully hydrolyzed with an effective pre-treatment with alkali and hydrogen peroxide. In the pre-treatment phase, hydrogen peroxide oxidizes the keratinocytes already present in the hair's microfibrils structure, leaving the hair more susceptible to thermal damage [21]. This process, depicted in (Fig. 3), oxidizes cystine amino acids to cysteic acids [16] under alkaline conditions, yielding a product abundant in sulfonic functional groups.

Collagen enlarges as a consequence of heightened osmotic pressure within the matrix, leading to the separation of fibre bundles. The increased surface area of broken fibres in collagen makes it more reactive to water. Thus, we treated collagen and keratin with alkaline hydrogen peroxide, which destabilized them both. Subsequently, heat treatment was utilized to cleave the polypeptide chains. The hydrolyzed segments notably display clearly identifiable functional groups, including amino, carboxyl, and sulfonic acid groups, as visualized in (Fig. 2). Using hydrogen peroxide as a pretreatment has many advantages. That is because (a) we toned down the original color of the results, making them suitable for a wider spectrum of pastel-hued products, and (b) we reduced their intensity. To ensure chemical linkages between the substance and the leather matrix, a sulfonic group is produced (More details about how this occurred are given below). (c) Oxygen and water were produced as hydrogen peroxide broke down. The hydrolyzed product was chilled and then separated to get rid of the fat and other insoluble parts. The liquid solution's pH was decreased to 8.0–8.5 before it was freeze dried. The grinding was used as a retanning agent throughout the leather-making process.

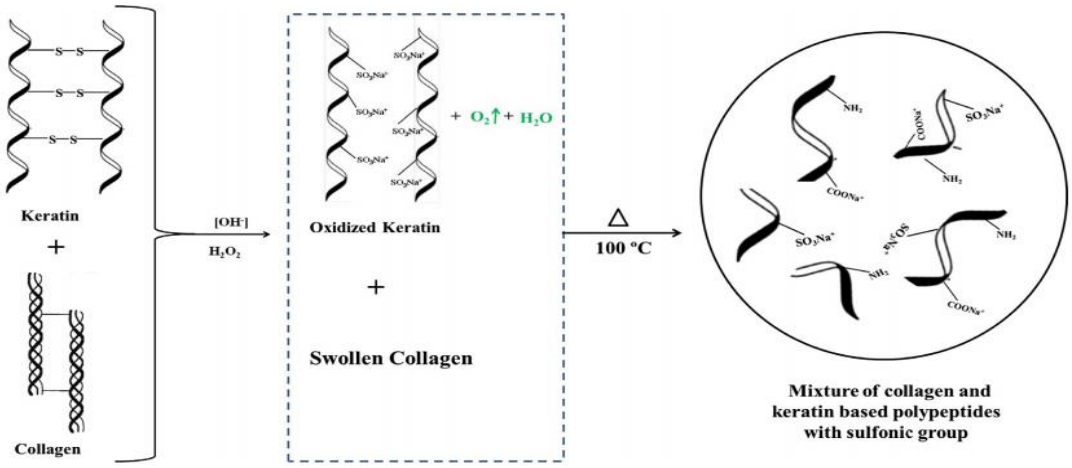

Figure 2. Fragment decomposition in an alkaline-hydrogen peroxide environment

(a) (b) (c) (d)

Figure 3. Progression from raw goat trimmings to the final retanning agent: (a) Rehydration of the raw trimmings, (b) Treatment of trimmings with Alkali-H_2O_2, (c) Protein hydrolysate, and (d) Development of the ultimate retanning agent

Hydrolysis of Sheep Hair: Process Optimization

The majority of the keratin found in red sheep hair is of the α-type and has α-helix structure [22]. To form a left-handed coiled-coil structure in the form of a dimer, two right-handed α-helices are linked together through disulfide bonds. Keratin's mechanical resilience is a result of a blend of factors, including hydrophobic interactions within the polypeptide chains, the existence of disulfide connections formed by cysteine amino acids, and the keratin's restricted ability to dissolve [23]. It takes a lot of time and expense to hydrolyze substances using enzymes. In addition to producing very modest amounts of hair wastage, acid hydrolysis is ineffective for entirely hydrolyzing hair. Alkali is a highly efficient method for hydrolyzing keratinous waste since it speeds up the process and reduces the amount of time needed [24]. Therefore, it is recommended to hydrolyze hair using the alkali approach. The alkali concentration, extraction duration, and temperature all affect how effectively hair is hydrolyzed. In a high-pH alkaline setting, surpassing a pH level of 9.2, sodium hydroxide disrupts the α-helix configuration of cystine and accelerates the breakdown of sturdy disulfide bonds and other covalent linkages.

This process leads to the creation of small, easily soluble peptides (Fig. 4). With increasing sodium hydroxide concentration, the effectiveness of hydrolyzing red sheep's hair gradually increases (Table 2). After two hours in contact with 2% NaOH at 90°C, the resulting hydrolysate shows no signs of significant hair filaments. Hence, it is safe to state that the process of dissolution is complete. Hair was hydrolyzed to a maximum of 91% with a cheap chemical, sodium hydroxide, at roughly 2% of its cost (Table 2). The fast hydrolysis time and simple process

used in the research can be applied on a larger scale in industry.

Development of Keratin Retanning Agent: Graft Polymerization

According to tests on hair hydrolysis, 2% sodium hydroxide proved successful for completely hydrolyzing hair. In the presence of the redox initiators $K_2S_2O_8/Na_2S_2O_5$, graft copolymerization of MAA monomers was carried out at 85 °C for 3 hours on the keratin hydrolysate backbone. The results showed that 53% of the grafts were successful and 89.7% of the grafts were efficient. The drafting success rate and drafting % were determined by analyzing the weight variation between the donor and recipient. Sulfate anion radicals were created when potassium persulfate was thermally induced to breakdown at 85 °C [25]. The radical produced triggers the initiation of active sites, leading to the generation of larger radicals responsible for kickstarting the graft copolymerization process of MAA onto the structure of KH. This ultimately leads to the development of a dense and thick substance known as KRA (Fig 6). To achieve this, a hydrogen radical is removed from one of the keratin hydrolysate's structural groups (-COOH, -SH, -OH, and -NH2) [26] (Fig. 5).

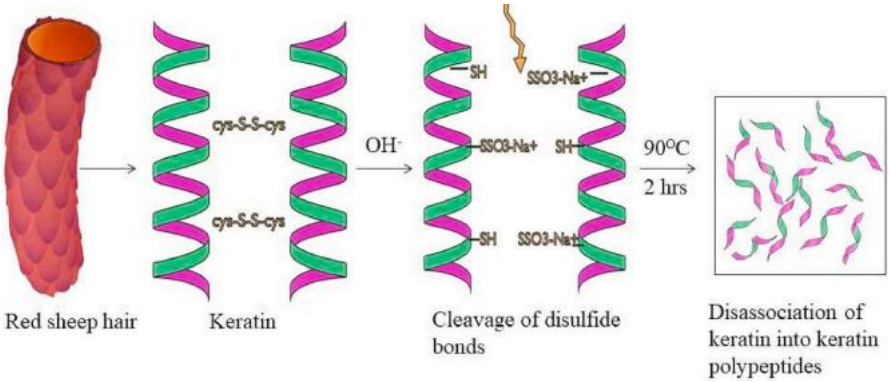

Figure 4. Hydrothermal and alkaline treatment of keratin, depicted schematically

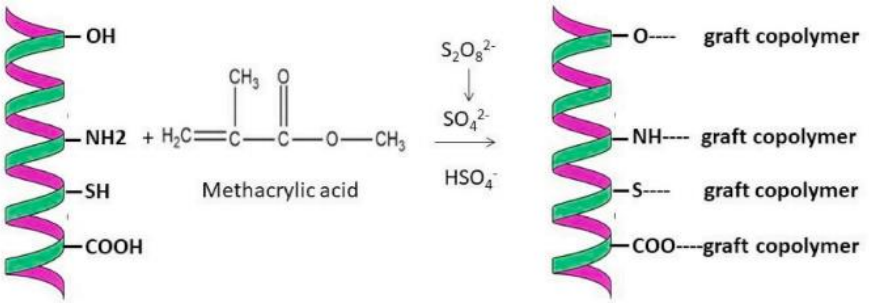

Figure 5. Schematic depiction of pendant functional groups in keratin hydrolysate, indicating potential grafting sites

(a) (b) (c) (d)

(e)

(f)

Figure 6. Enhancement of retanning agent derived from tannery waste hair, specifically addressing: (a) Hair waste, (b) Crushed hair, (c) Alkali hydrolysis, (d) Keratin hydrolysate (KH), (e) Graft polymerization process, (f) Developed retanning (KRA)

Developed Product Characterization

Moisture and Ash Content

The developed product (PHP) is a free-flowing powder with an approximate 7% w/w moisture content. Any retanning agent's ash content, which also affects how environment friendly a product is, as a crucial component. Wastewater treatment is a major problem for the leather industry because of the high salt load it contains; this load is exacerbated by the presence of retanning agents. Comparatively, the ash percentage in the newly formed product is approximately 15% (w/w), but it is between 30 and 40% (w/w) in technical retanning agents. The result revealed that produced product is hazardous substance-free and rich in organic content.

Table 3: Test of mechanical properties

Testing parameter / unit		LR+2%	LR+4%	LR+8%	LR+12%
Tensile strength (N/mm^2)	PHP Applied Leather	21.65	16.28	22.23	
	KRA Applied Leather		18.29	24.58	27.41
	Control LR	18.11			
Elongation at Break (%)	PHP Applied Leather	155.28	154.47	159.49	
	KRA Applied Leather		148.68	155.45	123.99
	Control LR	164.32			
Stitch Tear Strength (kg/cm)	PHP Applied Leather	87.5	91.2	78.7	
	KRA Applied Leather		123.6	158.7	168.00
	Control LR	103.8			
Load at Grain Crack (kg)	PHP Applied Leather	20	21	30	
	KRA Applied Leather		19	26	23
	Control LR	21			
Distension at Grain Crack (mm)	PHP Applied Leather	7.7	8.8	9.1	
	KRA Applied Leather		8.5	8.4	7.4
	Control LR	8			
Water Vapor Permeability	PHP Applied Leather	12.73	12.15	12.29	
	KRA Applied Leather		15.45	15.90	16.50
	Control LR	10.79			

*Protein hydrolysate powder (PHP), Keratin retanning agent (KRA), Leather (LR)

Color Rub Fastness Test

Table 4: Observation for leather (Dry condition)

Sample ID	Gray scale rating					
	32(rev)	64(rev)	128(rev)	256(rev)	512(rev)	1024(rev)
Control LR (0%)	5	5	5	5	5	5
LR+2%PHP	5	5	5	5	5	3/4
LR+4%PHP	5	5	5	5	5	4
LR+8%PHP	5	5	5	5	4	4/5
LR+4%PHP	5	5	5	5	4/5	4
LR+8%PHP	5	5	5	5	5	4/5
LR+12%PHP	5	5	5	5	4	3/5

Table 5: Observation for felt (Dry condition)

Sample ID	Gray scale rating					
	32 (rev)	64(rev)	128(rev)	256(rev)	512(rev)	1024(rev)
Control LR (0%)	5	5	5	5	5	2/3
LR+2%PHP	5	5	5	5	5	5
LR+4%PHP	5	5	5	5	5	5
LR+8%PHP	5	5	5	5	5	4/5
LR+4%PHP	5	5	5	5	4/5	4
LR+8%PHP	5	5	5	5	5	4/5
LR+12%PHP	5	5	5	5	4	4/5

Table 6: Perspiration Fastness Test

Sample ID	Gray scale Rating (1024 rev)	
	For Leather	For Multi-fiber
Control LR (0%)	2/3	2/3
LR+2%PHP	2/3	2/3
LR+4%PHP	4/5	3/4
LR+8%PHP	4/5	4
LR+4%PHP	4	4/5
LR+8%PHP	4/5	¾
LR+12%PHP	4/5	4

Analysis of Particle Size

The mean particle size of Protein Hydrolysate Powder (PHP) and KRA was determined Using DLS measurements. To assess whether a retanning agent interacts and penetrates the leather matrix sufficiently, its particle size must be measured. Insufficient penetration of the leather is caused by retanning agents with larger particle sizes, particularly those with a diameter of more than 1000 nm. PHP and KRA have particle diameters of 291 nm (7a) and 717 nm (7b) respectively, which are thought to be sufficient for penetrating the leather matrix.

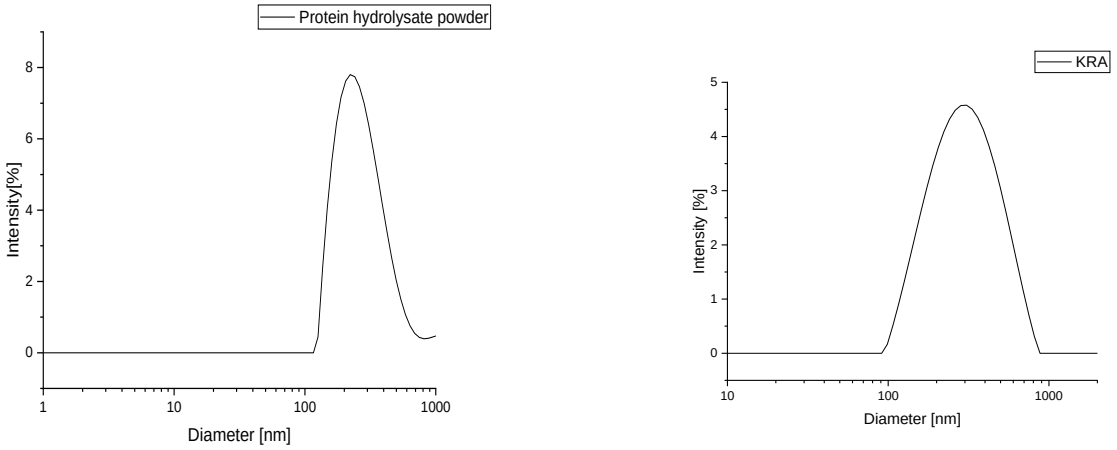

Figure 7. (a) Protein hydrolysate powder (PHP) particle size; (b) Size of the keratin-based retanning agent particles

FTIR Analysis

In Figure 8(a), the produced leather's FTIR spectrum and that of the protein retanning agent are displayed. Significant spectral signals may be found at 3369 cm^{-1} (N-H stretching vibration), 3304 cm^{-1} (CH2 asymmetrical stretching vibration), and 2923 cm^{-1} (N-H stretching vibration) for amides A and B, respectively. Each amide exhibits distinct peaks at 1647 cm^{-1}, 1640 cm^{-1}, 1537 cm^{-1}, 1546 cm^{-1}, 1327 cm^{-1}, and 1238 cm^{-1}, respectively. Specifically, Amide I corresponds to the stretching vibration of the C=O bond in the peptide backbone, while Amide II and Amide III denote the bending of N-H and the stretching vibration of C-N bonds, respectively. A peak at 1043 cm^{-1} and another at 1034 cm^{-1} show that the production process involved the use of cysteic acid, which contains sulfonic acid. These peaks agree with the stretching vibrations of S=O that are observed in cysteic acid, both symmetrically and asymmetrically [27]. The produced retanning agent has a significant amount of amino, carboxyl, and sulfonic functional groups, as shown by the results above.

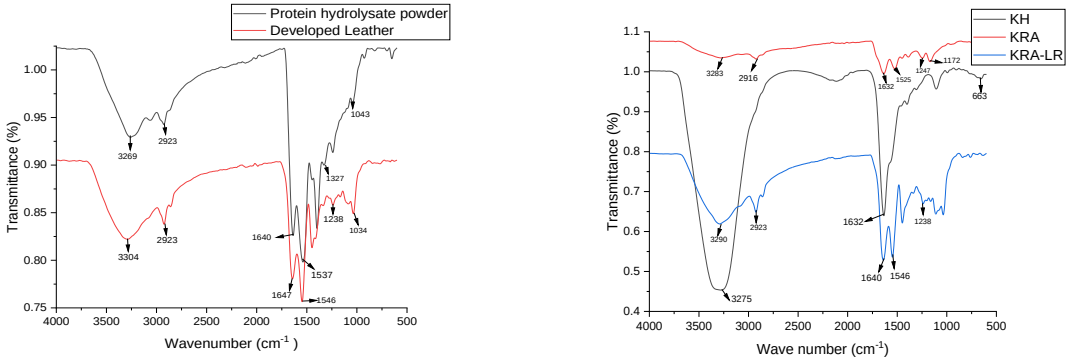

Figure 8. (a) FTIR spectrum of PHP and the leather produced through development, (b) FTIR spectrum of KH, KRA and developed leather (KRA-LR)

KH, KRA, and KRA-LR IR spectra are shown in Figure 8(b). Peptide N-H stretching vibration is responsible for the bands about 3310-3230 cm^{-1} (–CONH–). The bands at 2916 cm^{-1} and 2923 cm^{-1} in KRA and KRA-LR are indicative of the rotational oscillations of CH, CH_2, and CH_3. The frequency range from 1632 to 1640 cm^{-1} is characteristic of amide I. KRA and KRA-LR both showed amide II bands at 1525 cm^{-1} and 1546 cm^{-1}. C-S structural properties have been attributed to the 570-710 cm^{-1} bands (KH and KRA).

The stretching of keratin's -OH groups causes the bands in the KRA in the 3200–3600 cm^{-1} range. Absorption is seen in the range from 2550 to 3800 cm^{-1}, where both the carboxylate and alcoholic Maximum utilization bands are present. Moreover, there were supplementary spectral characteristics signifying the creation of graft copolymers, such as a prominent peak at 1172 cm^{-1} (representing the C-O-C component of PMMA) and approximately 1247 cm^{-1} (associated with C—O stretching), both of which were absent in the KH spectrum. The additional signature peak at 1689 cm^{-1} was observed in KRA (Fig. 7b), indicating grafting of the acrylic acid's carboxylic acid (-COOH) group (Fig. 8b) [28]. Alterations in the NH signals serve as evidence of the graft reaction occurring between the NH compounds and the free radicals of MMA, as evidenced by shifts at 3286, 3075, and 1592 cm^{-1}.

TGA Test

To examine the thermal behavior of the prepared leather sample, thermogravimetric analysis (TGA) was done. 50 °C was the initial temperature, and 1500 °C was the end temperature. The control sample and the leather samples numbered 1 through 4 were among the four samples used in the TGA test. Figure 9 shows the TGA graphs that were produced for those samples.

Each sample lost 5% of its weight, according to the TGA thermogram, which is consistent with a melting range of 50–80 °C. Weight loss was seen before the substance reached its melting point, demonstrating its hydrous character. When the temperature rises from 600 to 650 °C, there is a 13% weight loss. The melting peak is followed by the degradation peak, which starts to lose mass at temperatures of approximately 800 °C.

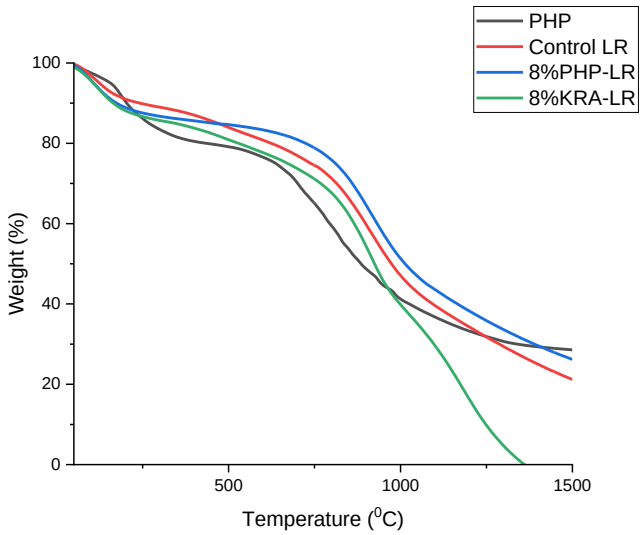

Figure 9. TGA data of different sample

XRD Analysis

The extracted keratin and protein hydrolysate powder (PHP) displayed in Fig. 10 were of high quality, according to the XRD data. In order to preserve the crystal, the extracted keratin was primarily supplied in a semi-crystalline form. Keratin molecules performed XRD examination, which revealed a strong peak at 22.46 degrees that indicated the existence of keratin [29]. The main peaks at 2θ = 9-10.50° and 19-34.8°, respectively, were attributed to the α-helix and β-sheet. The keratin exhibits the α-helix's diffraction characteristics at 2θ = 9.52 ° and the β-sheet's at 2θ = 22.46 °. The peak has an amorphous structure and a range that varies from 5 to 45 degrees. The results discussed above lead to the conclusion that keratin has two different crystal structures: α and β. On the other hand, keratin contains a greater amount of β-sheet. Amorphous keratin molecules are another characteristic. On the contrary, the PHP was obtained from raw trimming, which contains

two types of protein such as collagen and keratin. The XRD results of PHP showed amorphous structure and a strong peak at 2θ = 21.02°, which determined the presence of both proteins.

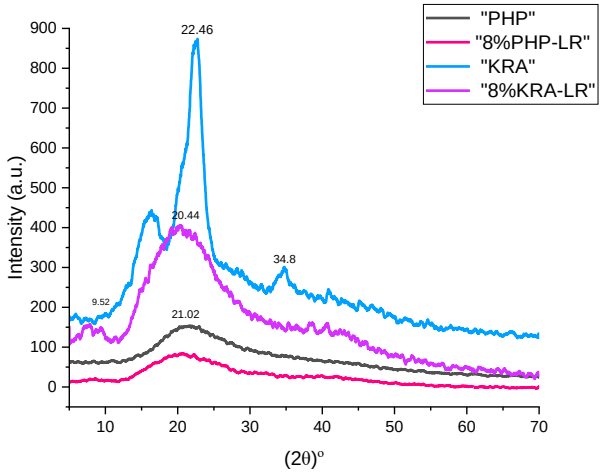

Figure 10. XRD graph of different sample

CONCLUSION

In this current study, we have developed an eco-friendly and biodegradable retanning solution using raw tannery waste trimmings and hair, all without the incorporation of any harmful substances or toxic compounds. Experiment leather was treated with 8% PHP and KRA which enhanced organoleptic and mechanical qualities compared to the control sample. In terms of fullness and roundness, the experimental leather was rated higher (8/10) than the control leather (7/10). The tensile strength, grain fracture resistance and color intensity of the experimental leather revealed higher vales than those of the control leather. Further, when compared to commercial retanning agents, the use of 8% PHP and KRA resulted in a lower emission of COD, TDS, TS and TSS, all of which were indicative of a smaller negative impact in the environment. This innovative approach involves creating an eco-friendly retanning agent using discarded trimmings and waste hair, providing an enhanced alternative to synthetic retanning agents in leather production. This not only exemplifies a sustainable business model but also plays a significant role in revolutionizing the tannery sector.

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INNOVATIVE TECHNOLOGIES FOR OBTAINING STRUCTURED EMULSIONS, BASED ON SEA BUCKTHORN EXTRACT AND TENSIDES

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INNOVATIVE TECHNOLOGIES FOR OBTAINING STRUCTURED EMULSIONS, BASED ON SEA BUCKTHORN EXTRACT AND TENSIDES

ABSTRACT. New structured emulsions were obtained by innovative technologies based on sea buckthorn extract (oil) and two surfactants, sodium dodecyl sulfate and Tween® 80 mixture: Es – sea buckthorn oil/sodium dodecyl sulfate/water; Et – sea buckthorn oil/Tween® 80/water; Est – sea buckthorn oil/sodium dodecyl sulfate and Tween® 80 (ratio 1:1)/water, for different concentrations of sea buckthorn extract oil, in order to improve surface properties with applications in leather industry. Sea buckthorn extract (oil) has a strong antimicrobial and antifungal effect due to its content in: vitamins C and E, phytosterols, fatty acids, antioxidants and amino acids. The order of introduction of the components in innovative technologies, the working conditions and especially the choice of the concentration of surfactants >CMC, are essential in the solubilization of sea buckthorn oil and in obtaining the structured emulsions. The emulsions were characterized by optical microscopy with sea buckthorn oil at 23-50°C. The changes in the aggregation process were observed for each type of emulsion, the influence of temperature and the solubilization of sea buckthorn oil. Dynamic light scattering (DLS) for the emulsions showed the stability, concentration, particle size, polydispersity, zeta potential. The antimicrobial properties were analyzed by microbiological tests. FTIR measurements highlighted the interaction mechanism of surfactants with sea buckthorn oil from the structured emulsions. The leather samples were microbiologically tested, and antimicrobial and antifungal effects were observed. The new structured emulsions are original due to the successful inclusion of sea buckthorn extract (oil) with high potential for improved surface properties with applications in the leather industry.

KEYWORDS: new structured emulsions, innovative technologies based on sea buckthorn extract and tensides, leathers processed

TEHNOLOGII INOVATOARE PENTRU OBȚINEREA UNOR EMULSII STRUCTURATE PE BAZĂ DE EXTRACT DE CĂTINĂ ȘI TENSIDE

REZUMAT. S-au obținut noi emulsii structurate prin tehnologii inovatoare bazate pe extract de cătină (ulei) și doi agenți tensioactivi, dodecil sulfat de sodiu și amestec Tween® 80: Es – ulei de cătină/dodecil sulfat de sodiu/apă; Et – ulei de cătină/Tween® 80/apă; Est – ulei de cătină/dodecil sulfat de sodiu și Tween® 80 (raport 1:1)/apă, pentru diferite concentrații de extract de cătină, în scopul îmbunătățirii proprietăților de suprafață cu aplicații în industria de pielărie. Extractul (uleiul) de cătină are un puternic efect antimicrobian și antifungic datorită conținutului său în: vitaminele C și E, fitosteroli, acizi grași, antioxidanți și aminoacizi. Ordinea introducerii componentelor în tehnologiile inovatoare, condițiile de lucru și mai ales alegerea concentraţiei de surfactanţi >CMC sunt esenţiale în solubilizarea uleiului de cătină și obținerea emulsiilor structurate. Emulsiile au fost caracterizate prin microscopie optică cu ulei de cătină la 23-50°C. S-au observat modificările procesului de agregare pentru fiecare tip de emulsie, influența temperaturii și solubilizarea uleiului de cătină. Dispersia dinamică a luminii (DLS) a arătat stabilitatea, concentrația, dimensiunea particulelor, polidispersitatea și potențialul zeta ale emulsiilor. Proprietățile antimicrobiene au fost analizate prin teste microbiologice. Măsurătorile FTIR au evidențiat mecanismul de interacțiune al agenților tensioactivi cu uleiul de cătină din emulsiile structurate. Probele de piele au fost testate microbiologic și s-au observat efecte antimicrobiene și antifungice. Noile emulsii structurate sunt originale datorită includerii cu succes a extractului de cătină (ulei), cu potențial ridicat de îmbunătățire a proprietăților de suprafață cu aplicații în industria de pielărie.

CUVINTE CHEIE: noi emulsii structurate, tehnologii inovatoare bazate pe extract de cătină și tenside, piei prelucrate

TECHNOLOGIES INNOVANTES POUR L'OBTENTION D'ÉMULSIONS STRUCTURÉES À BASE D'EXTRAIT D'ARGOUSIER ET DE TENSIOACTIFS

RÉSUMÉ. De nouvelles émulsions structurées ont été obtenues par des technologies innovantes à base d'extrait (huile) d'argousier et de deux tensioactifs, dodécylsulfate de sodium et mélange Tween® 80 : Es – huile d'argousier/dodécylsulfate de sodium/eau ; Et – huile d'argousier/ Tween® 80/eau ; Est – huile d'argousier/dodécylsulfate de sodium et Tween® 80 (rapport 1:1)/eau, pour différentes concentrations d'extrait d'argousier, afin d'améliorer les propriétés de surface avec des applications dans l'industrie du cuir. L'extrait (huile) d'argousier a un fort effet antimicrobien et antifongique grâce à sa teneur en : vitamines C et E, phytostérols, acides gras, antioxydants et acides aminés. L'ordre d'introduction des composants dans les technologies innovantes, les conditions de travail et surtout le choix de la concentration en tensioactifs >CMC sont essentiels à la solubilisation de l'huile d'argousier et à l'obtention des émulsions structurées. Les émulsions ont été caractérisées par microscopie optique avec de l'huile d'argousier à 23-50°C. Les changements dans le processus d'agrégation ont été observés pour chaque type d'émulsion, l'influence de la température et la solubilisation de l'huile d'argousier. La diffusion dynamique de la lumière (DLS) a montré la stabilité, la concentration, la taille des particules, la polydispersité et le potentiel zêta des émulsions. Les propriétés antimicrobiennes ont été analysées par des tests microbiologiques. Les mesures FTIR ont mis en évidence le mécanisme d'interaction des tensioactifs avec l'huile d'argousier dans les émulsions structurées. Les échantillons de cuir ont été testés microbiologiquement et des effets antimicrobiens et antifongiques ont été observés. Les nouvelles émulsions structurées sont originales en raison de l'inclusion réussie d'extrait (huile) d'argousier avec un potentiel élevé d'amélioration des propriétés de surface avec des applications dans l'industrie du cuir.

MOTS CLÉS : nouvelles émulsions structurées, technologies innovantes à base d'extrait d'argousier et de tensioactifs, traitement des cuirs

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INTRODUCTION

This paper presents innovative technologies to create new structured emulsions, based on sea buckthorn extract (oil) and two tensides: sodium dodecyl sulfate and/or Tween® 80, in order to improve surface properties with applications in leather industry.

Sea buckthorn (*Hippophae*) has its origins in China, but we can also find it in temperate areas of the world: Russia, Mongolia, Finland, France [1-4]. Sea buckthorn is a thorny shrub with yellow or orange berries, the leaves are long lanceolate and can reach a height of 7 m. *Hippophae rhamnoides* has nine subspecies that differ based on genetic variations [5-7]. Sea buckthorn is also called *Siberian pineapple* because of berries that have a bitter-sour taste similar to that of pineapple. Due to the dense arrangement of the berries and thorns (Figure 1), harvesting the berries is cumbersome and is done once every two years [8-10].

Figure 1. Sea buckthorn branch with berries [11]

Sea buckthorn is rich in bioactive compounds present in fruits, seeds and leaves. In sea buckthorn fruits we find a rich content of: ascorbic acid, phytosterols, carotenoids, flavonoids, polyphenols, caffeic acid, ferulic acid [12-24]. Buckthorn berries contain: 23% seeds; 7% peel, 69% pulp. Due to its nutritional properties and beneficial effect on health, sea buckthorn is used in cosmetics, medicine, pharmacy and food [25-32].

Tween 80 [33] is a polyethylene sorbitol ester, also known as Polysorbate 80, PEG (80) sorbitan monooleate, polyoxyethylenesorbitan monooleate. It has been used as emulsifying agent for the preparation of stable oil-in-water emulsions. Tween is a group of non-volatile surfactant derivatives derived from glycerol esters. The most important usage of Tween is its application as an oil absorber and emulsifier.

Sodium dodecyl sulfate (SDS), also called sodium lauryl sulfate (SLS), having the formula: $CH_3(CH_2)_{11}OSO_3Na$ is an anionic tenside used as a cleaning and hygiene products [33].

In this research the new structured emulsions created and leathers processed with them were analyzed by FTIR-ATR spectroscopy, DLS, optical microscopy and microbiological tests.

EXPERIMENTAL

Materials and Methods

In order to obtain new structured emulsions the following materials were used: sodium dodecyl sulfate and Tween 80 from Sigma-Aldrich; sea buckthorn oil from "BIOCA" company.

The experimental techniques used in this paper consist in:

- "MALVERN" zetasizer-nano equipment, with measuring range between 0.3 nm-60.0 microns and zeta potential determination with an accuracy of +/-2%;
- JASCO FTIR-ATR spectrophotometer;
- optical microscopy with an ELTA 90 Medical Research S.R.L. equipment.

A number of three samples of emulsions – Es, Et, Est – were prepared in the following working conditions: sodium dodecyl sulfate or/and Tween 80 at 1:1 ratio, temperature=50°C for 30 minutes with sea buckthorn extract (oil), Figure 2.

a) b) c) d)

Figure 2. Image of new structured emulsions: a) Es – sea buckthorn oil/sodium dodecyl sulfate/water; Et – sea buckthorn oil/Tween® 80/water; Est – sea buckthorn oil/sodium dodecyl sulfate and Tween® 80 (ratio 1:1)/water; b) sea buckthorn oil; c) sodium dodecyl sulfate; d) Tween 80

RESULTS AND DISCUSSION

Obtaining New Structured Emulsions Based on Sea Buckthorn Oil and Tensides

Aqueous emulsions were obtained using two tensides, sodium dodecyl sulfate and Tween 80, in which sea buckthorn oil was introduced. According to novel innovative technologies in Figure 3, three types of new structured emulsions were made: Es, Et, Est.

The antimicrobial and antifungal effects were improved with the increase in the amount of sea buckthorn oil.

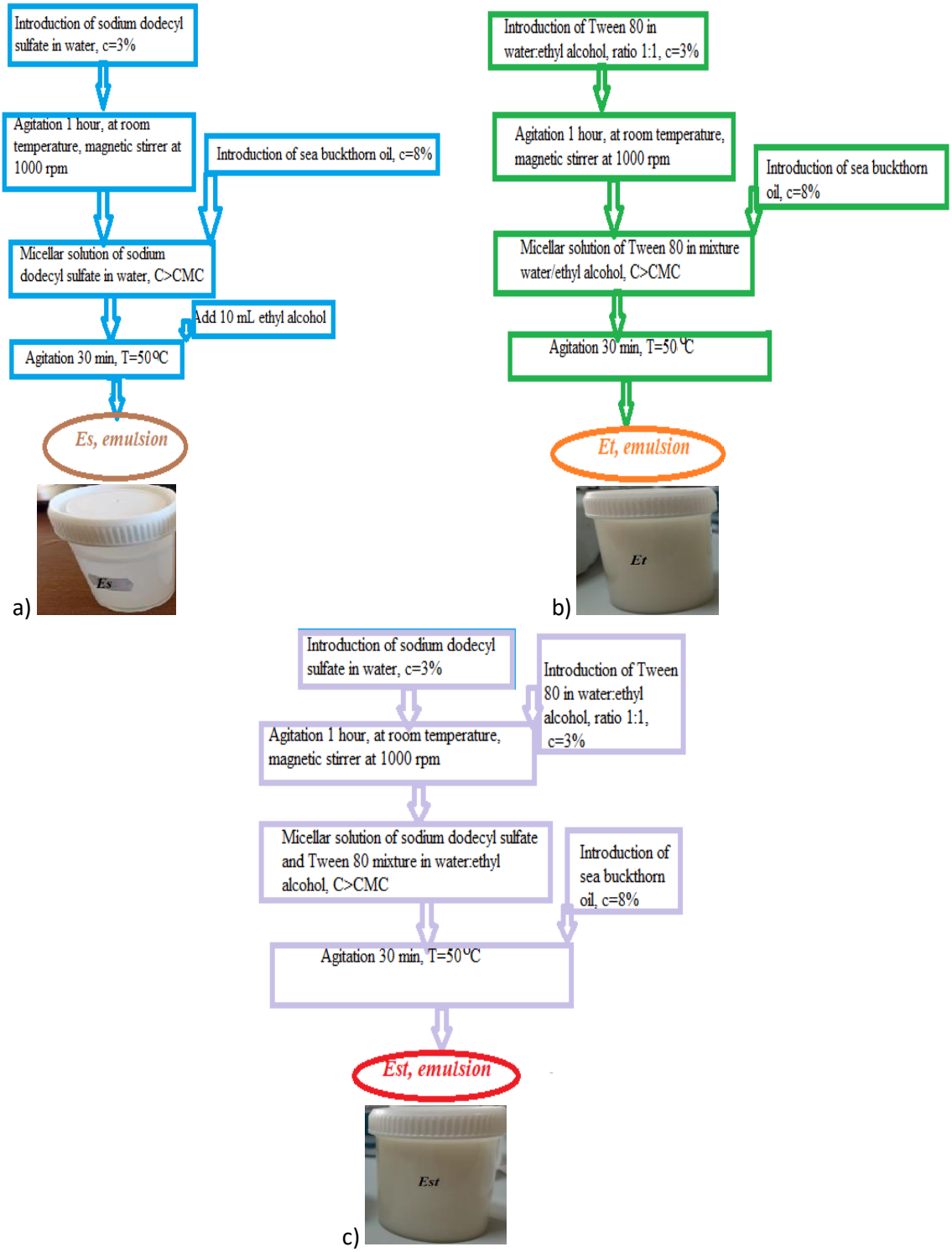


Figure 3. Innovative technologies for obtaining three types of emulsions with sea buckthorn oil:

a) Es; b) Et; c) Est

The Est emulsion variant with the two tensides sodium dodecyl sulfate and Tween 80 in a 1:1 ratio was selected because it is the most stable over time (1 month). The way of introducing tensides and sea buckthorn oil in obtaining emulsions is very important. The surfactant micellar solution is always made in water at a concentration above the micellar critical concentration – CMC and then the vegetable oil is added drop by drop and mixed. The chosen temperature is 50°C for a good solubilization of the vegetable oil in the surfactant micelles. When there are two tensides, micellar solutions in water are made separately for them, then the two solutions are mixed and mixed micelles in water are obtained. In the solution of mixed micelles, the vegetable oil is introduced drop by drop, stirring at the appropriate temperature. In the end, the emulsion is obtained with sea buckthorn oil solubilized in the mixed micelles. The yield of multiple drop formation decreases rapidly as the homogenization time increases. Structured emulsions are formed and the properties derive from the surfactants used, as well as the conditions and working parameters. This phenomenon is controlled by the concentration of: sea buckthorn oil, surfactants**,** temperature, pH=4.

Mechanism of Sea Buckthorn Oil Solubilization in Tenside Micelles

In this research, the interaction of sea buckthorn oil with two tensides, sodium dodecyl sulfate and Tween 80, was investigated. A mechanism for the solubilization of sea buckthorn oil in tenside micelles was proposed, Figure 4. The effect of the length of the carbon chain on the interaction was analyzed by FTIR-ATR spectroscopy. The experimental results suggested that Tween 80 was most efficient out of the two tensides taken for the study. The order of stability is given as sea buckthorn oil – Tween 80 > sea buckthorn oil – sodium dodecyl sulfate.

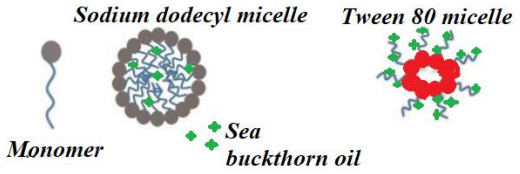


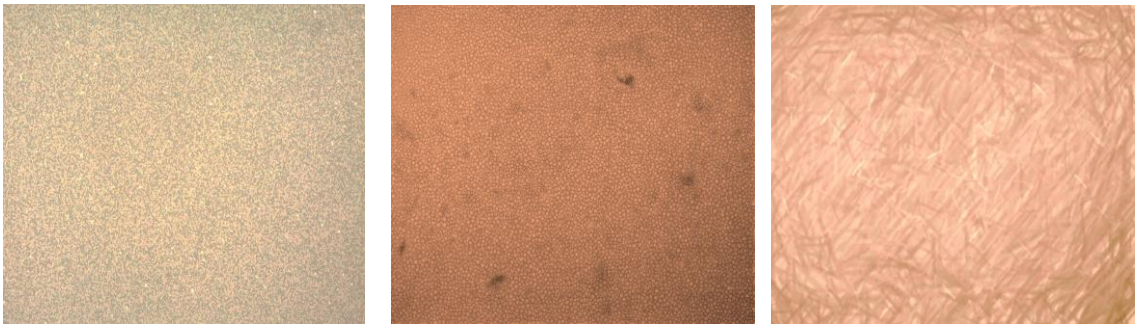
Figure 4. Proposed mechanism for solubilization of sea buckthorn oil in tensides: sodium dodecyl sulfate or Tween 80

Sea buckthorn oil is hydrophobic and gets stuck in the core of the micelles but also on the alkyl ends of the hydrophobic chains. For Tween 80, the amount of solubilized sea buckthorn oil is higher than in the case of sodium dodecyl sulfate, due to interaction forces.

Characterization of the Structured Emulsions Obtained and the Leathers Processed

Optical Microscopy Analyses of Structured Emulsions

The optical microscopy images from Figure 5 (a-f) show that all three emulsions obtained (at room temperature or 50 degrees) are structured like: irregular shapes (a, d), layer of balls (b, e) or bunches of needles (c, f) due to the influence of interaction between tensides and sea buckthorn oil.



a) b) c)

d) e) f)

Figure 5. Optical microscopy images of emulsions: a) Es at room temperature; b) Et at room temperature; c) Est at room temperature; d) Es at T=50°C; e) Et at T=50°C; f) Est at T=50°C

Dynamic Light Scattering (DLS) of Structured Emulsions

The average particle sizes of new structured emulsions showed dimensions between (10-2075 nm), confirming the formation of the complex aggregates, Table 1.

The three types of emulsions were analysed by dynamic light scattering (DLS), Table 1.

Table 1: Results of DLS for three emulsions: Es, Et, Est

Sample	Average diameter (nm)	% Intensity	Zeta Potential (mV)
Es	21	10	-55
	15	70	
	307	20	
Et	58	15	-38
	400	85	
Est	800	29	-70
	2075	71	

Characterization by FTIR-ATR Spectroscopy of Leathers Processed with Emulsions

The leathers were processed by spraying with the three obtained emulsions: Es, Et, Est, and were marked Esl, Etl, Estl (Figure 6) and then analyzed spectrophotometrically by FTIR-ATR.

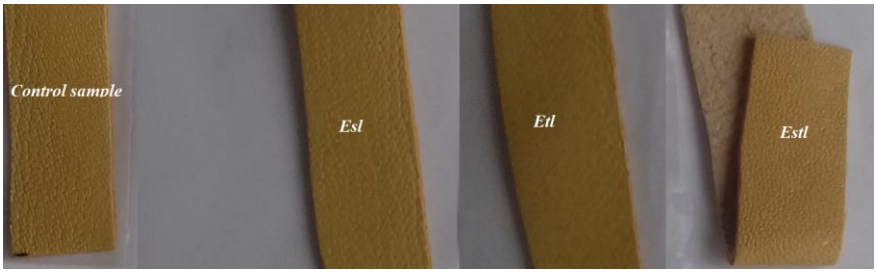


Figure 6. Image of the leathers processed with three structured emulsions: Es, Et, Est, and a control sample

From Figure 7 it can be seen that the largest amount of sea buckthorn oil is found in the leather treated with the Est emulsion (the spectrum intensity is the highest in the entire spectral range). The order of the sea buckthorn oil on the leather for the three emulsions is as follows: Estl>Etl>Esl.

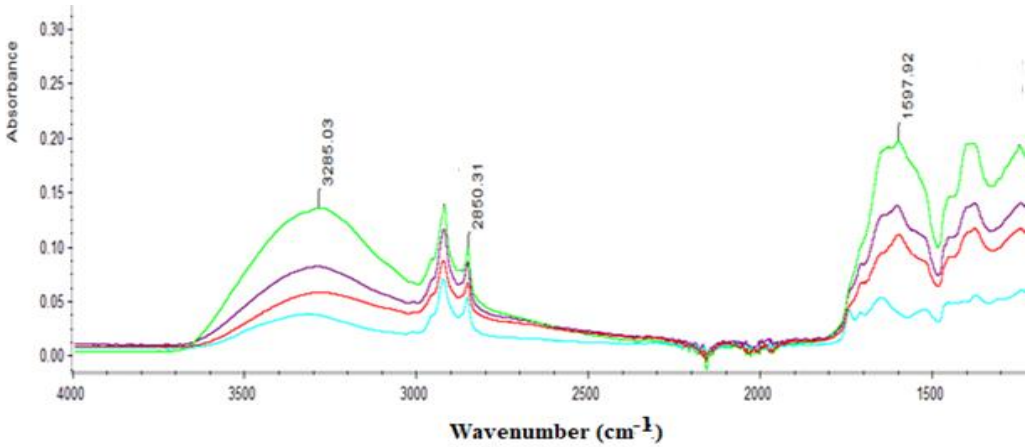


Figure 7. Overlay of FTIR-ATR spectra for leathers processed with emulsions: Esl---, Etl---, Estl--- control sample---

The Est emulsion is also the most stable, >1 month. The absorption maximum at the wavenumber ~1597 cm^{-1} is the result of the overlap of the CH_2 deformation with the asymmetric CH_3 deformation (the intensity of the absorption maximum being proportional to the number of CH_2 and CH_3 groups present).

The range of wavenumbers: 3400–3500 cm^{-1} is specific to sea buckthorn oil that has a high content of phenolic compounds and flavonoids. The absorption maximum at the wavenumber 2850 cm^{-1} represents a weak skeletal vibration of isopropyl ($R_1R_2C=CHR_3$), the deformation being out of plane for undeformed, weakly strained systems, i.e. for cyclohexene derivatives.

Microbiological Tests of Leathers Processed with Emulsions

The microbiological tests of leathers processed with three emulsions against the attack of *Staphylococcus aureus* ATCC 6538 and *Aspergillus niger* are presented in Table 2.

Table 2: Results of microbiological tests of leathers processed with three emulsions: Es, Et, Est

Sample	Result, UFC/mL	R%	Log_{10} red.	Sample	Result, UFC/mL	R%	Log_{10} red
Aspergillus niger, Inoculum concentration	$T_0=9.8x10^3$	-	-	*Staphylococcus aureus,* Inoculum concentration	$T_0=9.3x10^3$	-	-
Esl	$T_{24}=3.4x10$	99.65	2.46	Esl	$T_{24}=4.2x10$	99.55	2.35
Etl	$T_{24}=0$	100	4	Etl	$T_{24}=2$	99.98	3.67
Estl	$T_{24}=2.18x10^2$	97.78	1.44	Estl	$T_{24}=1.98x10^2$	97.87	1.67

CONCLUSIONS

1. The aim of this research was fulfilled to develop new emulsions and to study the influence of tensides and sea buckthorn oil in obtaining structures like: irregular shapes, layer of balls or bunches of needles. The structures of new emulsions were demonstrated by optical microscopy.

2. The emulsions with particle sizes of 10-2075 nm were obtained by DLS tests.

3. The new multiple structured emulsions are original due to the successful inclusion of sea buckthorn oil, with applications in the leather industry.

4. A mechanism of solubilization of sea buckthorn oil in tenside micelles was proposed. Sea buckthorn oil is hydrophobic and gets stuck in the core of the micelles but also on the alkyl ends of the hydrophobic chains. For Tween 80, the amount of solubilized sea buckthorn oil is higher than in the case of sodium dodecyl sulfate, because it has a larger hydrophobic chain, for which Van der Waals interaction forces are responsible.

5. The changes in the aggregation (structured) process were observed for each type of emulsion (Es, Et, Est), the solubilization

of sea buckthorn oil by dynamic light scattering and optical microscopy.

6. In the process of finishing the leathers by spraying with three types of structured emulsions obtained compared to an untreated leather, the antifungal and antimicrobial properties, as well as the softness and appearance of the leathers were improved.

Acknowledgments

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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, and were also published in the 2019-2022 issues of *Leather and Footwear Journal*. Newsletter 3 of 2023 is given below.

NEWS 3/2023

European Workshop on Accidents/Injuries at the Workplace

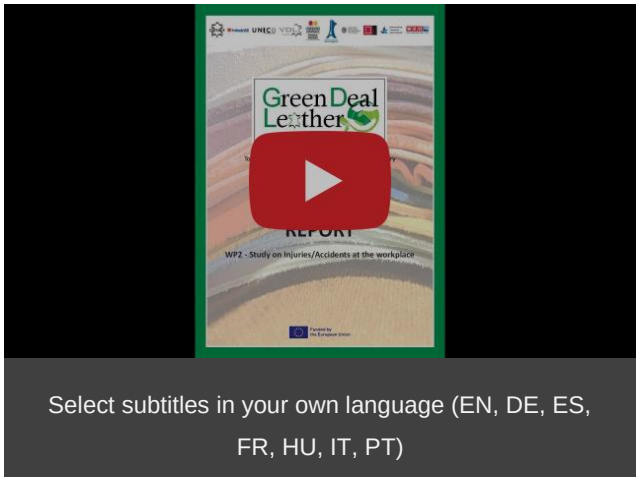
On 19 September 2023, on the premises of Lineapelle, the international leather fair in Milan, the European social partners for the tanning and leather sector, COTANCE and industriAll European Trade Union, held a European workshop to review the state of play in *Workplace Safety in European Tanneries.*

The workshop, developed as part of the EU-funded social dialogue project *''Towards Zero Adverse Impact of the European Leather Industry – GREEN DEAL LEATHER''*, brought together employers, trade unions and other stakeholders to review the results of a study on Injuries/Incidents at the workplace and discuss how to progress towards "Zero Impact".

(Left to right) Manuel Rios (President of COTANCE), Patrizia Pitronaci (industriAll-Europe), Gustavo Gonzalez-Quijano (COTANCE), Silvia Pedrana (UNIC)

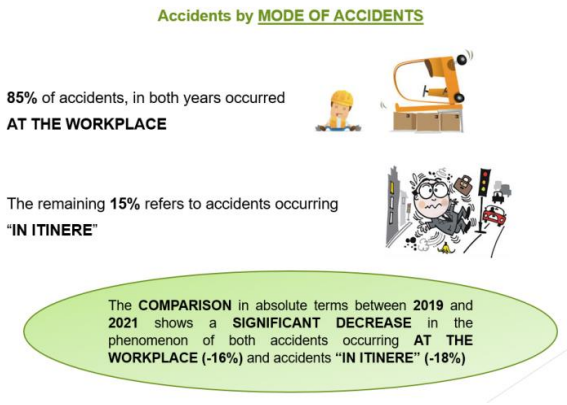
Opening the event, Manuel Rios, President of COTANCE, said:

*"Our common ambition is to **drive positive change in the global leather industry** by "leading by example". The present report pulls together all sector-specific information on tannery workplace accidents in Europe for better understanding them and drawing lessons for improved workplace safety in tanneries."*



COTANCE's Secretary General, Gustavo Gonzalez-Quijano**,** explained the context of the Green Deal Leather project, emphasising: "*Since COTANCE started the Social Sectoral Dialogue with its Trade Union counterparts some 25 years ago, **workers' health and safety has always been at the top of our agenda**. We understand that this concern ought to be the first priority when it comes to implementing Due Diligence in leather supply chains, as any accident at the workplace is irremediably a failure, with adverse consequences, above all, for the victim, but also for the employer."*

With 1102 accidents in 2021, the incidence of accidents at work in European tanneries is 3,2%. This figure includes accidents on the way to or from the workplace. Serious accidents are rare, most are wounds (49%), including superficial cuts concerning mainly the upper limbs (47%) with half involving hands (23%). **From 2019 to 2021 accidents have decreased by 16% (both female and males).**



In the words of Judith Kirston-Darling, Deputy General Secretary of industriAll-Europe:

*"**Quality social dialogue is essential to ensure a safe tanning and leather sector in Europe.** We encourage all employers to produce relevant data on occupational health and safety issues and to work closely with workers and their representatives at site level to ensure that all workers are properly trained, and that adequate health and safety measures are fully respected by both sides. By working together in an open and positive manner, we can eliminate accidents in the workplace and keep workers safe."*

The Green Deal Leather study on "Injuries/Incidents at the workplace" is available for download on COTANCE's website.

A recording of the Workshop is available on our You Tube channel.

edited by

Funded by the European Union

NEWS 4/2023

Szeged Slippers: Or How Leather Can Become a Part of a National Cultural Heritage

Leather has always been used to enhance everyday products and to create beauty and culture. Please meet Hungary's most famous shoe – **Szeged Slipper**.

Photo by Frank Yvette

The cultural treasure of Hungary that stands out for its beauty and history, and added to the UNESCO National Cultural Heritage List in 2018, Szeged slippers, also known as Szegedi papucs, are traditional Hungarian slippers originating from the city of Szeged. These handmade slippers, a symbol of tradition and comfort, have been crafted in the region for centuries and leather has always been the material of choice for their manufacture.

Originally, these slippers were worn at home during holidays or when receiving guests, and it was only by the end of the 19th century that they became a widespread favourite for outdoor and everyday elegance.

Nowadays, Szeged slippers are experiencing a rebirth, thanks to the efforts of a prominent Hungarian shoe designer, Zita Attalai. Collaborating with craftsman Tibor Sallay and his team, Ms Attalai aims not only to increase the popularity of Szeged but also to achieve a Hungarikum* status for them, which will empower designers to better preserve the Szeged tradition.

* “Hungarikum is a term that designates a value worthy of distinction within a unified system of qualification, classification and registration and that represents the high performance of the Hungarian people thanks to their typically Hungarian attributes, uniqueness, specialty and quality”, - according to Ms Attalai's description.

Photo by Ligetvári Csenge

Photo by Sallay Szegedi papucs

Szeged slippers are typically made from various materials such as leather and velvet and often feature intricate embroidery or other decorative elements. “The main characteristic of the Szegedi of that time was the material chosen for its manufacture, red velvet enriched with embroidery of wildflowers from the fields around Szeged. Szegedi were also part of the Hungarian wedding dress and it was customary for the groom to give the bride a pair in white as an engagement gift”, - says Ms Attalai in one of her interviews with Sara Sáez Garcia (Folkmania Traditional Fashion Legacy).

Valued for its outstanding quality, durability, and naturalness, leather was and still is a core constituent of Szeged slippers. Leather is utilised not only for the sole and upper parts of the slippers but also in the insoles and the lining, ensuring each part benefits from its softness and durability.

Photo by Sallay Handmade Elephant films

Designed with a symmetrical shape from a single-foot mould, the slippers can be worn on both feet. It is only during wearing that one can determine which slipper is best suited for the right or left

foot. Having leather as a core material not only helps to maintain the uniqueness of Szeged slippers but also enhances their longevity, making them a precious heirloom worth passing down from generation to generation.

"I work with genuine leather, and prefer to create objects with precise attention and care, which is why I represent the attitude of slow fashion", - says Zita Attalai.

So next time you are in Hungary, do not forget to get your own unique pair of Szeged leather slippers.

edited by COTANCE

in collaboration with ASSOCIATION OF HUNGARIAN LIGHT INDUSTRY

You want to know more:

Zita Attalai | **Web**

The Szegedi. A shoe full of history | **Folkmania, Traditional Fashion Legacy**

Documentary on Szeged slippers making | **Youtube**

Go for Slow Fashion - choose leather! | **COTANCE Newsletter 1/2022**

Leather for Christmas? - Of course! | **COTANCE Newsletter 8/2022**

NEWS 5/2023

Festive Leather Treasures: Perfect Gifts for December

There is something special in the air in December that instills a festive spirit in everyone. Crowded streets, glowing shop windows, and crowds hunting for the ideal holiday gift. Resistance is futile! So if you're seeking a gift that your loved ones will treasure for years or a personal reward that reflects your achievements, **think of leather!**

Leather is a choice that never disappoints. It's not just a gift; it's a lasting memory, a timeless treasure and an investment.

As a living, valuable material, leather requires care and evolves just like people. It's a statement, it reflects your personality, it boosts your confidence. As it ages, leather becomes an integral part of your personal story and treasured memories, with each scratch, crease, and patina telling its own unique narrative. And here's something interesting: as the years pass, leather only improves, much like a person.

So why not let leather tell your exceptional story?

A leather item can symbolise the beginning of a new chapter in your life or in a special relationship. It can become an immortal symbol of love or a promise made to yourself on New Year's Eve.

And you have plenty of choices: leather handbags, bags, wallets, or cardholders can boost your confidence and reinforce your status. Accessories such as cosmetic and toiletry bags, jewellery organizers, and belts or gloves can foster self-love. Leather charms, laptop pouches or leather trays/baskets can enhance your individuality. Meanwhile, backpacks, luggage tags, and passport covers offer added comfort, security, and a sense of self-respect.

Moreover, a leather item can become a precious heirloom worth passing down from generation to generation. Think of grandmother's beautiful leather handbag that has been with your family for generations. Quality vintage items like this never go out of fashion! Or think about your father's leather briefcase, a symbol of his hard work and dedication, or the leather couch you took from home when moving into your first apartment.

Why not start a family tradition by gifting a durable item? Such a gift can last for many years and serve as a constant reminder of you, your love, and your shared memories.

Why not start a family tradition by gifting a durable item?

Such a gift can last for many years and serve as a constant reminder of you, your love, and your shared memories.

Therefore, choosing leather as a gift transcends mere expenditure; it's an investment in all senses. Whether it’s purchasing a luxury bag that retains value over time or buying your child his/her first leather soccer ball, leather signifies more than just a material purchase.

It is also a significant contribution to a more sustainable, green and slow-fashion world. We do not want to annoy you with all these facts about how leather champions sustainability through its durability, biodegradability, and effective carbon storage. You can always deepen your knowledge by following the link.

What we really want is to offer you an alternative that ensures your success.

Still unsure about choosing a leather gift for this festive season? Discover 'Leather for Christmas' and explore another inspiring story that will encourage you to integrate more leather into your life.

News Release from the IULTCS

6th November 2023

Geoff Holmes Elected as IULTCS Vice President

The IULTCS Executive Committee is pleased to announce that Geoffrey Holmes has been elected as the new Vice President; he will take up the position in January 2024.

Geoff has a long history in the leather industry, having studied Leather Technology at the Leathersellers College at the University of Northampton. Prior to this he graduated with a BSc (Hons) in Applied Science at Kingston University, London.

The IULTCS Executive Committee is very confident that Geoff will make an excellent Vice President and move on to be a successful President in 2026. We look forward to working closely with him in the months and years ahead.

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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.
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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.
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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).
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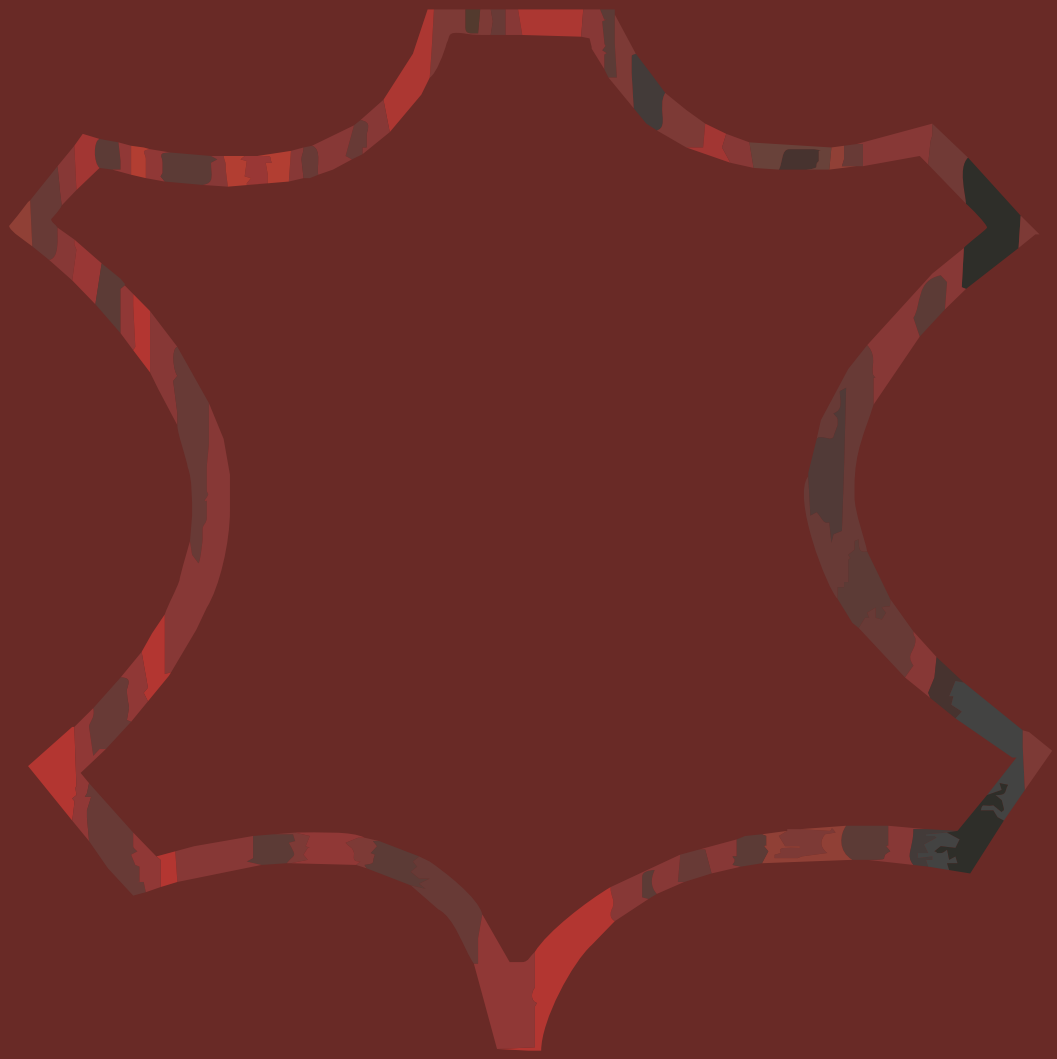

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