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	CONTENTS	*CUPRINS*	*SOMMAIRE*	
Juma Sharopovich AZIMOV **Maria Ivanovna MARKEVICH** **Tulkin Jumaevich KODIROV** **Shokhrukh Shukhratovich SHOYIMOV** **Akmal Yusupovich TOSHEV**	Estimation of the Regimes of Ablation of the Fabric of Karakul for Glutaraldehyde Tanning under the Exposure of a Laser on Yttrium Aluminum Garnet	Estimarea regimurilor de ablație a pielii de karakul pentru tăbăcire cu glutaraldehidă la expunere sub laser cu impulsuri de granat de ytriu-aluminiu	L'estimation des régimes d'ablation de la peau de karakul pour le tannage au glutaraldehyde lors de l'exposition au laser au grenat d'yttrium et d'aluminium	159
Demetra SIMION **Carmen GAIDĂU** **Gabriela PĂUN** **Maria STANCA** **Daniela BERECHET**	Obtaining Bioemulsions Structured as "Networks" by Innovative Technologies	Obținerea unor bioemulsii structurate sub formă de „rețele" prin tehnologii inovatoare	Obtenir des bioémulsions structurées en « réseaux » par des technologies innovantes	169
Qian LU **Shunxun LI** **Jin ZHOU** **Zhifeng YAO** **Wei LI**	The Validity and Reliability of TrueDepth Camera Embedded in the Phone for Foot Measurement	Validitatea și fiabilitatea camerei TrueDepth încorporate în telefon utilizate la măsurarea piciorului	La validité et la fiabilité de la caméra TrueDepth intégrée au téléphone pour la mesure du pied	175
Rodica Roxana CONSTANTINESCU **Mariana FERDEȘ** **Mădălina IGNAT** **Ciprian CHELARU** **Ana-Maria CIOBANU** **Denis DRUȘAN**	Enzymatic Biotechnology Applied to Pelt Waste	Biotehnologie enzimatică aplicată deșeurilor de piele gelatină	La biotechnologie enzymatique appliquée aux déchets de peau en tripe	185
Laurenţia ALEXANDRESCU **Mihai GEORGESCU** **Maria SÖNMEZ** **Mihaela NIȚUICĂ** **Maria-Daniela STELESCU** **Dana GURĂU**	Polymer Composite Based on Natural Rubber and Functionalized Rubber Waste	Compozit polimeric pe bază de cauciuc natural și deșeu de cauciuc funcționalizat	Composite polymère à base de caoutchouc naturel et de déchets de caoutchouc fonctionnalisés	197
Olga NICULESCU **Rodica Roxana CONSTANTINESCU** **Dana GURĂU**	Testing of Medical Sheep Fur with Antimicrobial Properties – Part 1	Testarea blănurilor medicale de oaie cu proprietăți antimicrobiene – Prima parte	Test des peaux de mouton médicales aux propriétés antimicrobiennes – Première partie	209
Demetra SIMION **Carmen GAIDĂU** **Gabriela PĂUN**	Preparation of Elastin Membranes Based on Surfactants and Separation Mechanism	Prepararea membranelor din elastină pe bază de surfactanți și un mecanism de separare	Préparation de membranes d'élastine à base de tensioactifs et mécanisme de séparation	217
Laurenția ALEXANDRESCU **Mihai GEORGESCU** **Maria SÖNMEZ** **Mihaela NIȚUICĂ** **Maria-Daniela STELESCU** **Dana GURĂU**	Biodegradable Polymeric Composites Based on Natural Rubber and Functionalized Post-Consumer Leather Waste	Compozite polimerice biodegradabile pe bază de cauciuc natural și deșeuri de piele post-consum funcționalizate	Composites polymères biodégradables à base de caoutchouc naturel et de déchets de cuir post-consommation fonctionnalisés	223
	European Research Area	Spațiul european al cercetării	Espace Européen de la Recherche	236
	National and International Events	Evenimente naționale și internaționale	Événements nationaux et internationaux	244

ESTIMATION OF THE REGIMES OF ABLATION OF THE FABRIC OF KARAKUL FOR GLUTARALDEHYDE TANNING UNDER THE EXPOSURE OF A LASER ON YTTRIUM ALUMINUM GARNET

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ESTIMATION OF THE REGIMES OF ABLATION OF THE FABRIC OF KARAKUL FOR GLUTARALDEHYDE TANNING UNDER THE EXPOSURE OF A LASER ON YTTRIUM ALUMINUM GARNET

ABSTRACT. The article discusses the activation of the surface of karakul (astrakhan) leather tissue by laser exposure, changes in the surface morphology of karakul leather tissue during laser processing and subsequent glutaraldehyde tanning combined with chrome tanning of karakul leather. The morphology of the surface of the sample was investigated by the methods of optical and scanning electron microscopy and the elemental analysis of the skin tissue of karakul under the action of laser radiation from the front side was carried out. Dry tanning was carried out after laser exposure. For the first time, the morphology of the surface of the skin tissue of karakul was investigated using a laser generating in a two-pulse mode (pulses are separated by a time interval of 3 μs, pulse duration of 10 ns) with a wavelength of 1064 nm in a wide range of deposited energies, which lead, as to the mode of ablation of the surface of the skin tissue of karakul and to its perforation followed by glutaraldehyde tanning. The possibility of changing the consumer parameters of the skin tissue of karakul due to the dermis dissociation, conformational changes, which lead to a change in the structure, is shown. At energies more than 30 J, the skin is perforated with carbonization of the edges of the holes.

KEY WORDS: Karakul skins, glutaraldehyde, morphology, hydrothermal destruction, laser radiation

ESTIMAREA REGIMURILOR DE ABLAȚIE A PIELII DE KARAKUL PENTRU TĂBĂCIRE CU GLUTARALDEHIDĂ LA EXPUNERE SUB LASER CU IMPULSURI DE GRANAT DE YTRIU-ALUMINIU

REZUMAT: Articolul discută despre activarea suprafeței pielii de karakul (astrahan) prin expunerea la laser, modificările morfologiei suprafeței pielii de karakul în timpul prelucrării cu laser, precum și tăbăcirea ulterioară cu glutaraldehidă combinată cu tăbăcire în crom a pielii de karakul. S-a investigat morfologia suprafeței probei prin metodele de microscopie electronică optică și de scanare și s-a efectuat analiza elementară a pielii de karakul sub acțiunea radiației laser din partea frontală. S-a efectuat tăbăcirea uscată după expunerea la laser. Pentru prima dată, morfologia suprafeței pielii de karakul a fost investigată folosind un laser care funcționează în modul cu două impulsuri (impulsurile sunt separate la un interval de timp de 3 μs, durata impulsului de 10 ns) cu o lungime de undă de 1064 nm într-o gamă largă de energii depuse, care generează ablația suprafeței pielii de karakul și perforarea acestuia, urmate de tăbăcirea cu glutaraldehidă. Se prezintă posibilitatea de a modifica parametrii de consum al pielii de karakul din cauza disocierii dermei și modificărilor conformaționale care conduc la o schimbare a structurii. La energii mai mari de 30 J, pielea este perforată, având loc carbonizarea marginilor orificiilor.

CUVINTE CHEIE: piele de karakul, glutaraldehidă, morfologie, distrugere hidrotermală, radiații laser

L'ESTIMATION DES RÉGIMES D'ABLATION DE LA PEAU DE KARAKUL POUR LE TANNAGE AU GLUTARALDEHYDE LORS DE L'EXPOSITION AU LASER AU GRENAT D'YTTRIUM ET D'ALUMINIUM

RÉSUMÉ. L'article traite de l'activation de la surface du cuir de karakul (astrakan) par exposition au laser, des modifications de la morphologie de surface du cuir de karakul pendant le traitement au laser et du tannage ultérieur au glutaraldéhyde combiné au tannage au chrome du cuir de karakul. La morphologie de surface de l'échantillon a été étudiée par les méthodes de microscopie optique et électronique à balayage, et l'analyse élémentaire de la peau de karakul sous l'action du rayonnement laser de la face avant a été effectuée. Le tannage à sec a été réalisé après exposition au laser. Pour la première fois, la morphologie de surface de la peau de karakul a été étudiée à l'aide d'un laser fonctionnant en mode à deux impulsions (les impulsions sont séparées par un intervalle de temps de 3 μs, durée d'impulsion de 10 ns) avec une longueur d'onde de 1064 nm dans un large gamme d'énergies déposées, qui génèrent l'ablation de la surface de la peau de karakul et sa perforation, suivie d'un tannage au glutaraldéhyde. La possibilité de modifier les paramètres de consommation de la peau de karakul en raison de la dissociation du derme et des changements de conformation conduisant à un changement de structure est présentée. Aux énergies supérieures à 30 J, la peau est perforée, carbonisant les bords des trous.

MOTS CLÉS : peau de karakul, glutaraldéhyde, morphologie, destruction hydrothermale, rayonnement laser

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INTRODUCTION

Karakul skins are the main products of karakul sheep. The beauty, peculiar shape and originality of curls, their variety, noble shine and silkiness of the hairline, elegance of drawings brought fame to karakul skins. Karakul skins are in great demand among the population [1]. Therefore, great attention is paid to the quality of the karakul products.

Chemicals are used in the leather and fur industry for tanning skins from karakul fur, sheepskin, goat and other skins [2]. This is a method of tanning skins using a tanning composition based on the reaction products of polyoxymethylene with a secondary amine and alcohol and which are after the reaction in the form of tertiary amino groups and ether groups [3].

Laser technologies are increasingly being introduced into the production of products from karakul leather fabric. Laser radiation has coherence, monochromaticity, collimation, which makes it unique. The interaction of laser radiation with the skin tissue of karakul is based on its physical properties [4-6].

The main physical parameters that determine the effect on natural skin are the generated wavelength and power density [4, 7]. It is also important to take into account the inhomogeneity of the spectral absorption of the karakul skin tissue, since hemoglobin has many absorption peaks, and the absorption of melanin gradually decreases as the wavelength of light increases. To activate chemical reactions on the surface of the skin tissue of karakul or to remove defects, ablation of the area of the affected skin tissue of karakul, including the epidermis, is carried out. Laser ablation is understood as a complex of processes that lead to an explosive ejection of a substance from the zone of exposure to laser radiation. Of interest are the modes in which the removal of the substance from the zone of action occurs quickly enough that the areas of the karakul skin tissue surrounding the laser crater do not have time to heat up due to the transfer of heat.

The aim of this work is to study the morphology of the surface of natural leather during laser ablation to establish the conditions for perforation of the leather tissue of karakul; glutaraldehyde tanning was combined with chrome tanning in the double pulse mode.

EXPERIMENTAL PART

Objects of Study

Karakul (Uzbekistan. Karakul – diminutive of “karakul, sheep of the Karakul breed”; from Uzbek. Karakul “Black Lake”, after the name of the city and area in Uzbekistan) – fur made from the skins of premature lambs (miscarriages in the last period of pregnancy) or fruits (extracted from the womb of slaughtered queens) of karakul sheep, as well as products made from this fur [8].

Karakul literally translates from Turkic, black as ash (karakul) – skin with fur, removed from lambs of the Karakul breed on 1-3 days after birth, when their wool is characterized by thick, elastic, silky hair, forming curls of various shapes and sizes [8].

Glutaraldehyde (glutaraldehyde, pentane dial) is an organic compound, an aldehyde with the chemical formula $C_5H_8O_2$. Transparent and colorless liquid, easily soluble in water, irritating to eyes and lungs. It is used as a tanning agent in the production of leather, and is used in the textile industry and microscopy [9].

Methodology and Research

Laser Radiation

In this work, we used laser processing in the mode of double pulses of a sample of karakul leather tissue. We used an LS-2134D yttrium aluminum garnet laser (LOTIS, Belarus) with a wavelength of 1064 nm, generating in a two-pulse mode (the pulses are separated by a time interval of 3 μs, the pulse duration is 10 ns). The sample was treated with laser radiation in the energy range of 1–30 J at exposure times of 1–30 s [10].

SEM Research and Elemental Analysis

The study of the surface morphology of the leather was carried out using a MIRA-3 scanning electron microscope (Czech Republic) with a system of micro analyzers from Oxford Instruments (Great Britain). The device allows

you to simultaneously study the surface morphology of the material, determine the distribution of chemical elements of the sample, and also obtain an image of the object in a wide range of magnifications. The thickness of the leather sample is ~500 µm [11].

Magnetic Resonance

Magnetic resonance studies were carried out on a specialized small-sized EPR analyzer Minsk 22 at room temperature. The working wavelength is 3 cm. The maximum value of the magnetic field induction is 450 mT. The modulation frequency of the magnetic field is 30 kHz. To calibrate the signal intensity of the objects of study, we used a sample from a ruby single crystal (Al_2O_3: Cr^{3+}). The optimal parameters for recording the working magnetic resonance spectra were chosen in the range of g-factors from 1.5–4.0. During measurements, an additional control of the stability of the spectrometer was carried out by measuring the calibration material of divalent manganese ($MgO{\cdot}Mn^{2+}$) [10].

RESULTS AND DISCUSSION

In this work, we used laser processing of leather tissue in the dual pulse mode. An LS-2134D yttrium aluminum garnet laser (LOTIS, Belarus) with a wavelength of 1064 nm was used, which generated in a two-pulse mode (pulses were separated by a time interval of 3 µs, pulse duration 10 ns) [11]. The energy input was determined by the exposure time and ranged from 1 to 30 J. During the research, we used unpainted waste of karakul leather fabric (made in Uzbekistan). Samples of tanning fabric karakul semi-finished product from the front side were treated with laser radiation. After pickling or fermentation, the skin tissue of the skin acquires strength, ductility and other useful qualities necessary in the manufacture of fur products. However, its strength can be compromised when wearing a finished fur product. Under the influence of moisture (rain or snow), peeling, swelling of the leather fabric of karakul fur can occur, and subsequently such fur products wrinkle and warp. To avoid these undesirable phenomena, tanning is carried out.

The purpose of tanning is to consolidate the properties obtained during pickling, to make the skin resistant to unfavorable factors – heat, moisture, chemicals and enzymes. Tanning agents of inorganic origin include compounds of aluminum, iron, titanium, zirconium and others, and organic ones – tannins, amino resins, aldehydes, highly unsaturated fats, etc. [12].

Tanning is a complex process that begins with the diffusion of tanning compounds into the structure of collagen protein, with which it then interacts, forming strong chemical compounds in the leather tissue of karakul fur. Under the influence of tanning compounds, collagen acquires new properties: its heat resistance, characterized by the welding temperature, increases, strength increases, porosity of the karakul leather tissue decreases, swelling disappears, and chemical resistance increases. When dressing skins (mostly sheepskins), glutaraldehyde tanning can be used.

In any case, it must be remembered that aldehydes are capable of dyeing fur white. Therefore, it is recommended to tan skins with white fur with aldehyde. Samples of tannery karakul semi-finished product were placed in a solution of sodium chloride (NaCl) with the addition of acetic acid (treatment for 2 hours), then glutaraldehyde was introduced (treatment for 4 hours), then baking soda was added (treatment for 1 hour).

Then the samples of the leather fabric of karakul fur were squeezed out and left to lie down, dried and kneaded. All processes were carried out at a temperature of 30°C. Leather treatment with glutaraldehyde, in addition to softness and elasticity, is characterized by a higher resistance to sweat and moisture in comparison with chrome tanning [13-15]. Glutaraldehyde tanning has been combined with chrome tanning.

Modern metallographic microscopes using various methods of optical contrasting make it possible to study the structures of non-metallic materials. In this work, an inverted metallographic microscope MI-1 was used to study changes in the surface morphology of the

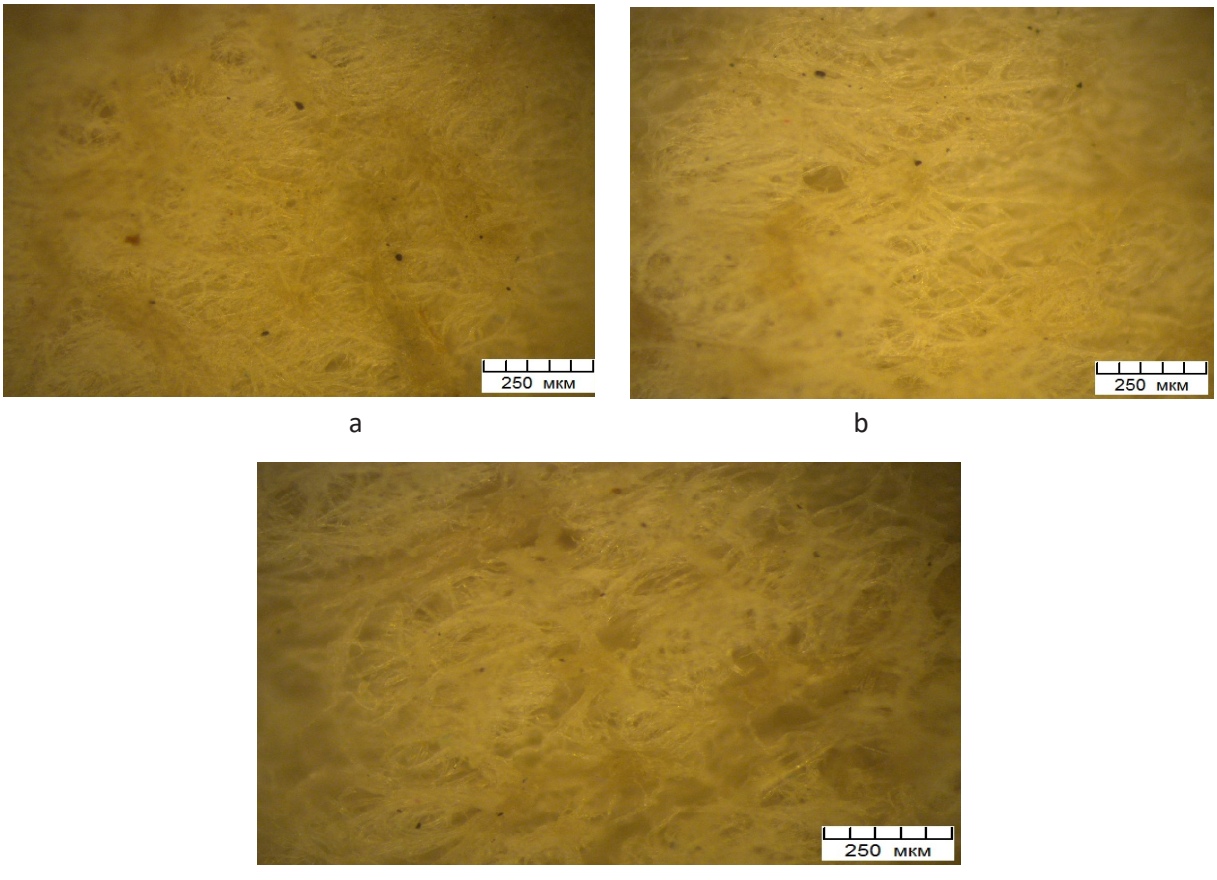
skin tissue of karakul. The analysis of the skin surface was carried out at 100x magnification using dark field illumination.

The study of the chemical composition of karakul leather tissue was carried out using a scanning electron microscope MIRA-3 (Czech Republic) with a system of micro analyzers from Oxford Instruments (Great Britain). The device allows you to simultaneously investigate the morphology of the material surface, determine the distribution of chemical elements of the sample under study, and obtain an image of the object in a wide range of magnifications.

In accordance with [4], under the influence of the first laser pulse, the substance evaporates, and a region with an increased temperature and a reduced density of air particles is formed in the near-surface layer, which leads to a more complete use of the energy of the second pulse for laser ablation [4]. It is known that when exposed to a series of nanosecond pulses, the main mechanism for removing a substance is thermo-mechanical ablation, which leads to the removal of the surface layer.

When exposed to IR laser radiation, energy is absorbed on the surface of the tanning fabric of the karakul semi-finished product. It is known that the nature of light erosion is largely determined by the characteristics of the material itself: optical, thermo-physical properties, structural in homogeneities, etc.

Figure 1 shows the surface of the karakul skin tissue that was not exposed to laser action and was exposed to laser action with different input energies.

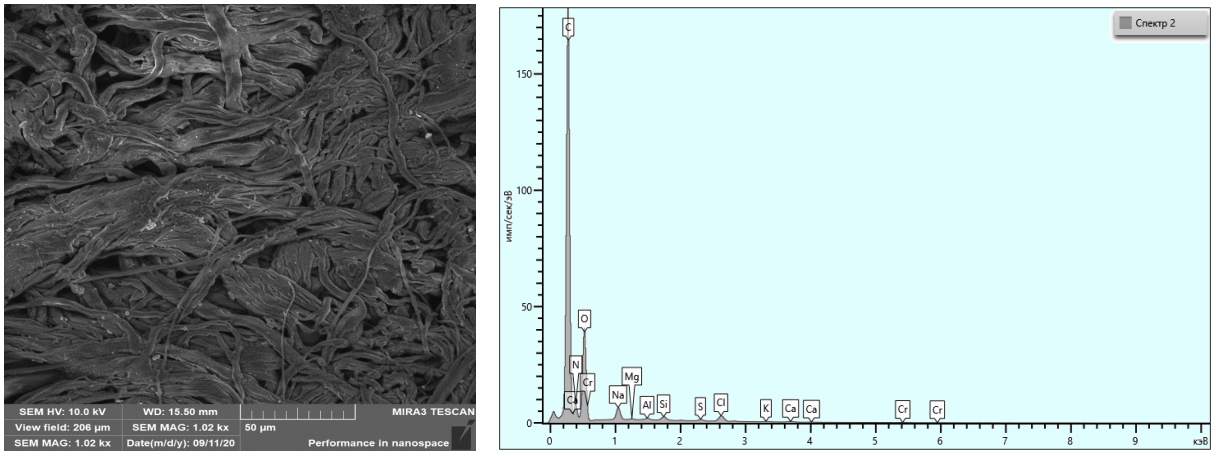


a b c

Figure 1. Morphology of the surface of the front side of the fabric of karakul before and after laser exposure: a) without exposure, b) after exposure (input energy 1 J, exposure time 1 s), c) after exposure (input energy 5 J, exposure time 5 s)

It follows from Figure 1 that with an increase in the energy deposited into the sample, the structure loosens (the fibers move apart) and the pore size increases. So, the size of the pores varies from 30 to 50 microns (Figure 1b) and from 50 to 125 microns (Figure 1c).

Figure 2 shows the structure and elemental composition of karakul leather fabric after chrome and glutaraldehyde tanning.



a b

Figure 2. Morphology of the surface of the face of the fabric of karakul after laser exposure: a) after exposure (input energy 5J, exposure time 5s)

Individual collagen fibers with a thickness of 1-2 microns are clearly visible, the joints of these collagen fibers form bundles of fibers 10-50 microns thick, intertwining in different directions to form a complex dermis tissue.

Figure 3 shows the morphology of the karakul skin tissue after laser exposure, during which the karakul skin tissue is perforated. Laser perforation is performed in the production of clothing, handbags and other products, mainly for decorative processing.

However, due to the porosity of the karakul leather tissue, there are also problematic issues, in particular, the combustion process when exposed to a laser beam, as well as the remnants of material inside the hole due to the fuzzy study of the hole in these modes. Therefore, it is necessary to investigate the modes of laser processing of karakul leather tissue in the process of its perforation.

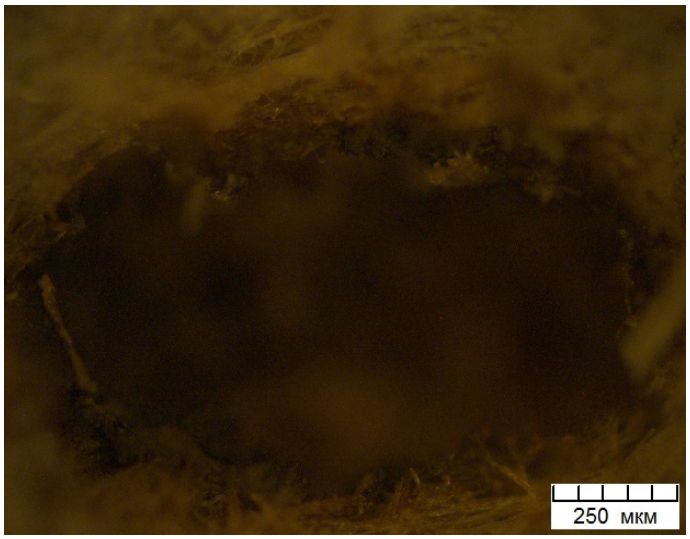


Figure 3. Morphology of the surface of the face of the fabric of karakul after laser exposure: after exposure (input energy 30 J, exposure time 30 s)

From Figure 3 it follows that at energies more than 30 J, perforation of the karakul leather tissue occurs and carbonization is observed at the edge of the hole, the size of the perforated hole reaches approximately 1100 microns.

Figure 4 shows the surface morphology and elemental composition of the karakul leather tissue (scanning microscopy) in the mode of its perforation.

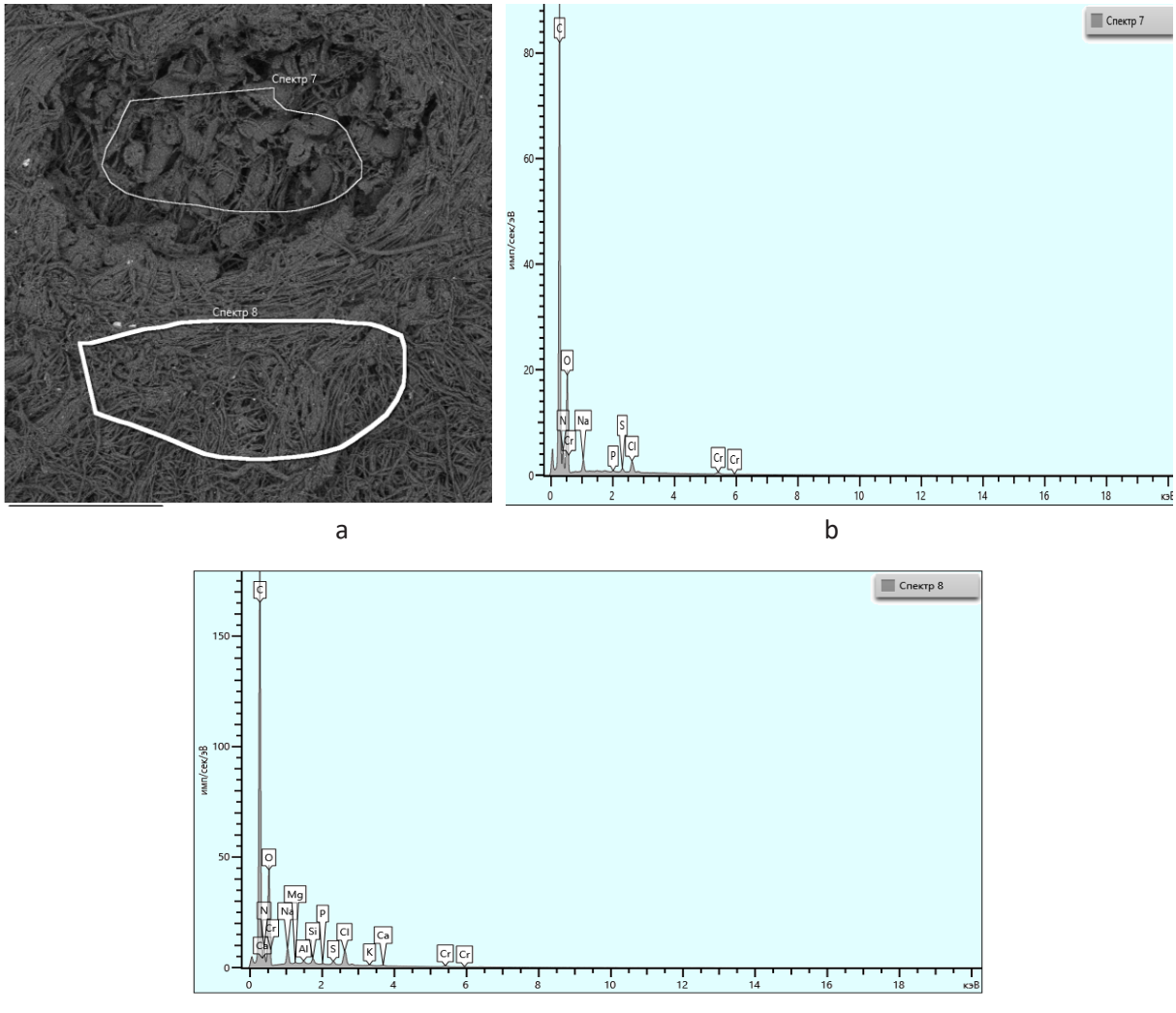


Figure 4. Surface morphology and elemental composition after laser exposure:
a) in the perforation zone (input energy 30J, exposure time 30 s), b) at the periphery of the exposure zone, c) spectra of the elemental composition of the peripheral crater

Table 1: Elemental analysis results

Result type	Spectrum label													
	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Total
Spectrum 7, wt%	56.74	15.01	25.21	0.88	-	-	-	0.09	0.28	1.06	-	-	0.73	100.00
Spectrum 8, wt%	55.73	13.29	26.64	1.25	0.16	0.25	0.34	0.15	0.27	1.46	0.13	0.15	0.45	100.00

As can be seen from Figure 4, in the perforation zone, there is a sharp change in the structure of the karakul leather tissue. The process of carbonization takes place, water is removed, and the pores increase to ~100 µm. There is also a change in the elemental composition, so in the perforation zone there is an increase in carbon and a change in the concentration of other elements, which is associated with the processes of carbonization of the leather tissue of karakul.

Thus, depending on the energy input, both the process of ablation of the karakul skin tissue and the process of its carbonization are observed.

At the next stage of research, the tanning action of glutaraldehyde, which is formed directly in the structure of the dermis, was studied. The polycondensation process was carried out due to acid tanning chromium compounds. The concentration of glutaraldehyde was 3.0 g/l, chromium compounds (calculated as Cr_2O_3) 1.0 g/l, CK = 8.0, temperature 35°C. The tanning effect was determined by the welding temperature of comparable samples of karakul leather by treatment with glutaraldehyde and formaldehyde (Figure 5).

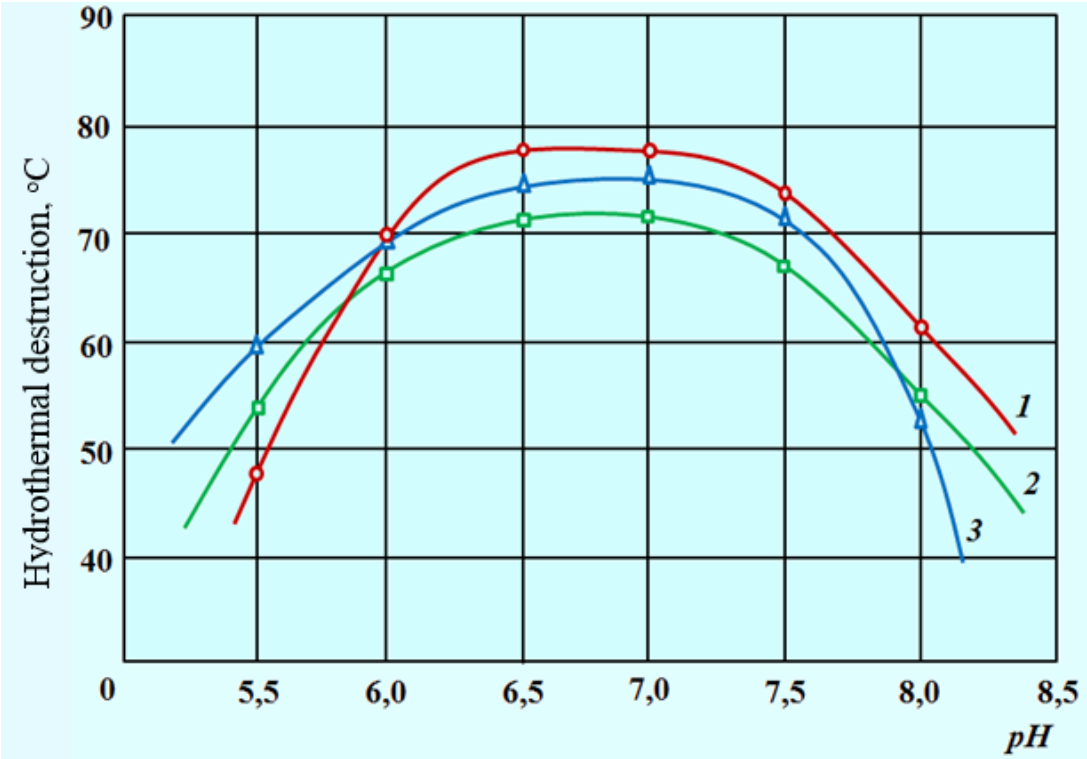


Figure 5. Dependence of hydrothermal degradation in the pH environment after tanning fabric of karakul semi-finished product
Treated variants: 1 - glutaraldehyde, 2 - formaldehyde and 3 - chromium compounds

As can be seen from Figure 5, the processing of karakul leather with glutaraldehyde gives the semi-finished product a higher welding temperature, which indicates a stronger tanning ability of glutaraldehyde. The reason for this is the stronger binding of the molecular chains of collagen by glutaraldehyde, which is formed in the structure of the dermis under the conditions of tanning, than when tanning with formaldehyde and chromium.

The results of the study of the physicochemical properties of karakul leather fabric for tanning with glutaraldehyde are presented in Table 2.

Table 2: Physicochemical properties of karakul leather fabric for glutaraldehyde tanning

№	Indicators	Control	Experienced	State standard 10151-2014
1	Free formaldehyde content, µg / g	33	18	no more than 300
2	Content of water washable chromium (VI), mg / kg	2.8	1.2	no more than 3.0
3	Temperature welding leather tissue, °C	73	78	at least 50
4	pH water hoods leather tissue	3.9	4.1	at least 3.5
5	Sustainability coloration hair cover to dry friction, points	4	5	at least 4
6	Color fastness of leather fabric to dry friction, points	4	4	at least 3

The glutaraldehyde tanned karakul leather fabric has a light brown color, is distinguished by its softness, high color fastness of the hairline and leather fabric to dry friction.

CONCLUSIONS

For the first time, the morphology of the surface of the skin tissue of karakul was investigated using a laser generating in a two-pulse mode (pulses are separated by a time interval of 3 µs, a pulse duration of 10 ns) with a wavelength of 1064 nm in a wide range of deposited energies, which lead, as a mode of ablation of the skin surface, followed by glutaraldehyde tanning, and to its perforation with an increase in the input energy. The modes of laser processing have been determined, which make it possible to switch from the ablation mode (removal of small defects and leveling the skin surface for further processing), and to the perforation mode (obtaining holes for cosmetic purposes).

The possibility of changing the consumer parameters of the skin tissue of karakul due to the dermis dissociation, conformational changes, which lead to a change in the structure, is shown. At energies more than 30J, perforation of the karakul leather tissue occurs with carbonization of the edges of the holes.

A decrease in tanning ability is clearly expressed in formaldehyde solutions, this provides a strong bond of dermal elements with glutaraldehyde. The leather fabric of karakul fur is more resistant to leather fabric to dry friction than leather fabric of karakul fur with formaldehyde and chrome tanning.

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OBTAINING BIOEMULSIONS STRUCTURED AS "NETWORKS" BY INNOVATIVE TECHNOLOGIES

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OBTAINING BIOEMULSIONS STRUCTURED AS "NETWORKS" BY INNOVATIVE TECHNOLOGIES

ABSTRACT. New bioemulsions structured like "networks" were created by innovative technologies based on: elastin/zinc hydroxide/ (bolaamphiphiles mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl ester] and/or sucrose diester)/ acetic acid/water, for improved surface properties development with applications in leather industry. We used in this research two "bolaamphiphiles". Bolaamphiphilic molecules contain a hydrophobic skeleton (e.g., one, two, or three alkyl chains, a steroid, or a porphyrin) and two water-soluble groups on both ends. The interaction of surfactants with biopolymers in aqueous medium results in the formation of different association structures. There are various morphologies of biopolymer-surfactant association complexes depending on the molecular structure of the biopolymer and surfactant, on the nature of interaction forces between solvents and surfactant or biopolymer. The innovation consists in the technologies for obtaining novel micro and nanostructured bioemulsions, and the compatibilisation with film forming polymers for leather surface finishing. Elastin/zinc hydroxide micro and nanocomposites have been stabilized with bolaamphiphilic surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl ester and sucrose diester in a 1:1 acetic acid/water ratio, to increase the uniformity of nanocomposites. Micro and nanostructured composites like "networks" developed as a result of biopolymer-surfactants interactions for elastin/zinc hydroxide/surfactants mixture couple in acetic acid/water system are reported by SEM microscopy and DLS analysis. A special class of micro and nanoarchitectures is represented by structures organized as "network" assemblies. The novel micro and nanocomposites can provide the hybrid film with increased resistance to rubbing and water, and to deformation. Environmentally-friendly substrates with smart multifunctional features can be obtained for various applications.

KEY WORDS: bolaamphiphiles, bioemulsions structured like "networks", innovative technologies, improved surface properties

OBȚINEREA UNOR BIOEMULSII STRUCTURATE SUB FORMĂ DE „REȚELE" PRIN TEHNOLOGII INOVATOARE

REZUMAT. S-au creat noi bioemulsii structurate sub formă de „rețele" utilizând tehnologii inovatoare bazate pe: elastină/hidroxid de zinc/ (amestec de bolaamfifile: bis [2-butil (bis-tioacetat de sodiu) dicarboxilat de sodiu 1,10 decanediil ester] și/sau diester de zaharoză)/ acid acetic/apă, pentru dezvoltarea unor proprietăți de suprafață îmbunătățite cu aplicații în industria pielii. Am folosit în această cercetare două „bolaamfifile". Moleculele bolaamfifile conțin un schelet hidrofob (de exemplu, unul, două sau trei lanțuri alchil, un steroid sau o porfirină) și două grupări solubile în apă la ambele capete. Interacțiunea agenților tensioactivi cu biopolimerii în mediu apos are ca rezultat formarea diferitelor structuri de asociere. Există diverse morfologii ale complexelor de asociere biopolimer-surfactant în funcție de structura moleculară a biopolimerului și agentului tensioactiv, de natura forțelor de interacțiune dintre solvenți și surfactant sau biopolimer. Inovația constă în tehnologiile pentru obținerea de noi bioemulsii micro și nanostructurate și compatibilitatea cu polimeri filmogeni pentru finisarea suprafeței pielii. Elastina/hidroxidul de zinc micro și nanocompozitele au fost stabilizate cu amestec de surfactanți bolaamfifili: bis [2-butil (bis-tioacetat de sodiu) dicarboxilat de sodiu 1,10 decandiil ester] și zaharoză diester într-un raport acid acetic/apă de 1:1, pentru a crește uniformitatea nanocompozitelor. Compozitele micro și nanostructurate sub formă de „rețele" dezvoltate ca rezultat al interacțiunilor biopolimer-surfactanți pentru amestecul de elastină/hidroxid de zinc/surfactanți în sistemul acid acetic/apă sunt raportate prin microscopia SEM și analiza DLS. O clasă specială de micro și nanoarhitecturi este reprezentată de structurile organizate ca ansambluri de „rețele". Noile micro și nanocompozite pot oferi filmului hibrid o rezistență sporită la frecare, la apă și la deformare. Se pot obține suporturi ecologice cu proprietăți multifuncționale inteligente pentru diverse aplicații.

CUVINTE CHEIE: bolaamfifile, bioemulsii structurate sub formă de „rețele", tehnologii inovatoare, proprietăți îmbunătățite ale suprafeței

OBTENIR DES BIOÉMULSIONS STRUCTURÉES EN « RÉSEAUX » PAR DES TECHNOLOGIES INNOVANTES

RÉSUMÉ. De nouvelles bioémulsions structurées en « réseaux » ont été créées par des technologies innovantes à base de : élastine/hydroxyde de zinc/ (mélange de bolaamphiphiles : bis [2-butyl (bis-thioacétate de sodium) dicarboxylate de sodium 1,10 décanediyl ester] et/ou diester de saccharose) / acide acétique/eau, pour le développement de propriétés de surface améliorées avec des applications dans l'industrie du cuir. On a utilisé dans cette recherche deux « bolamphiphiles ». Les molécules bolaamphiphiles contiennent un squelette hydrophobe (par exemple, une, deux ou trois chaînes alkyl, un stéroïde ou une porphyrine) et deux groupes hydrosolubles aux deux extrémités. L'interaction des tensioactifs avec les biopolymères en milieu aqueux conduit à la formation de différentes structures d'association. Il existe différentes morphologies de complexes d'association biopolymère-tensioactif en fonction de la structure moléculaire du biopolymère et du tensioactif, de la nature des forces d'interaction entre solvants et tensioactif ou biopolymère. L'innovation réside dans les technologies permettant d'obtenir de nouvelles bioémulsions micro et nanostructurées, et la compatibilisation avec des polymères filmogènes pour la finition de surface du cuir. Les micro et nanocomposites élastine/hydroxyde de zinc ont été stabilisés avec un mélange de tensioactifs bolaamphiphiles : bis [2-butyl (bis-thioacétate de sodium) dicarboxylate de sodium 1,10 décanediyl ester] et diester de saccharose dans un rapport acide acétique/eau de 1:1, pour augmenter l'uniformité des nanocomposites. Des composites de micro et nanostructures comme des « réseaux » développés à la suite d'interactions biopolymères-tensioactifs pour le couple mélange élastine/hydroxyde de zinc/tensioactifs dans un système acide acétique/eau sont rapportés par microscopie SEM et analyse DLS. Une classe particulière de micro et nanoarchitectures est représentée par des structures organisées en assemblages « en réseau ». Les nouveaux micro et nanocomposites permettent de conférer au film hybride une résistance accrue au frottement et à l'eau, à la déformation. Des supports respectueux de l'environnement avec des fonctionnalités multifonctionnelles intelligentes peuvent être obtenus pour diverses applications.

MOTS CLÉS : bolaamphiphiles, bioémulsions structurées en « réseau », technologies innovantes, propriétés de surface améliorées

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INTRODUCTION

This paper presents innovative technologies for obtaining structured bioemulsions with architectures represented by structures organized as "networks" assemblies, which have applications in leather industry, environmentally-friendly substrates. Micro and nanostructure composites like "networks" developed as the result of biopolymer-surfactants interactions for elastin/zinc hydroxide/ (surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl ester and sucrose diester) couple in a 1:1 acetic acid/water ratio system and are reported by SEM microscopy and DLS analysis.

Bolaamphiphiles are related to and often combined with "edge amphiphiles", where one flank of a hydrophobic core carries hydrophilic groups whereas the other edge is hydrophobic [1-7]. The terms "bolaform amphiphiles" or "bolaphiles" have also been used but do not make much sense. "Form" does not appear elsewhere in organic nomenclature, and a connection with "phile = friendly" makes sense with respect to a solvent ("amphiphile") or reaction center ("nucleophile") but not in connection with a noun describing a substitution pattern. Since the early 1980s the investigation of bipolar amphiphiles ("bolaamphiphiles") has been an expanding research area leading to an increasing number of annual publications. In 2004 several review articles appeared emphasizing the importance of this unusual class of amphiphilic molecules [1–7]. Elastin powder or hydrolyzed elastin is extracted from the bovine neck tendon or bovine heart canal by biotechnology and is processed into a hydrolysate, which makes it easier to use with most of the ingredients. It is fibrin composed of polypeptide subunits and is one of the most important structural proteins. This is because elastic protein can provide the ability to resist repeated compression and deformation. Studies have proved that elastic protein peptides have a certain degree of repair and increase moisturizing factors such as skin care [1-7].

Surfactants have the ability to change the surface tension in solution, which gives them the possibility to self-organize into structures with different shapes: core-shell, fibers, ribbons, tubes, layers, multilayers and even into "networks". These structured archetypes based on surfactants improve the properties of surfaces used as substrates.

EXPERIMENTAL

Materials and Methods

In order to obtain new nanostructured composites, the following materials have been used:

- zinc hydroxide and elastin powder from Sigma-Aldrich;
- sucrose from SERVA Feinbiochemica GmbH & Co;
- bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester obtained in an original method at ICECHIM in a PhD Thesis [1].

The experimental techniques used in this paper consist in electronic scanning (SEM) and dynamic light scattering tests:

- a "SEM QUANTA 200" equipment from FEI company, with EDAX coupled. The samples for SEM investigations were prepared by slow evaporation in clean atmosphere at room temperature;
- a "MALVERN" Zetasizer-Nano equipment, with measuring range between 0.3 nm-60.0 microns and zeta potential determination with an accuracy of +/-2%.

A number of 5 samples of elastin/surfactant (or not)/zinc hydroxide/ acetic acid/water were prepared in the working conditions: water-acetic acid solvents at 1:1 ratio, temperature=45°C for 50 minutes with elastin-c=0.1%; zinc hydroxide-c=0.1%, Figure 1.

The samples are:

- sample 1: elastin/zinc hydroxide/bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester/acetic acid/water with surfactant concentration: 1%, elastin concentration: 0.1%, zinc hydroxide-c=0.1%;
- sample 2: elastin/zinc hydroxide/sucrose diester/acetic acid/water with surfactant concentration: 1%, elastin concentration: 0.1%, zinc hydroxide-c=0.1%;
- sample 3: elastin/zinc hydroxide/sucrose diester and bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10

decanediyl] ester/acetic acid/water with sucrose diester concentration: 1%, elastin concentration: 0.1%, zinc hydroxide-c=0.1%; bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester concentration: 1%;

- sample 4: elastin/acetic acid/water with water-acetic acid solvents in 1:1 ratio, elastin concentration: 1-c = 0.1%;
- sample 5: elastin/zinc hydroxide/acetic acid/ water with water-acetic acid solvents in 1:1 ratio, elastin concentration: 1-c = 0.1%.

a) *b)* *c)*

Figure 1. a) Photographic image of the 5 samples; b) Image of elastin powder; c) Image of zinc hydroxide

The "network" architectures were observed only for samples 1, 2, 3 only with surfactants, not for samples 4 and 5. The experimental techniques used to analyse the new structured bioemulsions consist in electronic scanning and dynamic light scattering.

RESULTS AND DISCUSSIONS

This paper reports original innovative technologies for obtaining bioemulsions structured like "networks", Figure 2. Bioemulsions were created by the interaction of the elastin powder/zinc hydroxide/acetic acid/ water system with two surfactants used together or just one: sucrose diester and bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester.

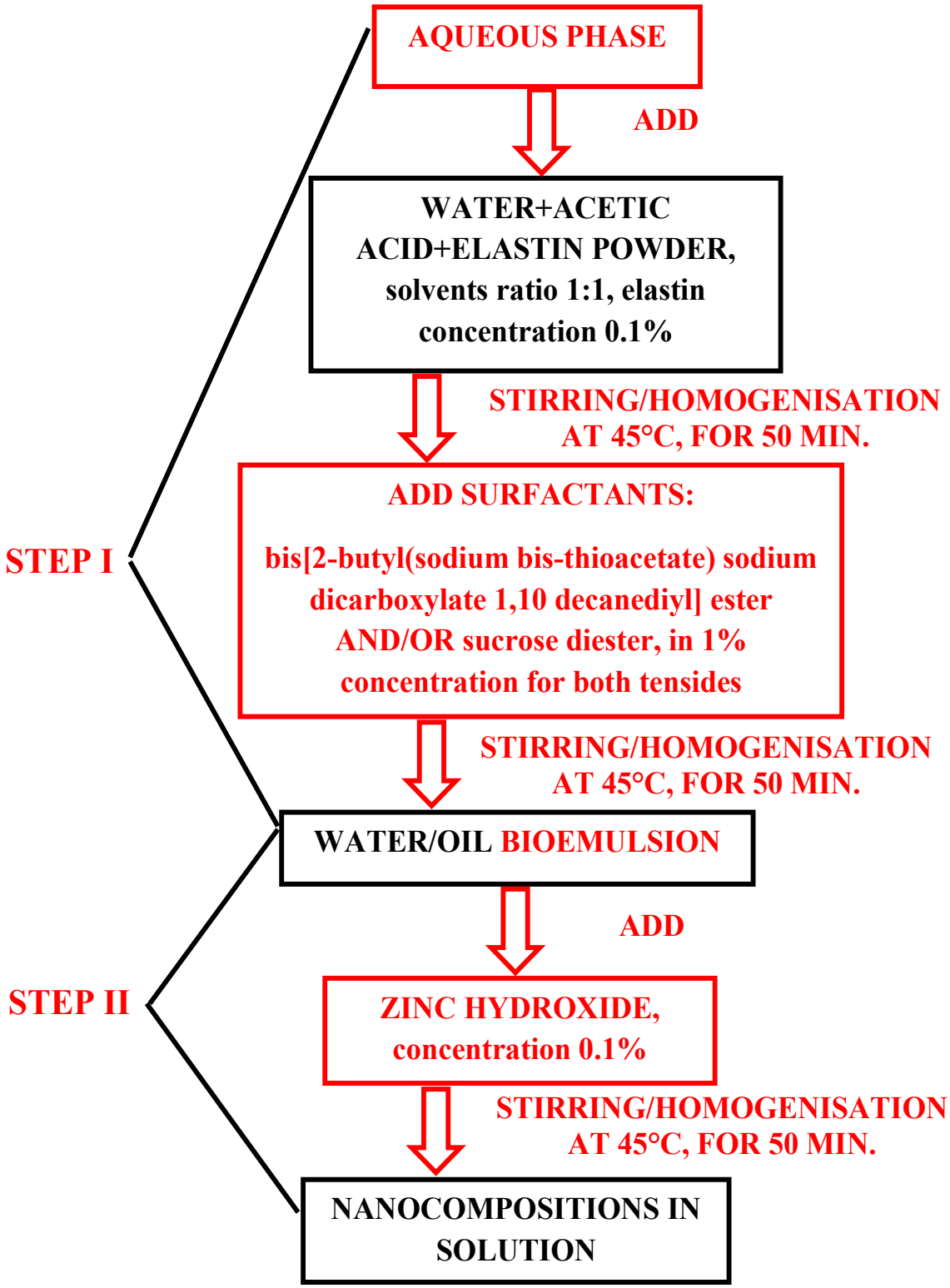


Figure 2. Two-step technological process of obtaining bioemulsion structured like “networks” and nanocompositions in solution

The original innovative technologies have two steps:

- Step I – obtaining the water-oil bioemulsion structured like "networks" by introducing in water/acetic acid at 1:1 ratio the elastin powder at concentration: 1% by stirring/ homogenization at 45°C for 50 minutes and after adding surfactants: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester, sucrose diester in 1:1 ratio, at concentration 1% (together or just one);
- Step II – creating the nanocompositions in solution by adding the zinc hydroxide (c=0.1%) in water-oil bioemulsion and homogenized/ stirring at 45°C for 50 minutes.

The responsible factors that control the appearance of bioemulsions structured like "networks" are: the type and concentration for surfactant and biopolymer, acetic acid/ water ratio, pH, the temperature and time of stirring, the concentration of zinc hydroxide, the hydrophilic nature of biopolymer.

The morphologies of "network" microstructures are due to the molecular structure of the biopolymer and surfactants mixtures, to the nature of interaction forces between solvents and surfactant or biopolymer in the elastin powder/sucrose diester and/or bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester/zinc hydroxide/acetic acid/water system.

The SEM micrograph of elastin powder is shown in Figure 3.

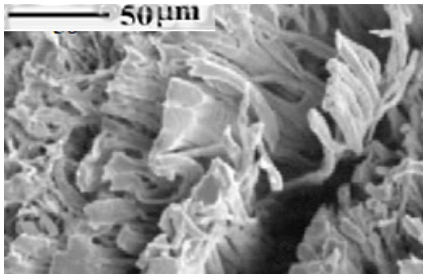
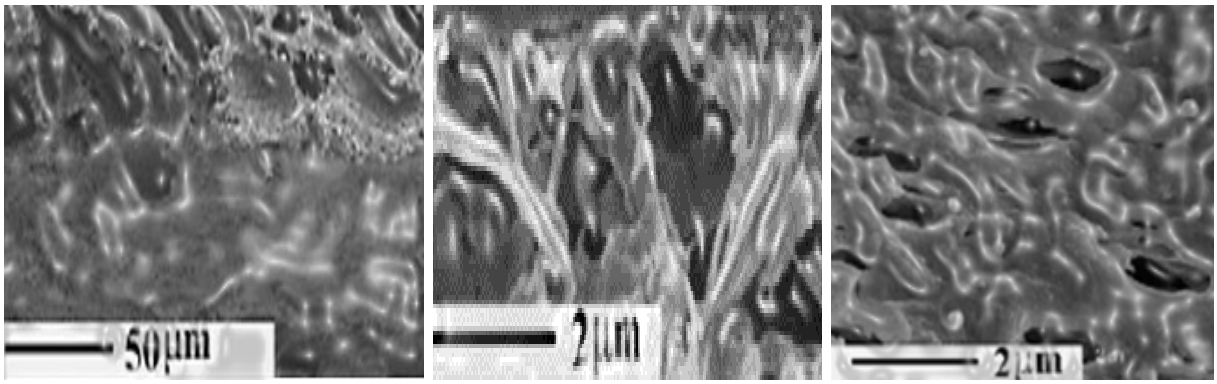


Figure 3. SEM micrograph of elastin

The association complexes with "network" morphologies appear only with surfactants, at a certain acetic acid/water/zinc hydroxide ratio, above critical concentration and for pH=4, as seen in Figure 4. SEM microscopy shows that the "network" architectures appeared only for samples: 1, 2, 3 with surfactants, not for samples 4 and 5 without tensides.



a) SEM micrograph for sample 1 *b) SEM micrograph for sample 2* *c) SEM micrograph for sample 3*

Figure 4. (a, b, c) SEM micrographs of "network" morphology in elastin/zinc hydroxide/ (surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester and/or sucrose diester)/ acetic acid/water

The cause of the appearance for these "network" structures are the complex interactions which involve both hydrogen bonds and chemical reactions between double chain bolaamphiphile surfactant- bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester and/or sucrose diester and elastin.

Dynamic light scattering test showed 2 types of composites: nano (50-200 nm) and microstructured (aggregate at 2mm-50 mm). The size, percentage of the particles and Zeta potential were determined and indicating the stability of nanocomposites.

CONCLUSIONS

The conducted research has led to the following results:

1. Preparation of novel micro and nanostructured bioemulsions by innovative technologies based on elastin/zinc hydroxide/ (surfactants mixture: bis [2-butyl (sodium bis-thioacetate) sodium dicarboxylate 1,10 decanediyl] ester and/or sucrose diester)/ acetic acid/water, to improve surface properties with applications in leather industry.

2. The above results bring forth aspects of the new "Smart" generation materials.

3. Further research proposes to analyse and test the possibilities of introducing other new auxiliaries (nanocomposite film) for the leather industry.

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THE VALIDITY AND RELIABILITY OF TRUEDEPTH CAMERA EMBEDDED IN THE PHONE FOR FOOT MEASUREMENT

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THE VALIDITY AND RELIABILITY OF TRUEDEPTH CAMERA EMBEDDED IN THE PHONE FOR FOOT MEASUREMENT

ABSTRACT. There are several laser or structured-light based foot scanners available on the market, which can be used to obtain accurate 3D foot models. Compared to those 3D scanning devices, TrueDepth cameras are portable, inexpensive and easy-to-use. However, the accuracy and reliability of their 3D foot scanning remain to be confirmed. This study aimed to verify the validity and reliability of structured light TrueDepth camera integrated into the mobile phone when it is used for foot measurement. Thirteen students without any kinds of foot abnormalities or foot diseases were recruited and their feet were measured by both Infoot 3D foot scanner and mobile phone with TrueDepth camera. Three parameters were measured including foot length, foot breadth and ball girth. Subsequently, the reliability and validity of the two methods were assessed by linear regression analyses, intraclass Correlation Coefficient and Bland-Altman analysis. The foot breadth and girth circumference measurements all showed high coefficients of determination (R^2>0.8) between the two methods and three measurements indicated good to excellent agreements (ICCs>0.9), although the length measurement was reported without significant coefficients of determination. Further, findings from Bland-Altman analysis demonstrated that the measurements from the TrueDepth camera had good agreements with those from Infoot and they could be used interchangeably. However, with the reconstruction algorithm updating in the near future, we could foresee the promotion in foot length measurement when using the TrueDepth camera from the phone. The TrueDepth camera utilizing structured-light and the customized application for foot measurement has fast, accurate and low-cost features and it is a convenient and economical method to obtain the foot 3D model. It can be widely applied for medical purposes and customization.

KEY WORDS: foot measurement, foot 3D model, structured-light, TrueDepth camera

VALIDITATEA ȘI FIABILITATEA CAMEREI TRUEDEPTH ÎNCORPORATE ÎN TELEFON UTILIZATE LA MĂSURAREA PICIORULUI

REZUMAT. Există mai multe scanere pe bază de laser sau cu lumină structurată disponibile pe piață, care pot fi utilizate pentru a obține modele 3D exacte ale piciorului. În comparație cu acele dispozitive de scanare 3D, camerele TrueDepth sunt portabile, ieftine și ușor de utilizat. Cu toate acestea, acuratețea și fiabilitatea acestora în cazul scanării 3D a piciorului trebuie confirmate. Acest studiu și-a propus să verifice validitatea și fiabilitatea camerei TrueDepth cu lumină structurată integrată în telefonul mobil atunci când este utilizată la măsurarea piciorului. S-au recrutat treisprezece studenți fără niciun fel de anomalii ale piciorului sau boli ale piciorului, iar picioarele acestora au fost măsurate atât cu ajutorul unui scaner 3D pentru picior, cât și cu un telefon mobil cu cameră TrueDepth. S-au măsurat trei parametri, și anume lungimea piciorului, lățimea piciorului și circumferința zonei metatarso-falangiene. Ulterior, fiabilitatea și validitatea celor două metode au fost evaluate prin analize de regresie liniară, coeficient de corelație intraclasă și analiză Bland-Altman. Măsurătorile lățimii și circumferinței piciorului au indicat coeficienți mari de determinare (R^2>0,8) între cele două metode și trei măsurători au indicat acorduri bune spre excelente (ICCs>0,9), deși măsurarea lungimii a fost raportată fără coeficienți de determinare semnificativi. Mai mult, descoperirile în urma analizei Bland-Altman au demonstrat că măsurătorile luate utilizând camera TrueDepth au avut acorduri bune cu cele luate cu scanerul Infoot și pot fi folosite interschimbabil. Cu toate acestea, odată cu actualizarea algoritmului de reconstrucție în viitorul apropiat, am putea prevedea progresul în măsurarea lungimii piciorului la utilizarea camerei TrueDepth a telefonului. Camera TrueDepth care utilizează lumina structurată și aplicația personalizată pentru măsurarea piciorului au caracteristici rapide, precise și ieftine și reprezintă o metodă convenabilă și economică de a obține modelul 3D al piciorului. Se poate aplica pe scară largă în scopuri medicale și de personalizare.

CUVINTE CHEIE: măsurarea piciorului, modelul 3D al piciorului, lumină structurată, cameră TrueDepth

LA VALIDITÉ ET LA FIABILITÉ DE LA CAMÉRA TRUEDEPTH INTÉGRÉE AU TÉLÉPHONE POUR LA MESURE DU PIED

RÉSUMÉ. Il existe plusieurs scanners laser ou à lumière structurée disponibles sur le marché, qui peuvent être utilisés pour obtenir des modèles de pieds 3D précis. Par rapport à ces appareils de numérisation 3D, les caméras TrueDepth sont portables, peu coûteuses et faciles à utiliser. Cependant, la précision et la fiabilité de leur scan 3D du pied restent à confirmer. Cette étude a le but à vérifier la validité et la fiabilité de la caméra TrueDepth à lumière structurée intégrée au téléphone mobile lorsqu'elle est utilisée pour la mesure du pied. Treize étudiants sans aucune sorte d'anomalie ou de maladie du pied ont été recrutés et leurs pieds ont été mesurés à la fois par un scanner de pied 3D et par un téléphone portable avec une caméra TrueDepth. Trois paramètres ont été mesurés, notamment la longueur du pied, la largeur du pied et le tour de pied. Par la suite, la fiabilité et la validité des deux méthodes ont été évaluées par des analyses de régression linéaire, par le coefficient de corrélation intraclasse et par l'analyse de Bland-Altman. Les mesures de la largeur du pied et de la circonférence ont montré des coefficients de détermination élevés (R^2 > 0,8) entre les deux méthodes et trois mesures ont indiqué des accords bons à excellents (ICC > 0,9), bien que la mesure de la longueur ait été rapportée sans coefficients de détermination significatifs. De plus, les résultats de l'analyse de Bland-Altman ont démontré que les mesures de la caméra TrueDepth avaient de bons accords avec celles du scanner Infoot et qu'elles pouvaient être utilisées de manière interchangeable. Cependant, avec la mise à jour de l'algorithme de reconstruction dans un proche avenir, nous pourrions prévoir le progrès de la mesure de la longueur du pied lors de l'utilisation de la caméra TrueDepth intégrée au téléphone. La caméra TrueDepth utilisant la lumière structurée et l'application personnalisée pour la mesure du pied ont des caractéristiques rapides, précises et peu coûteuses et représentent une méthode pratique et économique pour obtenir le modèle 3D du pied. On peut l'appliquer largement à des fins médicales et de personnalisation.

MOTS-CLÉS : mesure du pied, modèle 3D du pied, lumière structurée, caméra TrueDepth

INTRODUCTION

Foot measurements play an important role in the design of footwear, foot orthotics and insoles, which are related directly to fitting, comfort and health [1, 2]. Wearing poorly fitting shoes may increase the risk of lower extremity musculoskeletal problems such as foot pain or deformity [3]. Especially with the advent of mass customization in the area industry 4.0, accurate foot measurement and feasible foot model reconstructions are important considerations when choosing footwear for consumers [4].

There are several methods for measuring foot: manual measure, radiography scanning, laser scanning and optical scanning. Manual measurement is easy-to-use and pervasive, however, lacks repeatability and reliability. Other methods such as laser and magnetic resonance are precise but remain expensive, complex in structure and lack convenience [5], and they were mainly applied to industrial, clinical and research areas [6].

Researchers have compared the strengths and weaknesses of various foot measurements methods. In terms of optical scanning, radiographic such as X-rays allowed exact measurements of the bony structures, however, the radiation was harmful to health [7]. Laser scan such as Infoot 3D foot scanner exhibited good validity and reliability compared with X-rays and clinical measurements [8]. Mall [7] indicated that photographic and caliper measurements had good reliability and acceptable validity to radiographic measurements. Further, Niu [4] first collected 84 foot images with the mobile phone camera and used a magazine as the calibration; and then they constructed the model with Structure-from-Motion algorithm and Patch-based Multi-View System; finally they applied Meshlab to process and measure the foot model. The error of result was around 1mm compared to digital caliper and foot scanner; on the other hand, the operation was inconvenient.

With the advance in optoelectronic technology and mathematical modelling technology, optical scanning became more and more prevalent in the domain of measurement [9]. Both the detailed information on the contours, volume and cross-sectional of the object, and even the dynamic changes in anthropometric measurements [10, 11] could be assessed by optical scanning. With the birth of TrueDepth camera, it was enhanced by the computer vision technology and the advent of depth sensors and then breaks the limits of conventional optical scanning. Weiss *et al*. indicated that a single Microsoft Kinect sensor was capable to create 3D body models with the similar accuracy of expensive and a complex commercial laser scanner [12]. Meanwhile, Rogati *et al*. [13] assessed the accuracy of a Microsoft Kinect sensor by comparing it with a high-resolution laser scanner when scanning the foot plantar model. Ge Wu [14] first designed a system with six depth cameras PrimeSense scanning simultaneously, and then calibrated the system based on T-shaped checkerboards and iterative closest point algorithm, finally validated the accuracy of the scanner compared to manual measurement. Furthermore, Vogt *et al*. [15] evaluated the scanning precision of LiDAR and TrueDepth camera of iPad Pro by scanning Lego bricks compared with an industrial 3D scanner Artec Space Spider.

Since more and more mobile phones have integrated the TrueDepth camera, scanning with the phone would become a potential protocol in foot measurement owing to its convenient operation, low hardware price and mature software application. However, there was no literature reporting their accuracy and reliability. Therefore, this study aimed to verify the validity and reliability of the structured-light TrueDepth camera from the mobile phone. Based on the current cognition of TrueDepth camera scanning, we assumed that the scanning from the phone would generate good results both in the validity and the reliability in contrast with the professional scanner.

EXPERIMENTAL

Materials and Methods

Participants

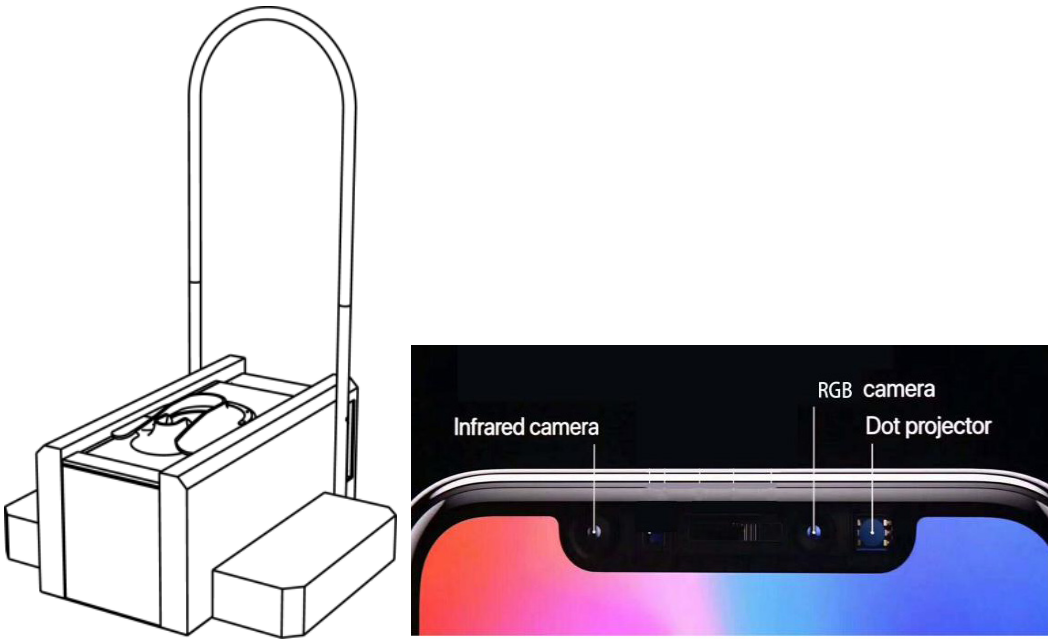
Thirteen students (1 male and 12 females; mean age: 22.7±1.1 years; mean height: 163.3±6.1cm; mean weight: 54.2±8.7 kg; BMI: 20.3±2.64) from Sichuan University were recruited for the experiment. None of them had any kinds of foot abnormalities or foot diseases.

Volunteers gave written informed consent before participation in this study. Due to the variation in the size of the left and right feet and the different size in standing and sitting posture, the two sides of the feet of subjects were measured in both standing and sitting conditions. The experiment was conducted based on principles of the Declaration of Helsinki and was approved by the Ethics Committee of the Sichuan University.

Two Measurement Methods

The feet shapes of the subject were captured using an traditional qualified laser scanner (Figure 1) (INFOOT USB:IFU-S-01, I-Ware Laboratory Co., Ltd., Japan), which is composed of 4 laser projectors and 8 charged-coupled devices (CCD) cameras capturing the lasers. It has shown high repeatability and could be applied directly to the static foot test. The equipment is designed with a multi-view laser path, which scanned a foot shape in less than 10 seconds and obtain high precision point cloud data. The procedure can refer to the operation in this article [16].

Another method was to scan the foot via an iPhone (iPhone XR, Apple inc. USA) with the application of LuxScan. LuxScan is an application based on TrueDepth camera of the phone and it is easy to scan foot models. The structured light-based depth camera (Figure 1) consists of a dot projector, infrared camera and an RGB camera. During the scanning process, the dot projector projects specially structured pattern called laser speckles onto the surface of objects; neural network algorithm in mobile phone bionic chips calculates the 3D shape and depth information of the object based on the distortion of the structured light observed by the infrared camera on the 3D physical surface [17]. The application can quickly generate .stl, .obj and .usdz files within approximately 10 seconds and files can be quickly transferred via sharing.



a b

Figure 1. Two foot-measurement methods. a: INFOOT USB:IFU-S-01;
b: The structured light-based depth camera from iPhone

The scanning process of LuxScan is shown below in Figure 2. With the screen side facing downwards, the starting position of the scan was located on outside of the heel diagonally behind the foot within 15-20 cm away from the foot; then the foot was scanned following a circle of 360 degrees within 10 seconds, ensuring that the foot was as still as possible.

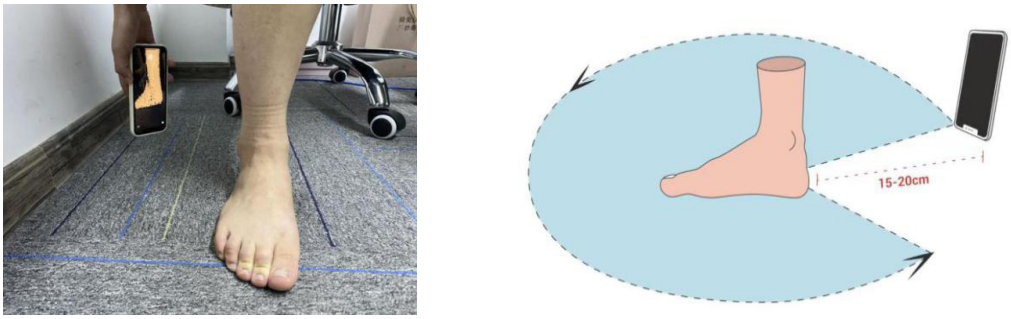


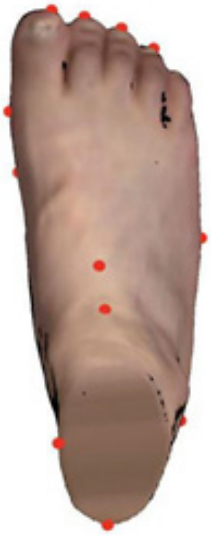
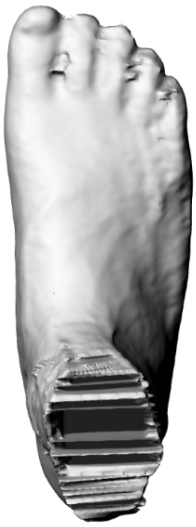
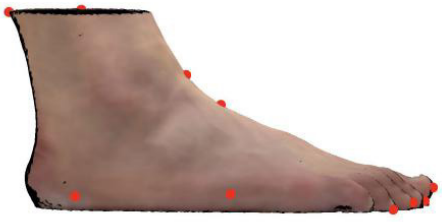
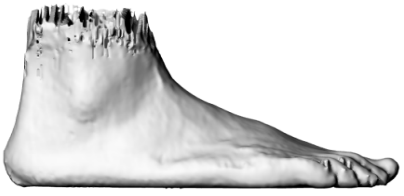
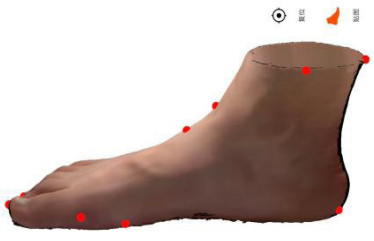
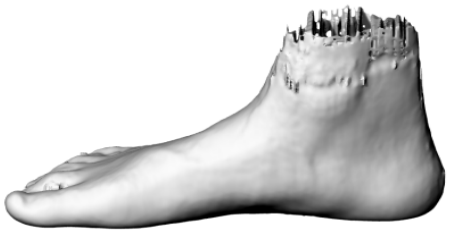
Figure 2. The scanning process of the LuxScan App

After the acquisition by structured light scanning, data were converted to the 3D floating point cloud and a surface reconstruction was conducted to obtain a triangular mesh model. Then, operations such as smoothing, denoising, point cloud alignment and hole repair were performed to obtain a better surface construction. Finally, curved surface reconstruction was carried out and the foot reconstruction data were exported from the scanner in the .obj file format.

Data Procedure and Analysis

In order to contrast the results between the two methods, we exported the STL file of the model and imported them into the Rhinoceros (Version 7.0, Robert McNeel, USA) to measure. An experienced researcher marked and measured the model (Table 1); furthermore, the model obtained from the LuxScan was measured three times for reliability assessment. The following parameters were considered: foot length is the distance from the prominent point of heel end to the tip of the longest toe; foot breadth is the maximum width from oblique length from the first metatarsophalangeal joint to the fifth metatarsophalangeal joint; ball girth circumference is the maximum distance around the circumference at the level of the first and the fifth metatarsophalangeal joint protrusion. These three parameters are most frequently used in the fitting and comfort assessment.

Table 1: An overview of foot 3D reconstruction with two methods

Angle of view	3D model by the structured light camera	3D model by Infoot
Top		
Lateral		
Medial		

With regard to the validity, the correlation between the results of LuxScan and Infoot was explored. Linear Regression Analyses was applied in the research, where results of the app were as independent variables, those from Infoot were as dependent variables. The coefficient of determination (R^2)<0.09 showed a small correlation; 0.09<R^2<0.25 represented a medium correlation; R^2>0.25 indicated a large correlation [18]. In addition, Bland-Altman analysis was used to compare the consistency of two measurements by quantifying their agreement accurately [19].

When considering the reliability, Intra-class correlation coefficients (ICCs (2,1)) were used to indicate the relative reliability of the measure [20]. The ICC<0.5 showed a poor agreement; 0.5<ICC<0.75 showed a moderate agreement; 0.75<ICC<0.9 represented a good agreement; ICC>0.9 showed an excellent agreement. Values of the 95% confidence interval of the ICC less than 0.5 indicate poor reliability. Values ranging from 0.5 to 0.75,0.75 to 0.90, above 0.90 indicated moderate reliability, good reliability and excellent reliability, respectively [21].

All statistical analyses were calculated using software SPSS (23, IBM, USA) with a significant level of 0.05 and a confidence interval of 95%.

RESULTS AND DISCUSSIONS

Results

The coefficients of determination (Table 2) of foot breadth and ball girth circumference were represented with large correlations (R^2=0.85, p=0.007<0.05; R^2=0.90, p=0.001<0.05). However, in terms of foot length, the coefficient of determination was nonsignificant (R^2=0.94, p=0.06).

The ICCs of foot length and foot breadth reached good to excellent agreements, ICC=0.94, p=0.00, 95% confidence interval =0.757 to 0.978 for foot length, ICC=0.92, p=0.00, 95% confidence interval =0.863 to 0.953 for foot breadth. It witnessed an excellent reliability for ball girth circumference (ICC=0.95, p=0.00 and 95% confidence interval =0.910 to 0.969).

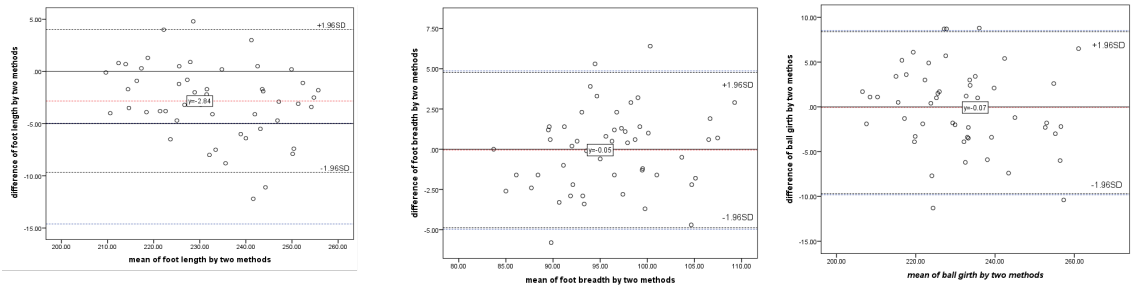
The Bland-Altman analysis was shown in Table 3. The mean bias between two measurements in foot breadth (-0.05±2.46, p=0.89>0.05, 95%LoA=-4.87 to 4.77) and ball girth circumference (-0.07±4.62, p=0.92>0.05, 95% LoA=-9.70 to 8.40) were low, but those in foot length became high (-2.84±3.49, p=0.00). It can be seen from Figure 3 that 6% (3/52) and 10% (5/52) plots were out of the 95% LoA and the discrepancies were accepted in the foot measurements of foot breadth and ball girth respectively. Those findings indicated that the new method can take place the traditional one in terms of the measurements for foot breadth and ball girth circumference, with p=0.919>0.05 and p=0.884>0.05 respectively and no statistically significant differences were found in measurement values. As regards length measurement, the difference of measurement methods was -2.84±3.49, 95% LoA = -9.68 to 4.0 and p=0.00, which indicated that the two methods showed a significant difference in foot length measurement.

Table 2: The regression models and the intraclass correlation coefficients [ICC (2, 1)] for three measured using Infoot and LuxScan

Parameters	Infoot	TrueDepth camera	R^2	ICC (2, 1)	95% CI for ICC (2, 1)
Foot length	231.4±12.53	234.0±13.55	0.936 (p=0.06)	0.943 (p=0.00)	0.757 to 0.978
foot breadth	96.0±6.28	96.0±5.84	0.846 (p=0.007<0.05)	0.919 (p=0.00)	0.863 to 0.953
Ball girth circumference	231.3±13.59	231.4±14.51	0.899 (p=0.001<0.05)	0.947 (p=0.00)	0.910 to 0.969

Table 3: Fixed biases by Bland-Altman analysis of foot measurements using Infoot and LuxScan

Parameters	mean difference ± SD	95% CI for bias (p value)	95% LoA	95% CI for lower LoA	95% CI for upper LoA
Foot length	-2.84±3.49	-3.81 to -1.87 (p=0.000)	-9.68 to 4.0	-14.61 to -4.75	-0.93 to 8.93
foot breadth	-0.05±2.46	-0.73 to 0.64(p=0.919>0.05)	-4.87 to 4.77	-4.96 to-4.78	4.68 to 4.86
Ball girth circumference	-0.07±4.62	-1.35 to 1.22 (p=0.884>0.05)	-9.70 to 8.40	-9.81 to -9.5	8.29 to 8.51



a b c

Figure 3. The plot of foot measurements difference against the mean of the two methods. a. foot length, b. foot breadth, c. ball girth

Discussion

A cognition for TrueDepth camera were established in the literature currently. Deng *et al*. [22] contrasted the consistency of the PrimeSense 3D sensor with conventional CT scan by scanning body surface, and ICC=0.56 for external Haller, 0.80 for depth ratios indices, r=0.63 for external Haller and r=0.84 for depth ratios. Vogt [15] evaluated the accuracy of iPad Pro (2020) TrueDepth camera using Heges app to scan simple Lego bricks and tolerance were 1 mm deviation in average on position, 1.03 mm deviation on profile of a surface, 4.92 mm on Profile of a line, 0.44 mm on straightness, 0.41 mm on flatness, 0.82 mm on cylindricity and 1.17 mm on roundness. Those finding above implied that the TrueDepth camera would be a qualified protocol in object dimension measurement. Very few were found in the literature to assess the accuracy of 3D foot model construction obtained by TrueDepth camera of the phone. A similar one was reported in our previous study. We [23] validated the accuracy of Intel RealSense SR300 camera with a traditional manual method which the results demonstrated that mean differences ranged from -1.3 mm to 5.2 mm and eight measurements parameters exhibited no significant differences. Results from this study further confirmed the above findings. At first, foot measurements from two methods were high-correlated, which witnessed its good measurement validity and accuracy. Then the ICCs of all three measurements all showed good to excellent agreements. At last, a discrepancy was found in foot length measurement using two methods, which might be due to the ambient lighting, inappropriate angle and distance of phone during the scanning [24, 25]. In addition, the meshing and surface fitting during processing was likely to lead to poor point cloud alignment and repair. Those defects can be improved by more tries of standard and steady operation posture and modified reconstruction algorithm. Therefore, our hypothesis was approved.

Although positive results were obtained, limitations still existed. On the one hand, the App requires high configuration and robustness of hardware and software, memory and computing power of the phone, and can only be installed on iPhones with TrueDepth camera at present. On the other hand, this new protocol requires users to keep the smartphone steady when they hold

and rotate in a circle around the foot during the scanning procedure.

Further research should be undertaken to investigate the precision of other parameters of the foot, such as planter 3D reconstruction and plantar pressure, which can be used medically and commercially to customize insoles for those associated with deformity and rheumatoid arthritis and enables widespread personal customization.

CONCLUSIONS

Overall, the scanning app utilizing structured-light TrueDepth camera has fast, accurate and low-cost features and it is an easy-to-use, convenient and low power consumption method to obtain the 3D foot model. It breaks the limitation of occasion, tedious operation and heavy costs like professional equipment and it can be widely applied for medical purposes such as orthopaedic shoe customization, medical diagnosis and surgical assistance.

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ENZYMATIC BIOTECHNOLOGY APPLIED TO PELT WASTE

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ENZYMATIC BIOTECHNOLOGY APPLIED TO PELT WASTE

ABSTRACT. Enzymes are the substances that speeds up a chemical reaction suitable for green chemistry and can be used to achieve ecological industrial processing in order to reduce the effects of industrial pollution. Microbiological degradation of pelt waste is amongst the permanent concerns of tanners. Several enzymes have been used in the leather industry to substitute the conventional process, mainly proteases. The objectives of this study were to isolate and identify bacteria which produced protease enzyme from tannery solid waste. The selected bacterial strains showed increased protease biosynthesis capacity, which had a significant hydrolytic action on pelt waste. The results obtained in this study demonstrated the ability of strains belonging to the *Bacillus* genus to synthesize increased amounts of proteolytic enzymes and to degrade pelt waste, as well as the possibility of using these microorganisms as a source of protease in various biotechnological processes.
KEY WORDS: leather waste, isolation of bacteria, protease enzyme

BIOTEHNOLOGIE ENZIMATICĂ APLICATĂ DEȘEURILOR DE PIELE GELATINĂ

REZUMAT. Enzimele sunt substanțele care accelerează o reacție chimică în acord cu chimia verde și pot fi utilizate în procese industriale ecologice pentru a reduce efectele poluării industriale. Degradarea microbiologică a deșeurilor de piele gelatină se numără printre preocupările permanente ale tăbăcarilor. Mai multe enzime au fost folosite în industria de pielărie pentru a înlocui procesul convențional, în principal proteaze. Obiectivele acestui studiu au fost de a izola și identifica bacteriile care produc enzima protează din deșeurile solide din tăbăcărie. Tulpinile bacteriene selectate au prezentat o capacitate crescută de biosinteză a proteazei, care a avut o acțiune hidrolitică semnificativă asupra deșeurilor de piele gelatină. Rezultatele obținute în acest studiu au demonstrat capacitatea tulpinilor aparținând genului *Bacillus* de a sintetiza cantități crescute de enzime proteolitice și de a degrada deșeurile de piele gelatină, precum și posibilitatea utilizării acestor microorganisme ca sursă de protează în diferite procese biotehnologice.
CUVINTE CHEIE: deșeuri de piele, izolarea bacteriilor, enzimă protează

LA BIOTECHNOLOGIE ENZYMATIQUE APPLIQUÉE AUX DÉCHETS DE PEAU EN TRIPE

RÉSUMÉ. Les enzymes sont les substances qui accélèrent une réaction chimique conformément à la chimie verte et peuvent être utilisées pour réaliser un traitement industriel écologique afin de réduire les effets de la pollution industrielle. La dégradation microbiologique des déchets de peau en tripe fait partie des préoccupations permanentes des tanneurs. Plusieurs enzymes ont été utilisées dans l'industrie du cuir pour remplacer le procédé conventionnel, principalement des protéases. Les objectifs de cette étude étaient d'isoler et d'identifier les bactéries qui produisent l'enzyme protéase à partir des déchets solides de la tannerie. Les souches bactériennes sélectionnées ont montré une capacité accrue de biosynthèse des protéases, qui a eu une action hydrolytique significative sur les déchets de peau en tripe. Les résultats obtenus dans cette étude ont démontré la capacité des souches appartenant au genre *Bacillus* à synthétiser des quantités accrues d'enzymes protéolytiques et à dégrader les déchets de peau en tripe, ainsi que la possibilité d'utiliser ces micro-organismes comme source de protéase dans divers procédés biotechnologiques.
MOTS CLÉS : déchets de cuir, isolement de bactéries, enzyme protéase

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INTRODUCTION

The leather processing industry generates a huge highly polluting quantum of solid wastes relative to the main product – leather, while processing animal hides for leather making. The pollution effect caused by the present inefficient disposal of these solid wastes impedes the industry's path towards sustainable growth. In order to comply with pollution and discharge restrictions imposed by environmental regulatory agencies, leather industries around the world are shifting to cleaner and milder technology, such as enzyme biotechnology [1]. Current technology allows for the isolation, immobilization and purification of the specific enzymes required for the desired function. Proteases can be used in several biotechnological processes including leather, food and detergent industries. In addition to facilitating the tanning process, the enzymes can also replace chemicals, which means a reduction in the amount of chemical waste [2, 3]. Therefore, the production of enzymes is needed for the leather tanning process.

In recent years, there has been an increased interest in the use of biological degradation of pelt waste. Leather has a complex composition comprising collagen, keratin, elastin, albumins and globulins [4, 5]. Each of these compounds can be degraded under certain environmental conditions (pH, temperature, substrate selectivity, humidity) under the action of enzyme complexes synthesized by a variety of microorganisms (bacteria and molds). Pelt waste degradation occurs by means of proteolytic enzymes [6]. Microbiological degradation of pelt waste is amongst the permanent concerns of leather processing units. Microorganisms (bacteria and molds) play an important role in solving these problems [7].

Among various enzymes proteases have long been used in the bating stage of leather processing, because of their ability to execute reactions with excellent efficiency and selectivity; as a result, enzyme has emerged as a popular tool in green processing applied in the leather sector [8-10].

Protease enzyme can be produced from animals, plants and microorganism products. However, the use of enzymes derived from animal and plant products may have drawbacks. Protease enzymes used in the industry are generally produced from microorganisms [11]. They can be easily produced on a large scale, they have a relatively short production time, and they can be produced in a sustainable manner with a relatively low cost.

Several microorganisms that had been known as protease-producers in commercial applications were *Bacillus cereus*, *Saccharomyces cerevisiae*, *Pseudomonas aeruginosa*, *Aspergillus oryzae* and *Aspergillus flavipes* [12-14]. There are several types of *Bacillus* bacteria capable of producing protease [15, 16].

The objectives of this research were to identify and isolate the bacteria producing protease enzyme from tannery solid waste. The protease is characterized for enzymatic activities. Results of this study are proposed as alternate source of protease enzyme contributing to tanner industry, as well as the possibility of using these microorganisms as a source of protease in various biotechnological processes. The studies have shown that employing enzymes in leather manufacturing can result in higher quality leather.

EXPERIMENTAL

Materials and Methods

Samples

Ground pieces of grey-yellowish pelt waste of hard, slightly wet and gelatinous consistency were used in the experiments (Figure 1).

Figure 1. The macroscopic appearance of pelt waste samples used in degradation experiments

Microorganisms

Three strains with high proteolytical activity were used: P_1, P_2, P_3, strains of the *Bacillus* genus.

To obtain a preinoculum, strains were transplanted in tubes with inclined solidified nutrient medium (agar), which were incubated in a thermostat at 28°C for 24 hours. Subsequently, from the exponentially growing cultures, the bacterial inoculum was made in Erlenmeyer flasks with nutrient broth, which were incubated in a thermostat at 28°C for 24 hours.

Growth Conditions

In order to obtain the bacterial cultures used in pelt degradation experiments, the inoculum was then seeded in a 1/10 ratio in nutrient broth with different pH values (5, 7, 9) in Erlenmeyer flasks which were incubated in a thermostat at 20, 28 and 37°C, respectively, under static conditions for 72 hours.

After this interval, ground samples of pelt, with a known weight of 2.02-2.05 g, were added to the bacterial cultures developed in liquid medium. The Erlenmeyer flasks containing the pelt sample and the bacterial cultures with high proteolytic activity were incubated in a thermostat at different temperature values (20, 28, 37°C), in static conditions for 21 days.

In order to determine the proteolytic activity of the selected strains, culture fluids were harvested at intervals of 7, 14 and 21 days from bacterial cultures developed on a nutrient medium with different pH values and incubated at different temperatures (20, 28 and 37°C).

Enzymatic activity was determined spectrophotometrically at 280 nm and expressed in mg casein/ml.

The decomposition of pelt waste was assessed by macroscopic observations of samples from bacterial cultures and gravimetric determination of their weight, after 21 days of incubation, for each experimental variant.

RESULTS AND DISCUSSION

The obtained results showed that the synthesis of proteases by bacterial strains P_1, P_2, P_3 intensified during the incubation period, the maximum values of enzymatic activity being determined in all experimental variants after 21 days of contact with pelt samples (Figures 1-9).

Bacterial strain P_1 showed maximum proteolytic activity under incubation conditions at 37°C at all pH values of culture media (5, 7, 9), but the highest enzymatic activity was found in the nutrient medium with pH=5 (5.798 mg casein/ml). It was also found that the biosynthesis activity of protease decreased with increasing pH of the culture medium to 7 and 9, respectively (5.295 and 5.123 mg casein/ml) (Figures 1, 2, 3).

Macroscopic observations made after 21 days of culture of the bacterial strain P_1 in the presence of pelt samples indicated a very good development in the incubation conditions at higher temperatures (28 and 37°) at all pH values of the culture media.

It was also found that strain P_1 caused complete degradation of pelt samples in culture

media with pH=5 at 28°C, pH=7 at 28 and 37°C and pH=9 at all three temperature values tested. In these experimental variants, the pelt samples lost their structural integrity, resulting in colloidal solutions, with a cloudy appearance, containing bacterial biomass and particles of different sizes (Table 1).

In comparison, in the case of cultures developed in the medium with pH=5 incubated at 20 and 37°C and of the culture in the medium with pH=7 incubated at 20°C, partial degradation of the pelt samples was observed after 21 days.

Table 1: Pelt waste degradation by fungal treatment

Strain code	pH and temperature (°C)	Initial weight (g)	Weight loss (g)
P_1	pH 5, 20°C	2.03	0.69
	pH 5, 28°C	2.04	-
	pH 5, 37°C	2.04	0.83
P_2	pH 5, 20°C	2.05	remnants
	pH 5, 28°C	2.03	remnants
	pH 5, 37°C	2.04	-
P_3	pH 5, 20°C	2.05	remnants
	pH 5, 28°C	2.03	-
	pH 5, 37°C	2.04	-
P_1	pH 7, 20°C	2.04	0.46
	pH 7, 28°C	2.02	-
	pH 7, 37°C	2.02	-
P_2	pH 7, 20°C	2.02	-
	pH 7, 28°C	2.02	-
	pH 7, 37°C	2.03	remnants
P_3	pH 7, 20°C	2.04	0.24
	pH 7, 28°C	2.03	-
	pH 7, 37°C	2.03	-
P_1	pH 9, 20°C	2.03	remnants
	pH 9, 28°C	2.03	remnants
	pH 9, 37°C	2.04	-
P_2	pH 9, 20°C	2.03	-
	pH 9, 28°C	2.04	-
	pH 9, 37°C	2.04	remnants
P_3	pH 9, 20°C	2.04	remnants
	pH 9, 28°C	2.04	remnants
	pH 9, 37°C	2.03	remnants

Thus, in these experimental variants, colloidal solutions with a cloudy appearance were obtained, made up of bacterial biomass, different particles, as well as pelt residues with small dimensions and wet weight of 0.69 g, 0.83 g and 0.46 g, respectively (Table 1).

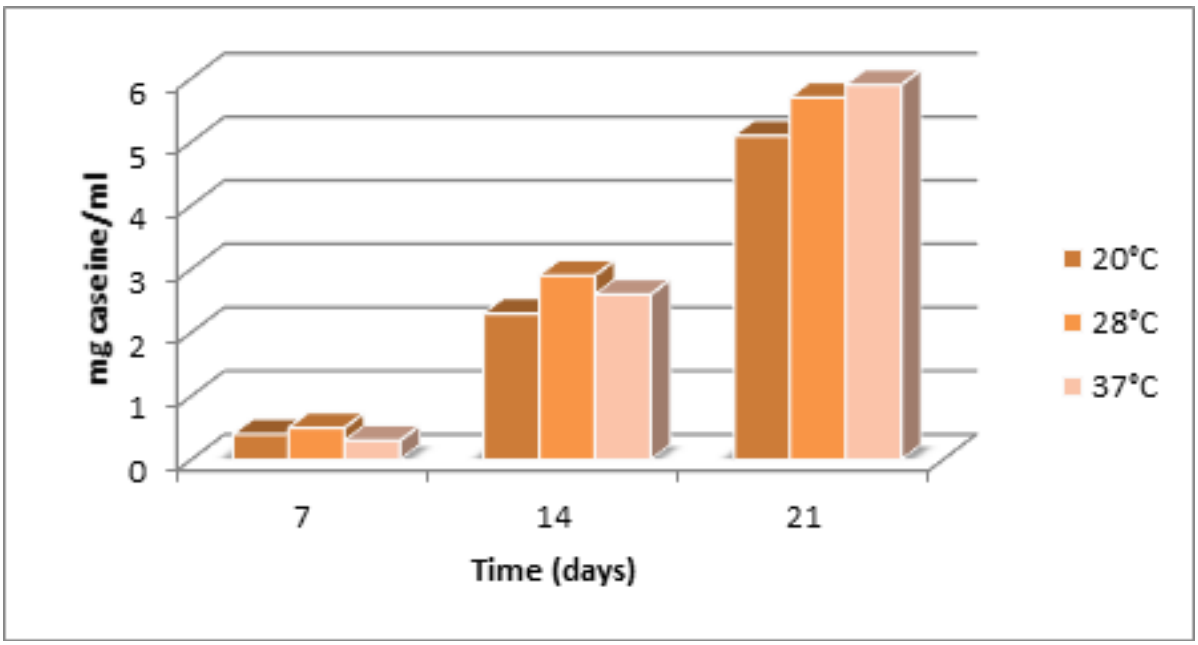

Figure 1. Dynamics of proteolytic activity of bacterial strain P_1 in the culture medium with pH=5, under different temperature conditions

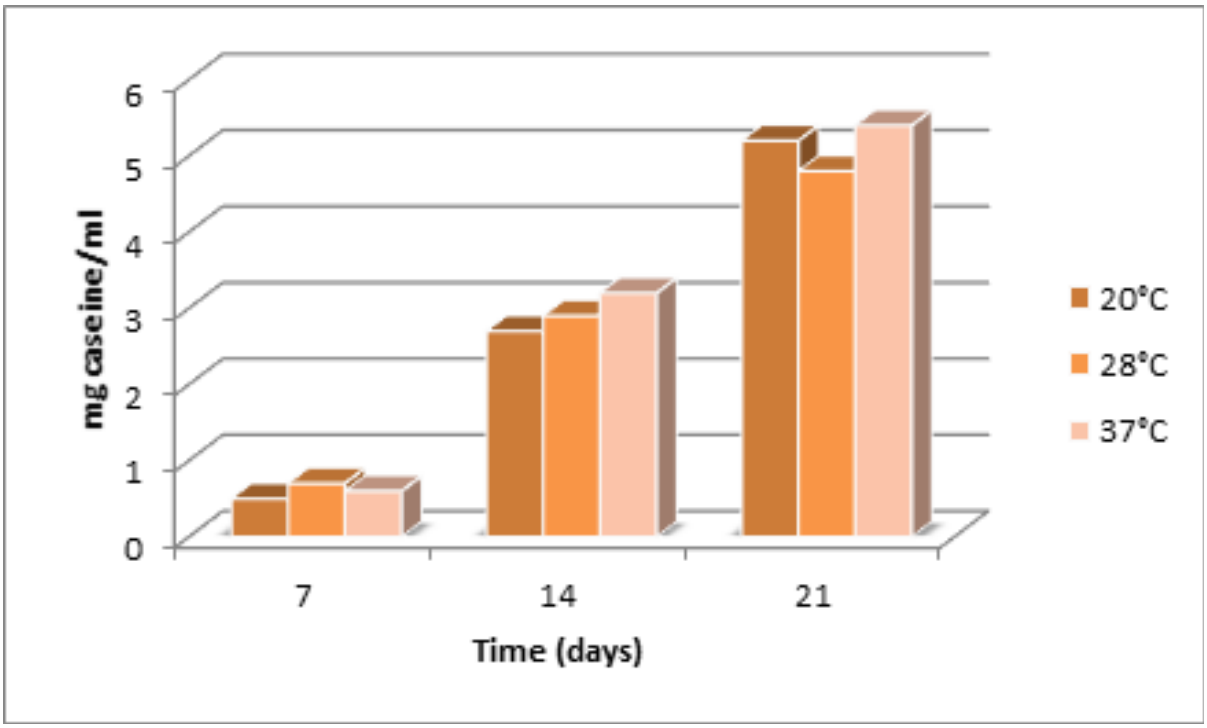

Figure 2. Dynamics of proteolytic activity of bacterial strain P_1 in the culture medium with pH=7, under different temperature conditions

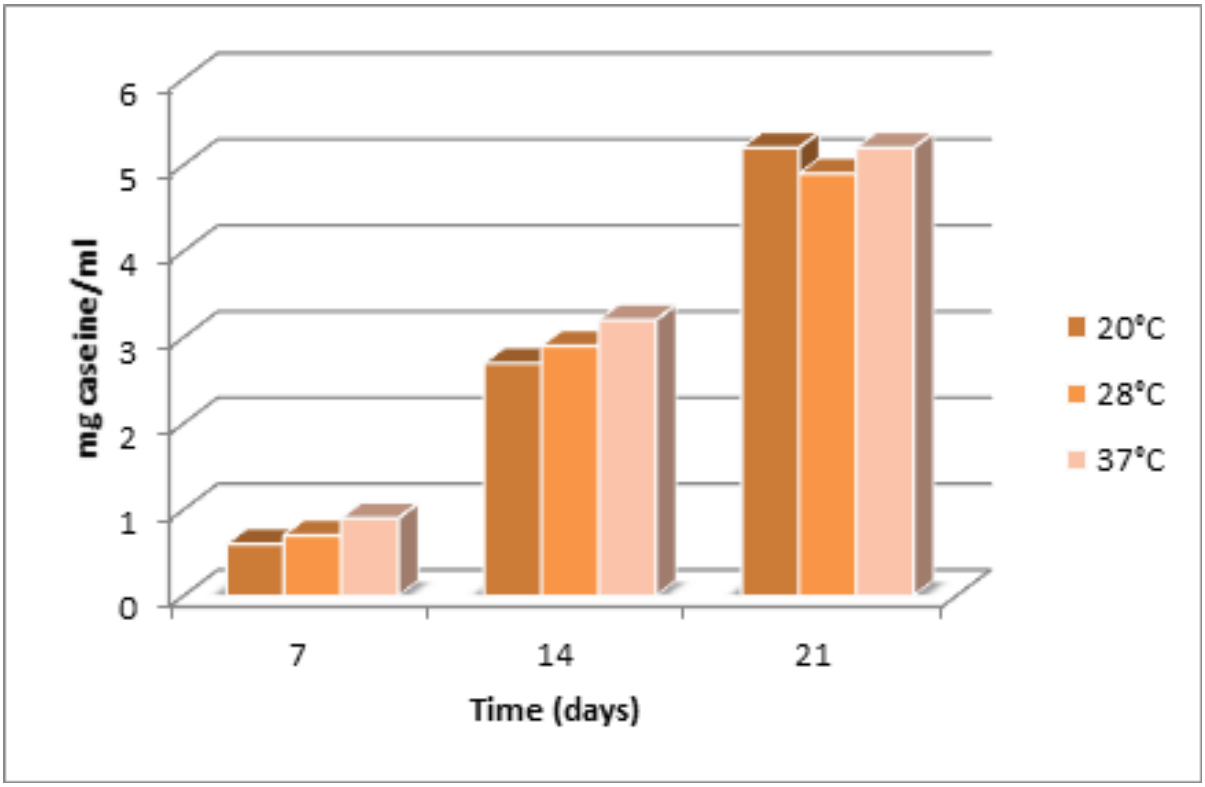

Figure 3. Dynamics of proteolytic activity of bacterial strain P_1 in the culture medium with pH=9, under different temperature conditions

The bacterial strain P_2 showed maximum proteolytic activity under the conditions of incubation at 20°C in the medium with pH=9 (5.397 mg casein/ml), but close values were also determined at the temperature of 28°C in the medium with pH=5 (5.41 mg casein/ml) and in the medium at 20°C with pH=7 (5.312 mg casein/ml) (Figures 4, 5, 6).

Macroscopic observations made after 21 days of culturing the bacterial strain $P_{3/1}$ in the presence of pelt samples indicated a very good development of the culture media in all pH conditions and at all temperature values tested.

It was also found that the very good development of the $P_{3/1}$ strain was correlated with the complete degradation of the pelt samples in culture media with pH=5, 7, and 9 at temperatures of 20, 28, and 37°C. Thus, in all experimental variants, strain $P_{3/1}$ showed high proteolytic activity, causing the loss of structural integrity of pelt samples, their decomposition and obtaining colloidal solutions, with cloudy appearance, containing bacterial biomass and particles of different sizes (Table 1).

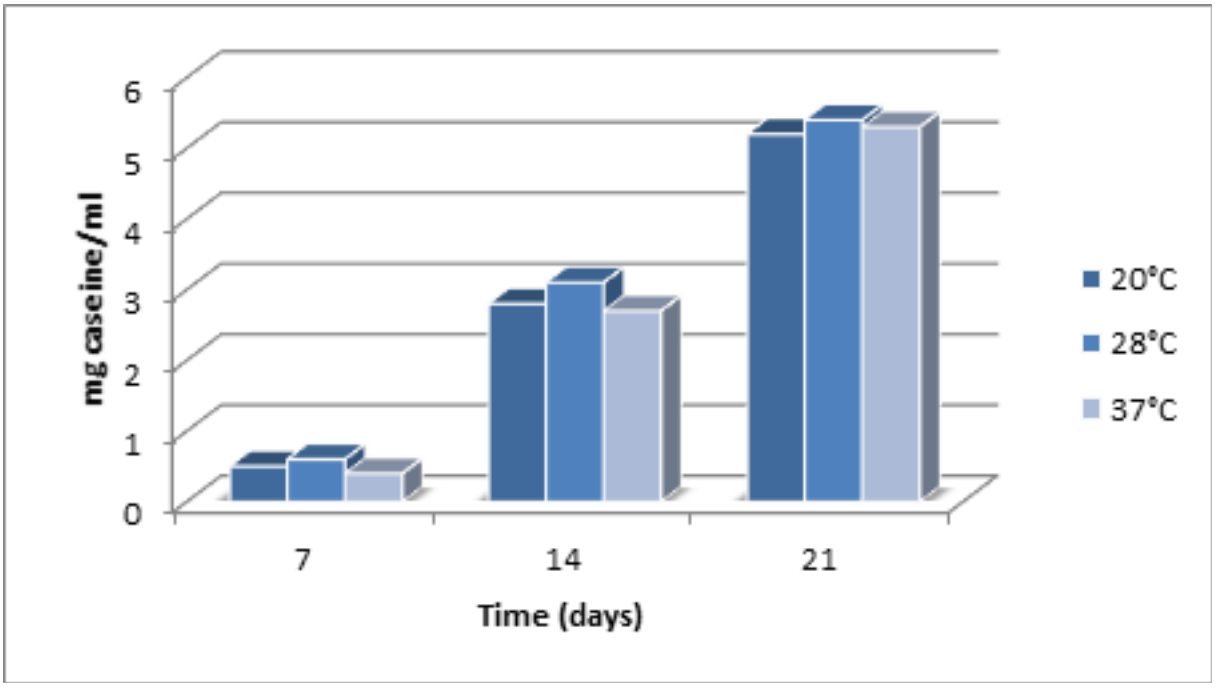

Figure 4. Dynamics of proteolytic activity of bacterial strain P_2 in the culture medium with pH=5, under different temperature conditions

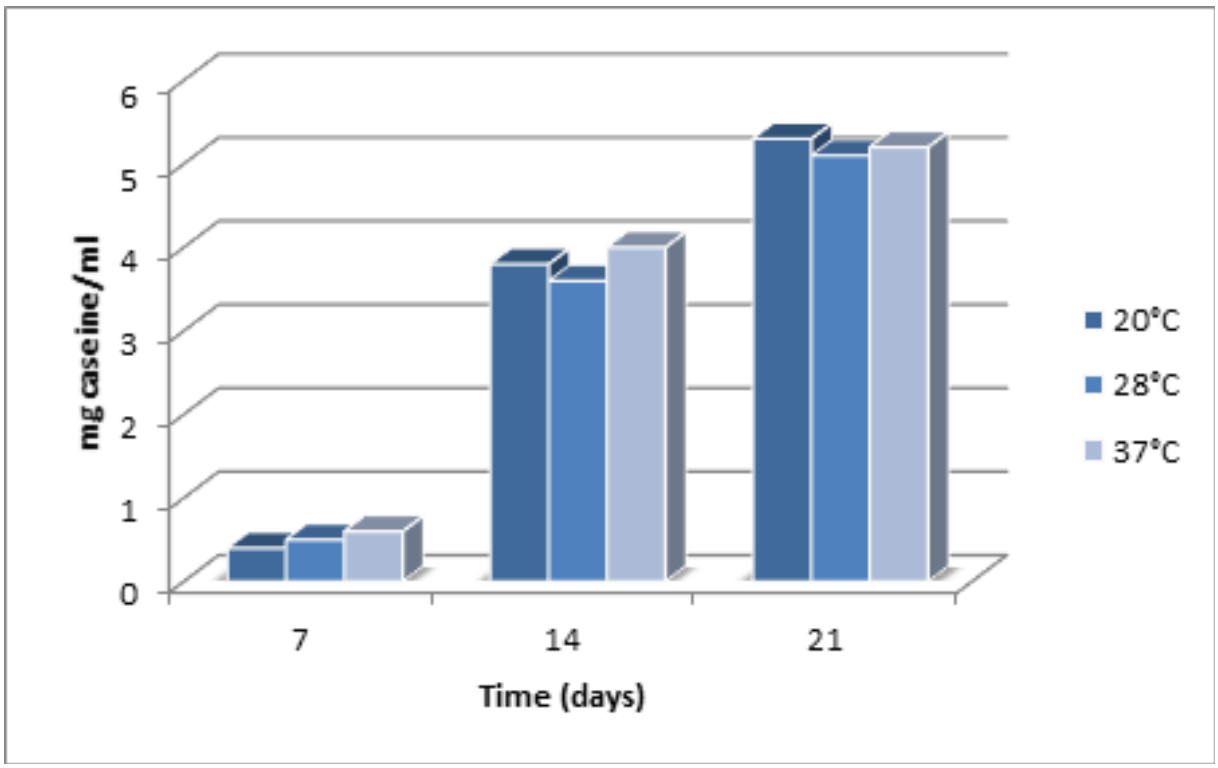

Figure 5. Dynamics of proteolytic activity of bacterial strain P_2 in the culture medium with pH=7, under different temperature conditions

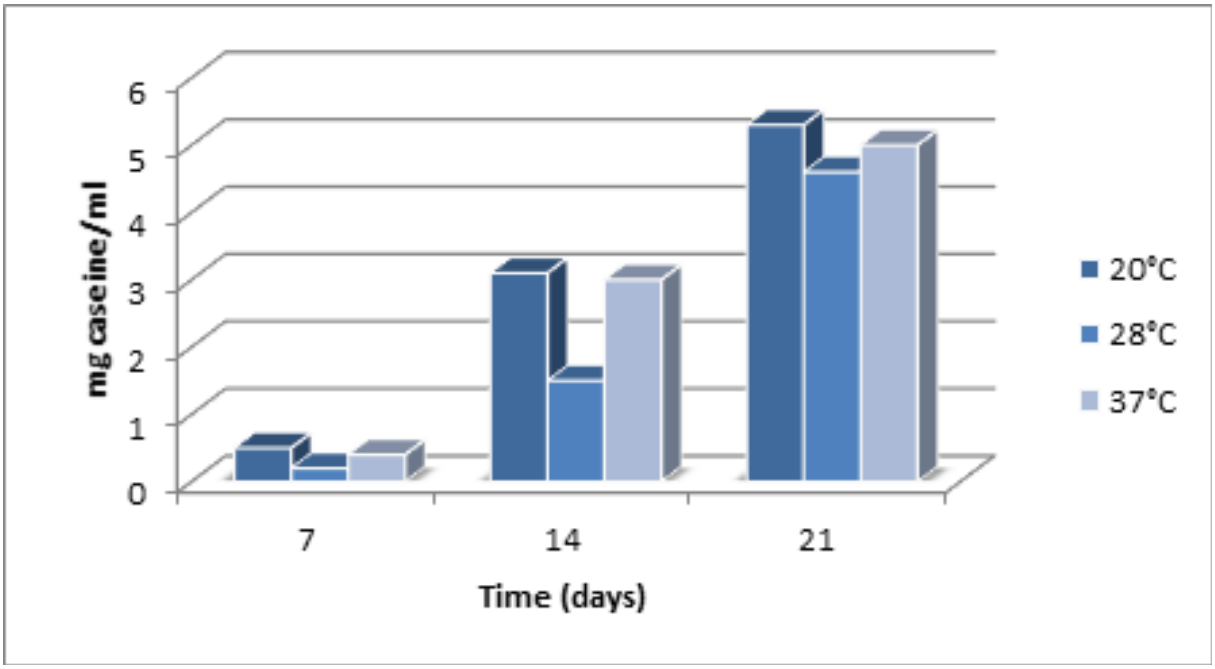

Figure 6. Dynamics of proteolytic activity of bacterial strain P_2 in the culture medium with pH=9, under different temperature conditions

Bacterial strain P_3 showed maximum proteolytic activity under incubation conditions at 37°C, in culture medium with pH=5 (5.5745 mg casein/ml), but high enzymatic activity at the same temperature was also achieved by the culture developed in the nutrient medium with pH=9 (5.4808 mg casein/ml).

In comparison, in the case of culturing the P_3 strain in the medium with pH=7, the highest activity of protease biosynthesis was found in the variant incubated at 20°C (5.3132 mg casein/ml) (Figures 7, 8, 9).

Macroscopic observations made after 21 days of culturing the $P_{4/1}$ strain in the presence of pelt samples indicated a very good development in all experimental variants, which was correlated with a high proteolytic activity, which determined the complete degradation of the samples, losing their structural integrity. Thus, at the end of the incubation period, colloidal solutions were obtained, with a cloudy appearance, which contained bacterial biomass and particles of different sizes (Table 1).

An exception was noticed in the cultivation of strain P_3 on medium with pH=7 and incubated at 20°C, in which partial degradation of the pelt samples was observed after 21 days and a cloudy colloidal solution consisting of bacterial biomass, various particles, as well as small-sized pelt debris and wet weight of 0.25 g was obtained (Table 1).

The partial degradation of the pelt samples in the case of this experimental variant may be due to a decreased enzymatic activity, determined by the low temperature value at which the bacterial culture was incubated with the pelt sample.

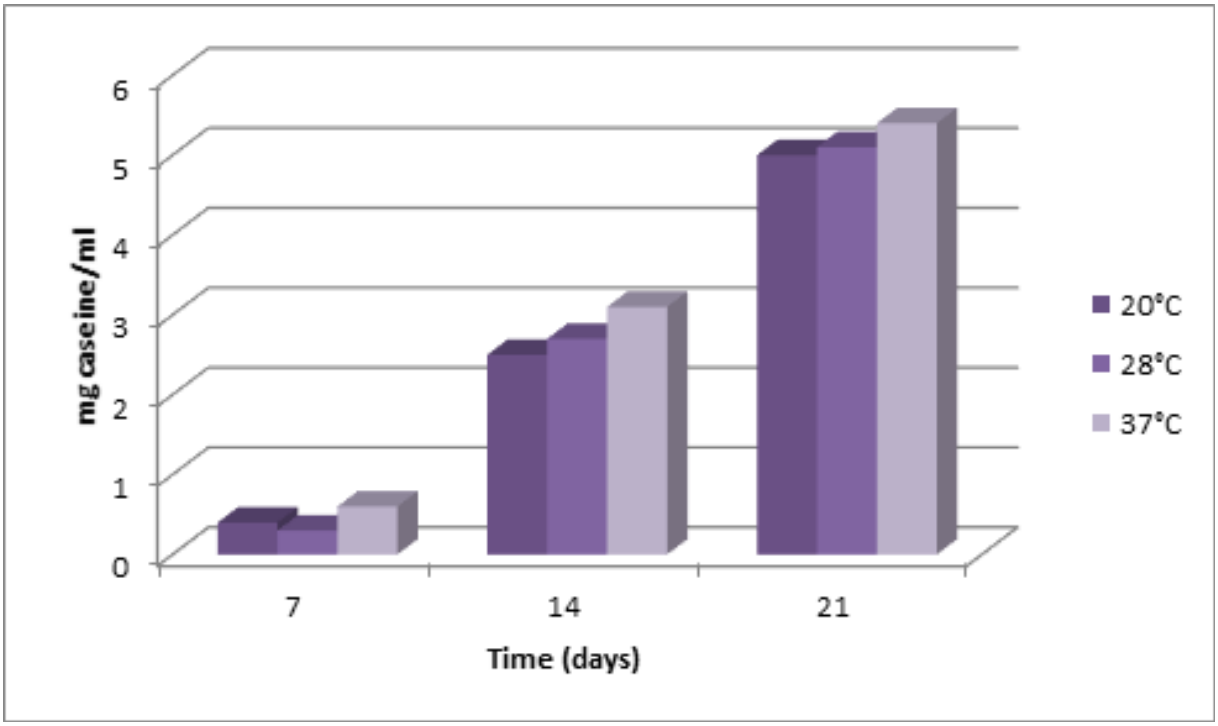

Figure 7. Dynamics of proteolytic activity of bacterial strain P_3 in the culture medium with pH=5, under different temperature conditions

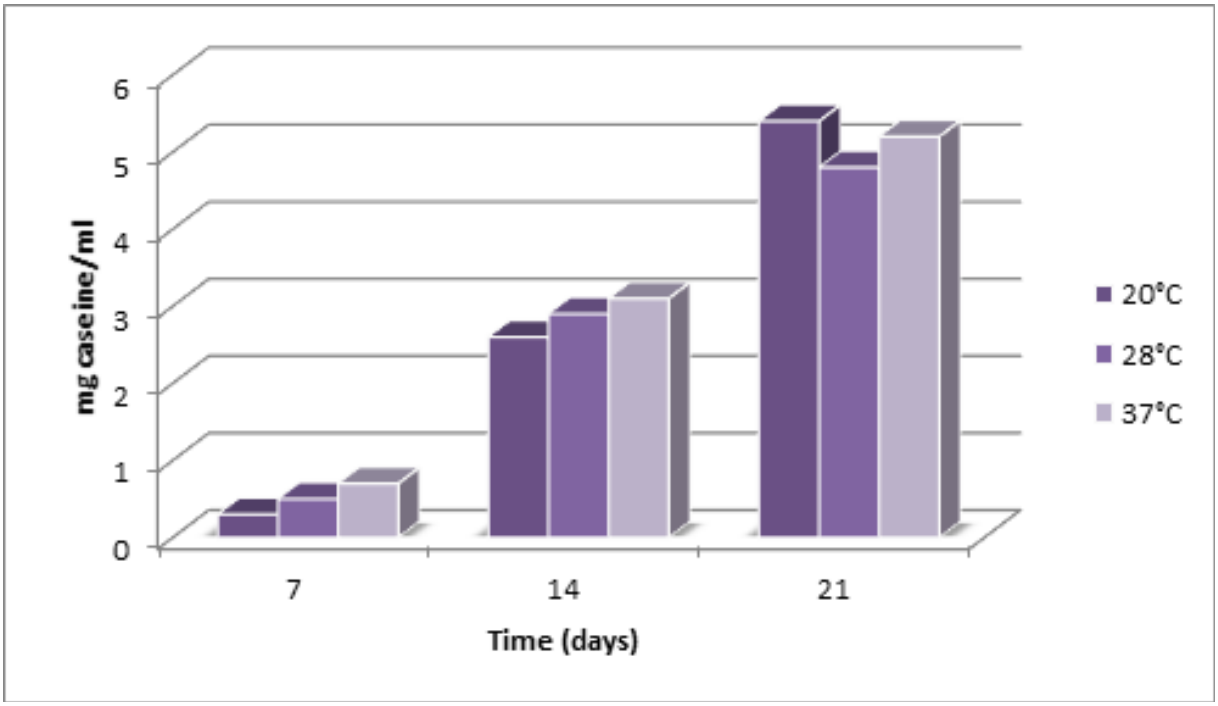

Figure 8. Dynamics of proteolytic activity of bacterial strain P_3 in the culture medium with pH=7, under different temperature conditions

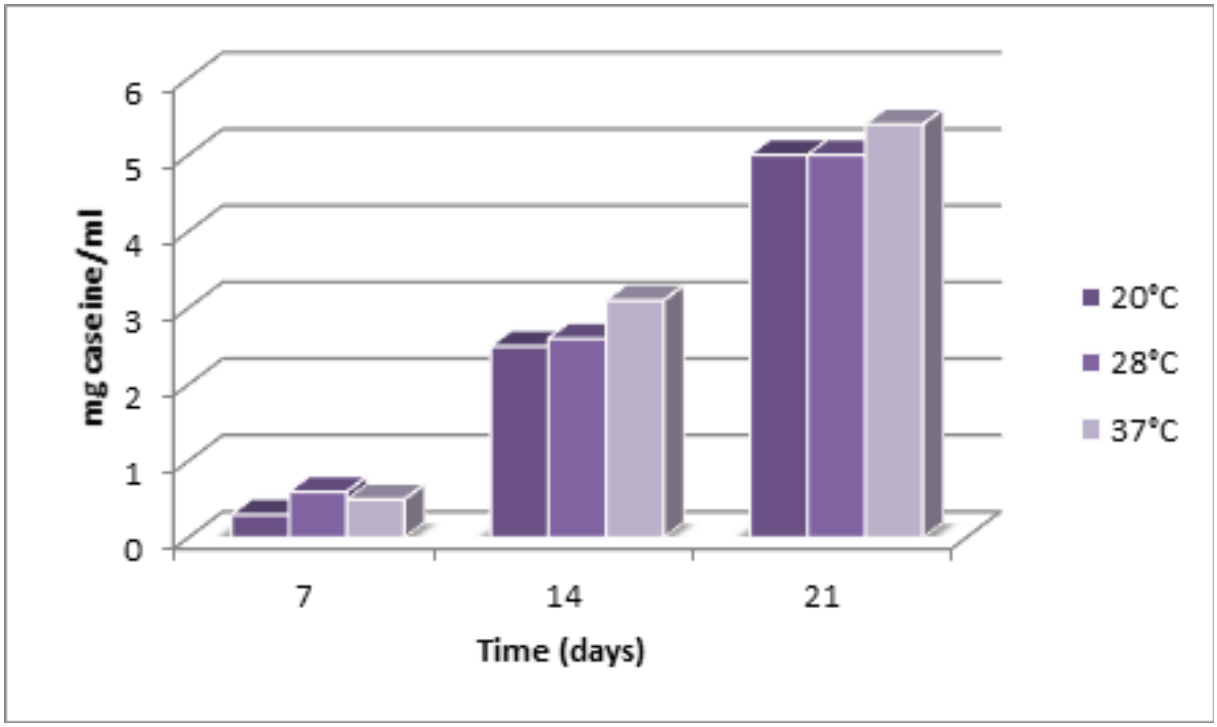

Figure 9. Dynamics of proteolytic activity of bacterial strain P_3 in the culture medium with pH=9, under different temperature conditions

CONCLUSIONS

The selected bacterial strains showed increased protease biosynthesis capacity, which had a significant hydrolytic action on pelt waste.

The quantitative determination of the enzymatic activity showed that the proteolytic activity on the pelt waste medium was specific for each of the three bacterial strains tested. Also, in the case of each strain there were differences depending on the pH value of the culture medium and the incubation temperature. Thus, strains P_1 and P_3 showed maximum protease synthesis activity on the medium with pH=5, under the conditions of incubation at 37°C. In comparison, in the case of P_2 strain the highest proteolytic activity was determined at lower temperatures (20°C) and at a higher pH value of the culture medium (9).

Some differences were found among the bacterial strains tested for the degradation capacity of the pelt samples. Thus, in the case of the bacterial strain $P_{1/1}$, the complete degradation of the pelt samples was obtained in the environment variant with a higher pH, at all the tested temperature values. In contrast, strains P_2 and P_3 showed superior ability to degrade pelt waste, causing loss of structural integrity of the samples and their decomposition at all pH values of the culture media and at all incubation temperatures tested.

The synthesis of proteases by the tested bacterial strains intensified during the incubation period, the maximum values of the enzymatic activity being determined in all experimental variants after 21 days of contact with the pelt samples.

The results obtained in this study demonstrated the ability of strains belonging to the *Bacillus* genus to synthesize increased amounts of proteolytic enzymes and to degrade pelt waste, as well as the possibility of using these microorganisms as a source of protease in various biotechnological processes.

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POLYMER COMPOSITE BASED ON NATURAL RUBBER AND FUNCTIONALIZED RUBBER WASTE

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POLYMER COMPOSITE BASED ON NATURAL RUBBER AND FUNCTIONALIZED RUBBER WASTE

ABSTRACT. In this work, biodegradable polymer composites were made based on natural rubber and post-consumer vulcanized rubber waste functionalized with potassium oleate, in various proportions (5, 10, 20, 30, 50%), cryogenically ground to dimensions of min. 500 nm and polyethylene grafted with maleic anhydride as compatibilizer between the two phases. This composite will be made into a low-density product, with low cost, and last but not least, biodegradable, with the recovery and reuse of waste, containing post-consumer polymers. The methodology for making the new materials involves the following steps: sorting waste, grinding, functionalization and compounding. These operations are easy to manage and do not involve new equipment. Compounding, the most important operation, is carried out on a roller and the mixtures are processed into finished products by compression in an electric press. The tested biodegradable composites were structurally and physico-mechanically characterized. Waste transformation (ground and functionalized) into new value-added products will lead to remarkable improvements in the life cycle of raw materials and the sustainable use of this waste, contributing to sustainability, improving eco-efficiency and economic efficiency and reducing the "pressure" of waste on the environment.
KEY WORDS: biodegradability, polymer composite, post-consumer

COMPOZIT POLIMERIC PE BAZĂ DE CAUCIUC NATURAL ȘI DEȘEU DE CAUCIUC FUNCȚIONALIZAT

REZUMAT. În această lucrare s-au realizat compozite polimerice biodegradabile pe bază de cauciuc natural și deșeuri de cauciuc vulcanizate post-consum funcționalitate cu oleat de potasiu, în proporții variate (5, 10, 20, 30, 50%), măcinat criogenic la dimensiuni de min. 500 nm și compatibilizator între cele două faze, polietilenă grefată cu anhidridă maleică. Acest compozit va fi transformat într-un produs cu densitate scăzută, cu costuri reduse, și nu în ultimul rând, biodegradabil, valorificând și reutilizând deșeurile care conțin polimeri post-consum. Metodologia de realizare a noilor materiale implică următoarele etape: sortarea deșeurilor, măcinarea, funcționalizarea și amestecarea. Aceste operațiuni sunt ușor de gestionat și nu implică echipamente noi. Compoundarea, cea mai important operațiune, se realizează pe un valț, iar amestecurile sunt procesate în produse finite prin compresie într-o presă electrică. Compozitele biodegradabile experimentate au fost caracterizate structural și fizico-mecanic. Transformarea deșeurilor (măcinate și funcționalizate) în noi produse cu valoare adăugată va duce la îmbunătățiri remarcabile ale ciclului de viață al materiilor prime și la utilizarea durabilă a acestor deșeuri, contribuind la sustenabilitate, îmbunătățirea eco-eficienței și a eficienței economice, precum și la reducerea „presiunii" deșeurilor asupra mediului.
CUVINTE CHEIE: biodegradabilitate, compozit polimeric, post-consum

COMPOSITE POLYMÈRE À BASE DE CAOUTCHOUC NATUREL ET DE DÉCHETS DE CAOUTCHOUC FONCTIONNALISÉS

RÉSUMÉ. Dans ce travail, des composites polymères biodégradables ont été fabriqués à base de caoutchouc naturel et de déchets de caoutchouc vulcanisé post-consommation fonctionnalisés avec de l'oléate de potassium, dans diverses proportions (5, 10, 20, 30, 50 %), broyés cryogéniquement à des dimensions de min. 500 nm et compatibilisant entre les deux phases, polyéthylène greffé anhydride maléique. Ce composite sera transformé en un produit à faible densité, à faible coût, et, enfin et surtout, biodégradable, en récupérant et en réutilisant des déchets contenant des polymères post-consommation. La méthodologie de fabrication des nouveaux matériaux comprend les étapes suivantes: tri des déchets, broyage, fonctionnalisation et compoundage. Ces opérations sont faciles à gérer et n'impliquent pas de nouveaux équipements. Le compoundage, opération la plus importante, est réalisé sur rouleau et les mélanges sont transformés en produits finis par compression dans une presse électrique. Les composites biodégradables testés ont été caractérisés structurellement et physico-mécaniquement. La transformation des déchets (broyés et fonctionnalisés) en nouveaux produits à valeur ajoutée conduira à des améliorations remarquables du cycle de vie des matières premières et à l'utilisation durable de ces déchets, contribuant à la durabilité, améliorant l'éco-efficacité et l'efficacité économique et réduisant la « pression » des déchets sur l'environnement.
MOTS CLÉS: biodégradabilité, composite polymère, post-consommation

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INTRODUCTION

The European Commission adopted the new Circular Economy Action Plan to stimulate Europe's transition from a linear towards a circular economy. This ambitious initiative: "Closing the Loop - An EU Action Plan for the Circular Economy" is promoting the transition to a more circular economy, where the value of products, materials and resources is maintained in the economy for as long as possible and the generation of waste is minimized, being an essential contribution to the EU's efforts to develop a sustainable, low carbon, resource efficient and competitive economy. Nowadays, the circular economy is an irreversible, global trend. It was foreseen that the proposed actions would contribute to "closing the loop" of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy [1-5]. The paper presents a recycling route for post consumption rubber wastes in order to obtain biodegradable composites for green products manufacturing. Composites represent a very valuable group of materials, which can solve a series of existing problems in various applications/industries, because they facilitate the introduction of new properties in materials. Recycling and using renewable natural resources offer a new dimension in the discovery of new materials.

The dynamic increase in the production of rubber products, especially those used in the automotive industry, is responsible for obtaining a large amount of vulcanized rubber waste, especially in the form of used tires, of which more than 17 million tons are globally generated every year. China, the European Union (EU), the USA, Japan and India produce the largest amounts of used tire waste – almost 88% of the total number of tires withdrawn worldwide [6, 7]. The diversification of chemical compositions and three-dimensional structures existing in vulcanized rubber from tires is the main reason why they are highly resistant to biodegradation, photochemical decomposition, chemical reagents and high temperatures. The increased number of used tires makes them a serious threat to the natural environment. End-of-life tires and other rubber waste (containing high-quality natural and synthetic rubbers) have become the source of materials for obtaining "environmentally friendly" composites with utilitarian properties. The advantages of using such materials include the sustainable management of the large quantities of used polymer articles that currently burden the environment and the reduction of costs of composite materials produced from cheap polymer waste [8]. The increasing level of consumption of rubber recycling products shows that rubber waste is used in the rubber industry as a raw material for the production of composites with practical utilitarian properties and in an economical way. For high-quality and high-strength rubber products, the use of rubber waste is limited. Therefore, rubber composites obtained using rubber waste are used in practice for the manufacture of inexpensive items where strength is not a priority, such as: floor materials, windshield wipers, washers, tapes, molds, cable housings and shoe soles [9].

Currently, the amount of used tires recycled by grinding in the EU, USA, Japan and China is estimated at about 3.6 million tons/year. According to the analysis of the tire recycling market, it can be said that rubber powder is no longer considered a cheap filler, but a valuable component of durable rubber composites, used in large-scale applications by manufacturers of molded and extruded products, gaskets, manufacturers of playgrounds, artificial sports surfaces, or in the automotive industry, etc. [6, 7, 9-13]. It is known in the literature that the properties of rubber powder depend on the method of obtaining them (cryogenic grinding or at ambient temperature), the grain size, crosslinking, filler content and the type of natural or synthetic rubber that the initial products had. The mechanical properties and performances of the polymer composites obtained from rubber powder from waste, depend on the type of polymer matrix used and, therefore, on the nature of the interactions between the matrices, the type and size of the rubber granules and their amount in the composites. For example, the studies carried out by Yehia [8] on compounds based on natural rubber with 0-50 phr HAF and 0-50 phr rubber powder with a particle size of 125-500 µm, showed that by oxidizing the surface of the rubber particles from the powder, there is an improvement in traction and accelerated aging properties. The same conclusions were reached by Zhang *et al*. [14], who modified the

surface of the rubber particles from the powder using plasma treatment. They made composites based on acrylonitrile-butadiene rubber (NBR) with 0-20 phr rubber powder with a rubber particle size of 250 µm, and observed that by using the powder modified by plasma treatment there is an improvement of the interfacial adhesion between the components, which leads to an improvement of the mechanical properties compared to the composites in which the unmodified powder was used.

The aim of this paper is to study the properties of natural rubber reinforced composites with differential rubber waste contents (10, 20, 30 and 50 wt%). Tensile strength, tear strength, elasticity, hardness, elongation of break, attrition and morphological study (FT-IR) of Natural Rubber/ Waste Rubber composites were examined.

EXPERIMENTAL

Materials and Methods

Materials

Materials used were: (1) natural rubber (NR rubber): purity 99%; Mooney viscosity (100%) – 32±3; density – 0.96 g/cm^3; (2) stearin: white flakes; moisture – 0.5% max; (3) zinc oxide microparticles (ZnO): yellow powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g; (4) silicon dioxide (SiO_2): density – 1.9-4.29 g/cm^3, molar mass – 60.1 g/mol; (5) precipitated chalk: white powder, purity 99.09%; (6) rubber waste – ground rubber functionalized with potassium oleate from the footwear industry; (7) mineral oil; (8) N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD 4010): density – 1.1 g/cm^3, solidification point over 76.5°C, flat granules coloured brown to dark purple); (9) sulphur (S): vulcanization agent, fine yellow powder, insoluble in water, melting point: 115°C, faint odor; (10) N-cyclohexylbenzothiazole-2-sulphenamide (Cz): curing agent, density – 1.26g/cm^3, melting point 93-100°C; (11) diphenyl guanidine (D): curing agent, density – 1.34g/cm^3; (12) PEG – Polyethylene glycol: plasticizer, white pellets.

Preparation of Various Types of Biodegradable Polymer Composite

Table 1 presents the formulations for polymer composites based on natural rubber, with semi-active white mineral charge – ZnO and precipitated chalk, formulations based on the recipe for processing caps for antibiotic bottles for zootechnical use. In order to obtain polymer composites based on natural rubber and elastomeric waste, the basic recipe was modified by adding rubber waste functionalized with potassium oleate in different proportions, respectively 10, 20, 30, 50%, waste relative to the amount of elastomer.

Table 1: Polymer composites based on natural rubber compounded with elastomeric waste functionalized with potassium oleate

Material	UM	N0	NC1	NC2	NC3	NC4
Brabender mixer processing						
Natural rubber	g	190	190	190	190	190
Stearic acid	g	3.8	3.8	3.8	3.8	3.8
Zinc oxide	g	9.5	9.5	9.5	9.5	9.5
Precipitated chalk	g	95	76	57	38	0
Elastomeric waste	g	-	19	38	57	95
Mineral oil	g	4.5	5.7	5.7	5.7	5.7
IPPD antioxidant	g	4.5	5.7	5.7	5.7	5.7
PEG 4000	g	1,14	1.14	1.14	1.14	1.14
Roller processing						
Sulfur	g	4.85	4.85	4.85	4.85	4.85
Cz accelerator	g	2.28	2.28	2.28	2.28	2.28
D accelerator	g	0.29	0.285	0.285	0.285	0.285

N0, NC1-NC4 composites were mechanically mixed in Brabender Plasti-Corder PLE 360 at 45°C and 80 rpm for 3 minutes and 2 min. at 23°C for homogenisation. The total time was 5 min. from the Brabender mixing diagrams, Figure 1.

According to the diagrams (Figures 1-2), the following can be observed: in the first portion (A-B), the elastomer is introduced into the mixer and the torque increases. The first loading peak, A, corresponds to the introduction of elastomers. As the torque increases, so does the temperature due to friction. The torque starts to decrease until B, mainly due to the homogenization and plasticization of the elastomer, as well as due to the increase in temperature as a result of the shear forces. The other ingredients are introduced and the rotational speed is reduced to 20 rpm, and the mixer is kept open. Between point B and point X, the torque starts to increase due to the incorporation of the ingredients. After incorporating the fillers and the other ingredients, the second loading peak, X, is observed, when a maximum torque appears. The torque begins to decrease, indicating the homogenization of the mixture. As a result, a maximum torque value is obtained due to the compaction and homogenization of the rubber mixture. This is generally followed by a decrease in the value of the torque, which indicates both the homogenization of the mixture and the increase in the temperature of the mixture due to friction at a higher rotational speed (60 rpm) with the mixer closed.

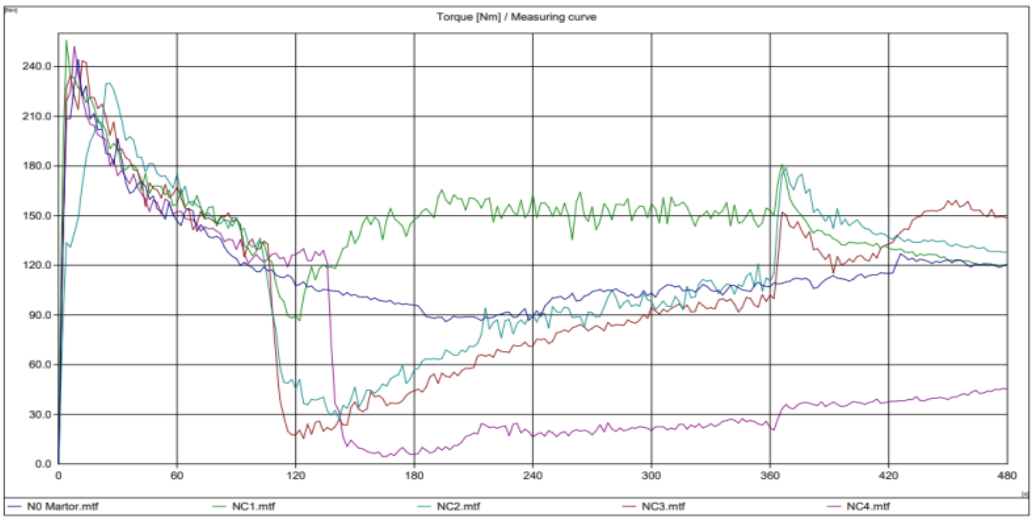
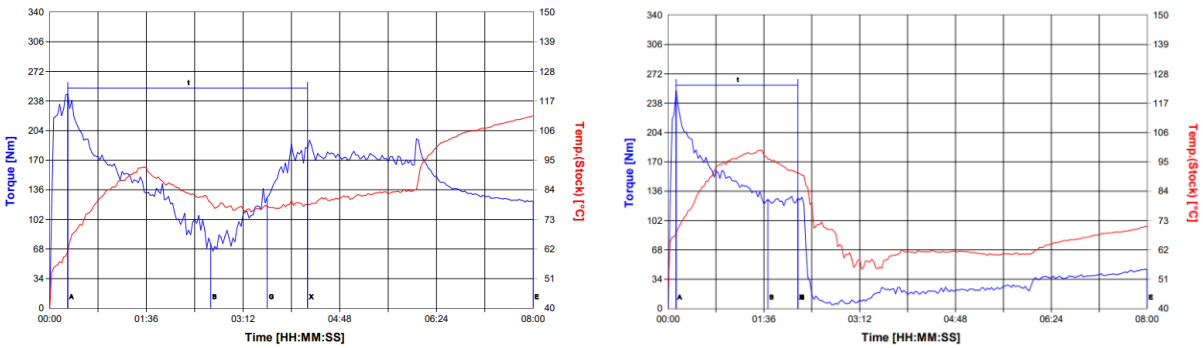


Figure 1. Torque variation with time recorded using the Brabender Plasti-Corder when obtaining NC rubber mixtures



N0 mixture NC4 mixture

Figure 2. Torque and temperature variation with time recorded using the Brabender Plasti-Corder when obtaining N0 and NC4 samples

From the diagrams shown in Figures 1 and 2, it can be seen that the temperature in the mixing chamber increases, depending on the percentage of elastomeric waste introduced into the polymer composite (starting from 78-80°C, it decreases to 69°C – NC3 then increases to 91°C – NC4, the last being the composite with a percentage of 50% elastomeric waste). Also, the mixing forces increase proportionally with the percentage of elastomeric waste in the composite, starting at a temperature of 61°C and reaching a maximum at 30 seconds of mixing of 246 Nm for sample N0 and increasing proportionally to 252.1 Nm for sample NC4. The maximum torque is reached when the natural rubber plasticizes, mixes with the mixing ingredients (plasticizer, filler, antioxidants) and begins to disperse the waste rubber particles. After reaching the maximum torque, it decreases uniformly (171.4-128.2), being constant in the last minute, which indicates the homogenization of the mixture. This decrease is due to the elastic behavior of the rubber waste and its functionalization with potassium oleate, which also acts as a plasticizer. Table 2 shows the processing characteristics presented in the Brabender diagrams, for each processed composite.

Table 2: Characteristics presented in Brabender processing diagrams for NC polymer composites

Characteristics	Sample code				
	N0	NC1	NC2	NC3	NC4
Temperature at peak load, °C	61	64	66	63	68
Temperature at the inflection point, °C	78	80	77	69	91
Maximum temperature, °C	112	109	112	107	91
Energy at the peak load, Nm	246.0	255.9	230.0	243.6	252.1
Maximum energy, Nm	183.5	171.4	169.6	159.1	128.2
Gelation zone energy, kNM	10.3	33.7	33.1	94.7	1.0
Specific energy, kNm/g	0.7	0.8	0.6	0.6	0.3
Gelation rate, Nm/min.	142.5	171.2	22.0	26.3	-52.5

Vulcanizing agents are added to the mixtures made using the Brabender Plasti-Corder on the roller. The working method on the laboratory electric roller for adding vulcanizing agents to the mixtures is as follows, with the mixture executed on the roller at a temperature of 23-30°C, roller friction 1:2 and 50 rotations/min:

- The composite is plasticized;
- The vulcanization agents are added and mixed for approximately 5-10 minutes;
- The mixture is homogenized on the roller for 1-2 minutes and taken out in the form of a 1-2 mm thick sheet.

The Monsanto 100S Rheometer was used to determine the vulcanization parameters of the tested composites, which describes their vulcanization and processing parameters. The analysis is carried out as follows: a sample is sealed in a cavity of the device, at a controlled and constant temperature (in this case a temperature of 165°C was used), which surrounds a rotor with oscillations at a frequency of 1.67 Hz (100 cpm). The output correlates with the degree of vulcanization depending on vulcanization time.

From the experimental data (Table 3) it can be seen that by replacing the amount of inactive filler (precipitated chalk) with functionalized elastomeric waste, the rheological characteristics of the mixtures are changed as follows:

- the minimum torque (ML) shows a variation of +5 – (-20)%, the maximum torque (MH) shows a decrease of max. 28%, and the torque variation (ΔM) decreases by a maximum of 41% as the amount of waste increases, indicating the decrease in the stiffness of the rubber mixtures in the vulcanized state;

- for all the samples, the reversion phenomenon is observed, indicating a degradation of the mixtures at high temperatures through the breaking of some cross-linking bonds.

- the scorching time (ts2) decreases as the amount of rubber powder increases and the amount of precipitated chalk decreases, and the optimal vulcanization time shows a slight increase by replacing the precipitated chalk with elastomeric waste.

Table 3: Rheological characteristics of NC mixtures

Rheological characteristics at 165°C	Sample codes				
	N0	NC1	NC2	NC3	NC4
ML (dNm)	8	7.6	8.9	10	10.2
MH (dNm)	54.3	54.4	45.2	39	37.4
ΔM = MH-ML (dNm)	46.3	46.8	36.3	29	27.2
Mf - Reversion (dNm)	47	48.5	43	35	35
t_{s2} (min)	1.2	1.07	1.01	0.99	1.04
t_{50} (min)	1.67	1.74	1.79	1.79	2
t_{90} (min)	2.54	2.75	3.15	3.26	4.06

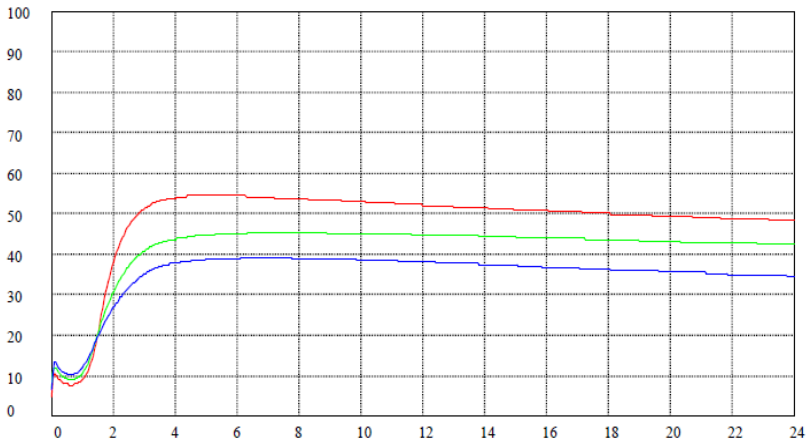


Figure 3. Torque variation expressed in dNm (OY axis) with time expressed in minutes (OX axis) for mixtures based on natural rubber: NC1 (red), NC2 (green) and NC3 (blue)

The vulcanization parameters were established based on the data from the rheograms, presented in Table 4.

Table 4: Vulcanization parameters for making samples in the press for NC mixtures based on natural rubber and elastomeric waste)

Vulcanization parameters	Sample code				
	N0	NC1	NC2	NC3	NC4
Vulcanization temperature	165°C	165°C	165°C	165°C	165°C
Vulcanization time - T_{90}	4 min	4 min	4 min	4 min	4 min
Pressing force	300 kN	300 kN	300 kN	300 kN	300 kN
Cooling temperature	45°C	45°C	45°C	45°C	45°C
Cooling time	10’	10’	10’	10’	10’
Pressing force	300 kN	300 kN	300 kN	300 kN	300 kN

The compounds were then compression-molded (using an electrically heated laboratory press) to obtain a sheet of about 2 mm thick. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore "A" Durometer according to SR ISO 7619-1:2011.

Abrasion resistance was carried out according to ISO 4649/2010, the cylinder method, using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Repeated flexions - Ross Flex - SR ISO 132/2018 is the test that determines the resistance of the specimens to the appearance and propagation of cracks when they are subjected to repeated bending at an angle of 90°C, on a mandrel with a diameter of 10mm, up to 30,000 cycles or until the crack appears or the material breaks.

FT-IR spectroscopy was done using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range 2000-530 cm^{-1}.

RESULTS AND DISCUSSIONS

Physical-mechanical tests were carried out in the Investigation laboratory from INCDTP - Division ICPI, accredited by RENAR, and materialized in the determination of hardness, elasticity, tensile and tear strength, attrition, residual elongation and elongation at break for thermo-oxidative aging (168h x 100°C) and normal state (Table 5).

Table 5: Physical-mechanical characteristics of NC mixtures

Physical-mechanical characteristics	Sample code				
	N0	NC1	NC2	NC3	NC4
Normal state					
Hardness, °Sh A	44	35	32	30	30
Elasticity, %	32	24	22	22	24
100% modulus, N/mm^2	1.0	0.51	0.05	0.046	0.046
300% modulus, N/mm^2	2.0	1.02	0.84	0.77	1.21
500% modulus, N/mm^2	4.52	2.21	1.68	1.97	2.88
Tensile strength, N/mm^2	14.23	10.46	6.2	3.17	5.31
Elongation at break, %	740	800	780	620	660
Residual elongation, %	28	30	26	24	20
Tear strength, N/mm	24.39	19.23	16.9	15	23
Specific weight, g/cm^3	1.2	1.16	1.11	1.08	1.02
Abrasion resistance, mm^3	123.45	320	-	265.36	231.71
Rossflex repeated flexions SR ISO 132/2018	Resist up to 150.000 cycles			90.000 cycles crack appears, resist up to 109.000 cycles	
After accelerated ageing for 168 hours at 70°C					
Hardness, °Sh A	51	41	39	36	35
Elasticity, %	34	38	32	34	24
100% modulus, N/mm^2	1.22	1.0	0.84	0.06	0.06
300% modulus, N/mm^2	2.8	1.5	1.0	1.3	1.28
Tensile strength, N/mm^2	11.3	6.6	8.3	4.7	4.3
Elongation at break, %	620	660	780	580	620
Residual elongation, %	32	28	30	24	20
Tear strength, N/mm	29.2	25.6	21.4	20.7	16.1

- The hardness decreases by 9-14 °ShA, from 44 °ShA in the control sample to 30 °ShA in the composite based on natural rubber with functionalized rubber waste in a proportion of 30-50%. The decrease in hardness is due to the increase in plasticizer from the rubber waste functionalization process and its low density. After accelerated aging, the hardness increases due to the loss of plasticizer when the samples are kept at a temperature of 70°C for 168 h.

- Elasticity decreases by 25-38%, but the variations are uneven.

- The modulus, tensile strength and tear strength values decrease as the inactive filler (precipitated chalk) is replaced by the elastomeric waste. When the precipitated chalk is completely replaced with rubber powder, an increase in these characteristics is observed, but without exceeding the values of the control sample.

- Elongation at break shows good values, over 620%.

- Abrasion resistance increases in samples with elastomeric waste.

- The density of the mixtures decreases as the amount of powder increases and the amount of precipitated chalk decreases, because the density of elastomeric waste is lower than that of chalk.

- Repeated flexions - Ross Flex - The footwear standards in force specify values of 100,000 cycles for vulcanized rubber shoe soles when determining repeated flexions. The values presented in Table 5 show that only the composites NC3 and NC4 with rubber waste content of 30% and 50% respectively, do not fall within this value (crack appears after 90,000 cycles, resist up to 109,000 cycles). The others have values over 150,000 cycles, higher than the values imposed by the standard.

- IR spectrum represents the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 µm. IR domain for usual organic chemistry is between 2.5 and 25 µm. The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm^{-1}, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the natural rubber and rubber waste elastomeric spectrum. The FTIR spectra of the analyzed materials are presented in Figure 5. In the spectrum recorded on the unvulcanized natural rubber, the most important bands that allow its qualitative and quantitative identification can be highlighted. The band at 2960.79 and 2851.81 cm^{-1} can be attributed to asymmetric (ν_{as}) and symmetric (ν_{s}) stretching of $-CH_3$ bonds, and the one at 1375.58 cm^{-1} represents the in-plane deformation vibration, namely the shear (δ^{s}) of $-CH_3$ bonds, the band at 841.97cm^{-1} represents the out-of-plane deformation vibration (γ) of -CH-CH bonds originating from cis-1,4 units. The band at 1444.82 cm^{-1} is associated with deformation bonds of CH_2 groups, the band at 1375.58 cm^{-1} comes from the shear vibration of $-CH_3$ bonds and the one at 1663.01 cm^{-1} represents the stretching vibration of C=C bonds [15].

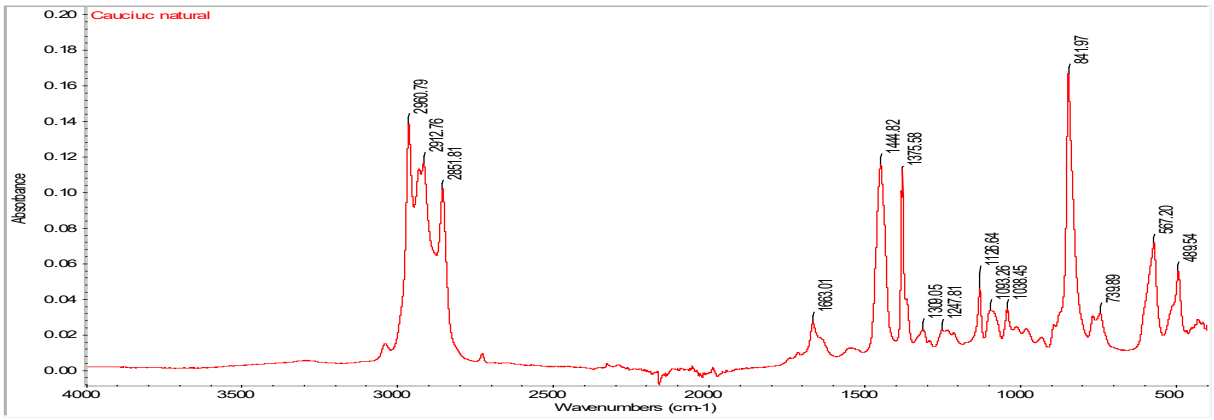


Figure 4. FTIR spectrum of unvulcanized natural rubber

In the case of the elastomeric waste used as filler in the tested composites, both the bands characteristic of SBR rubber and bands originating from other specific processing additives can be identified. Thus, in the spectrum recorded on the unmodified elastomeric waste, the bands characteristic of the functional groups in SBR can be highlighted. Thus, the band at 962.41 cm^{-1} is attributed to 1,4 group from trans-butadiene and the one at 907.46 cm^{-1} is attributed to 1,2 units from butadiene. The bands at 2914.39 and 2847.55 cm^{-1} correspond to CH bond deformations originating from the aromatic styrene ring. In the case of the elastomeric waste modified on the surface with potassium oleate, the appearance of peaks at 1560.84 and at 1413.25 cm^{-1} are characteristic of the mode of asymmetric and symmetric stretching of COO^- bonds. The band at 1463.59 cm^{-1} comes from the CH_2 bond vibration [16]. The band at 719.08 cm^{-1} is due to - $(CH_2)_n$ – bond deformation [17].

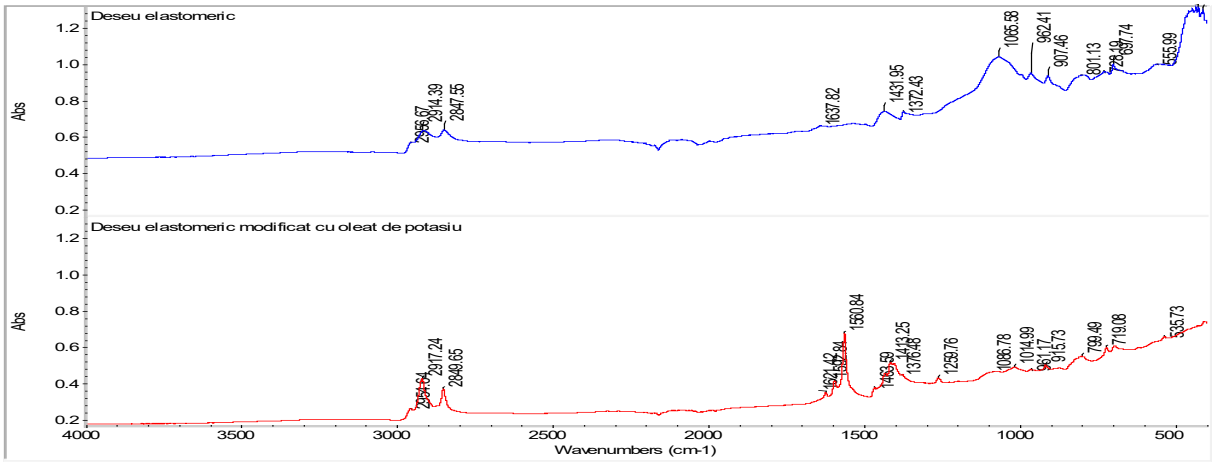


Figure 5. FTIR spectrum of unmodified elastomeric waste and modified with potassium oleate

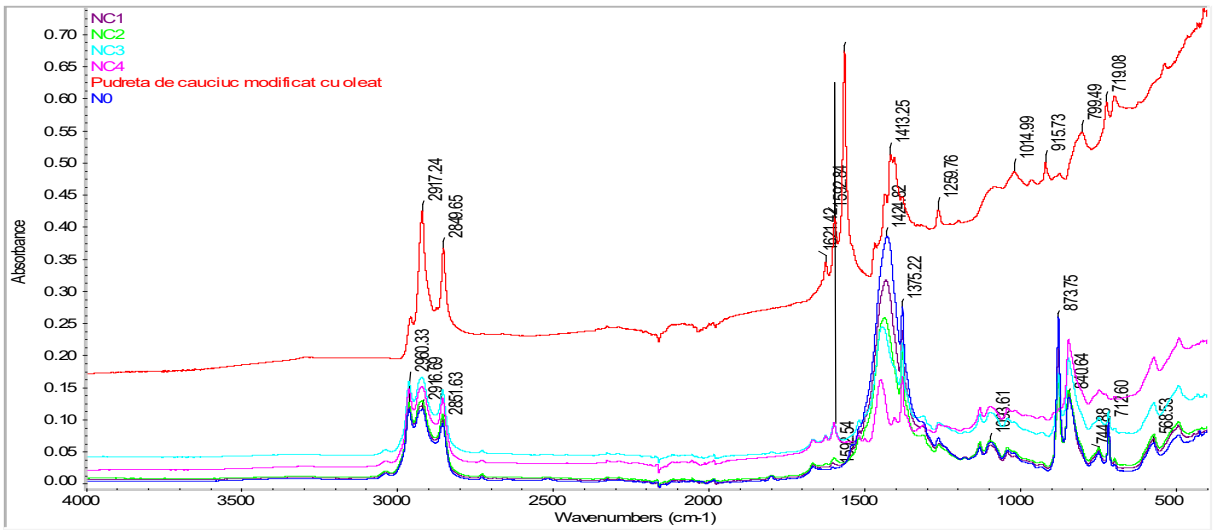


Figure 6. FTIR spectra of mixtures based on natural rubber reinforced with varying percentages of elastomeric waste modified with oleate

In the case of the N0 mixture (control sample without elastomeric waste), besides the bands characteristic of natural rubber, the presence of very intense bands due to the groups originating from calcium carbonate at 1424.82, 873.75 and 712.6 cm^{-1} can be highlighted. The intensity of these bands is directly proportional to the amount of calcium carbonate introduced into the mixtures. Thus, the control mixture N0 contains the highest amount of calcium carbonate, following that in the mixtures NC1-NC3 the amount of carbonate is gradually replaced with the elastomeric waste modified with oleate. Instead, in the case of the NC4 mixture, the calcium carbonate was completely replaced with rubber waste, which led to the disappearance of the bands associated with $CaCO_3$. The characteristic bands of the rubber waste modified with oleate, and especially the band at ~1592 cm^{-1} (due to the vibration of the C=C bonds in the aromatic styrene ring) and 1621 cm^{-1} (the stretching vibration of the C=O bonds in the oleate) can be visualized in all processed mixtures NC1-NC4, their intensity being the greater the greater the amount of rubber waste modified with oleate [18]. In the case of vulcanized mixtures, it can be observed that the band at 1663.01 cm^{-1} associated with the stretching vibration of C=C bonds (clearly detectable in the spectrum obtained on the unvulcanized natural rubber) is consumed during the sulfur vulcanization process, its relative intensity decreasing.

CONCLUSIONS

The recipe based on natural rubber used in the processing of antibiotic bottle stoppers for zootechnical use was modified by replacing the inactive filler (precipitated calcium carbonate) with cryogenically ground post-consumer rubber waste with a particle size of 500nm and functionalized with potassium oleate. These polymer composites were processed on a Brabender mixer and laboratory roller using elastomeric waste with different proportions (10, 20, 30 and 50%). The polymer composite samples with percentages of 10 and 20% post-consumer elastomeric waste presented the best physical-mechanical performances compared to those with higher percentages of elastomeric waste (30 and 50%), characteristics that fall within the specific values for the control sample without waste. Properties such as elongation at break and elasticity showed a slight reduction compared to the control sample – NC0, and the hardness decreased by 9-14 units. The tensile strength of the composition decreased to about half that of NC0. Although the values are lower, the NC1-NC3 composites, with a percentage of 10-30% functionalized elastomeric waste, fall within the standardized physical-mechanical values. The physical-mechanical values obtained after accelerated aging are slightly modified, corresponding to the standardized ones.

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TESTING OF MEDICAL SHEEP FUR WITH ANTIMICROBIAL PROPERTIES – PART 1

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TESTING OF MEDICAL SHEEP FUR WITH ANTIMICROBIAL PROPERTIES – PART 1

ABSTRACT. The medical treatment of patients with rheumatic, joint and muscle diseases can be improved by alternative methods. The essential oils extracted from different plants have certain analgesic, anti-inflammatory, antiseptic, antibacterial, immunostimulating properties, etc. Products have been made based on essential oils with therapeutic properties (mint, cajeput, eucalyptus), which can be used to treat the surface of finished sheep fur for medical purposes. The sheep furs were tanned (without metals) with syntans based on phenolsulfonic acids and aromatic oxysulfones and treated with products based on essential oils with therapeutic properties, to be used to make medical fur articles (lumbar and cervical belts, knee pads, elbow pads, etc.). They can improve rheumatic, muscular and circulatory conditions, complementing the medical treatment of patients suffering from these conditions. The work presents the chemical, physical-mechanical and microbiological characterization of natural furs for medical use.

KEY WORDS: medical fur, essential oils, antimicrobial properties

TESTAREA BLĂNURILOR MEDICALE DE OAIE CU PROPRIETĂȚI ANTIMICROBIENE – PRIMA PARTE

REZUMAT. Tratamentul medical al pacienților cu afecțiuni reumatismale, articulare și musculare poate fi îmbunătățit prin metode alternative. Uleiurile esențiale extrase din diferite plante au anumite proprietăți analgezice, antiinflamatoare, antiseptice, antibacteriene, imunostimulante etc. S-au realizat produse pe bază de uleiuri esențiale cu proprietăți terapeutice (mentă, cajeput, eucalipt), care pot fi utilizate pentru tratarea suprafeței blănurilor de oaie finite în scopuri medicale. Blănurile de oaie au fost tăbăcite (fără metale) cu sintani pe bază de acizi fenolsulfonici și oxisulfone aromatice și tratate cu produse pe bază de uleiuri esențiale cu proprietăți terapeutice, pentru a fi utilizate la realizarea unor articole din blană de uz medical (centuri lombare și cervicale, genunchiere, cotiere etc.). Acestea pot ameliora afecțiunile reumatismale, musculare, circulatorii, completând tratamentul medical al pacienților care suferă de aceste afecțiuni. Lucrarea prezintă caracterizarea chimică, fizico-mecanică și microbiologică a blănurilor naturale de uz medical.

CUVINTE CHEIE: blănuri medicale, uleiuri esențiale, proprietăți antimicrobiene

TEST DES PEAUX DE MOUTON MÉDICALES AUX PROPRIÉTÉS ANTIMICROBIENNES – PREMIÈRE PARTIE

RÉSUMÉ. Le traitement médical des patients atteints de maladies rhumatismales, articulaires et musculaires peut être amélioré par des méthodes alternatives. Les huiles essentielles extraites de différentes plantes possèdent certaines propriétés analgésiques, anti-inflammatoires, antiseptiques, antibactériennes, immunostimulantes, etc. Des produits ont été élaborés à base d'huiles essentielles aux propriétés thérapeutiques (menthe, cajeput, eucalyptus), qui peuvent être utilisées pour traiter la surface de la peau de mouton finie à des fins médicales. Les peaux de moutons ont été tannées (sans métaux) avec des syntans à base d'acides phénolsulfoniques et d'oxysulfones aromatiques et traitées avec des produits à base d'huiles essentielles aux propriétés thérapeutiques, destinés à la confection d'articles médicaux en fourrure (ceintures lombaires et minerves, genouillères, coudières, etc.). Ils peuvent améliorer les affections rhumatismales, musculaires et circulatoires, en complément du traitement médical des patients souffrant de ces affections. L'article présente la caractérisation chimique, physico-mécanique et microbiologique des fourrures naturelles à usage médical.

MOTS CLÉS : fourrures médicales, huiles essentielles, propriétés antimicrobiennes

INTRODUCTION

The essential oils extracted from different plants have certain analgesic, anti-inflammatory, antiseptic, antibacterial, immunostimulating properties, etc. [1-5]. The antioxidant, antimicrobial, antifungal, flavoring properties demonstrated by the many studies conducted in recent years on the composition of essential oils make them important in areas such as the chemical, pharmaceutical, food and perfumery industries and medicine. Essential oils (EOs) are mixtures of aromatic, volatile, lipophilic biomolecules, extracted from regions of plants. They are formed of complex mixtures of hydrophobic molecules, which exhibit a broad spectrum of antimicrobial activity against bacteria, fungi, and viruses [6-11].

The medical treatment of patients with rheumatic, joint and muscle diseases can be improved by alternative methods. Ecological requirements as well as requirements related to fur assortment characteristics have led to the development of new fur processing technologies, such as:

- wet-white tanning of fur to eliminate or reduce the amount of complex salts of trivalent chromium;

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- tanning using chemically modified vegetable tannins or small molecular phenolic and polyphenolic compounds, including those derived from cellulose-making and refining techniques;

- sanitation of natural fur by binding some therapeutic species to the dermis and/or the hair.

In this research study, sheep furs were tanned (without metals) with syntans based on phenolsulfonic acids and aromatic oxysulfones and treated with products based on essential oils with therapeutic properties, to be used to make medical fur articles (lumbar and cervical belts, knee pads, elbow pads, etc.) [12-15]. The antibacterial properties of the sheepskins were subsequently evaluated by standardized methods [16-18]. Products have been made based on essential oils with therapeutic properties (mint, cajeput, eucalyptus), which can be used to treat the surface of finished sheep fur for medical purposes [19]. The medical fur articles can improve rheumatic, muscular and circulatory conditions, complementing the medical treatment of patients suffering from these conditions.

EXPERIMENTAL

Materials

- Sheepskins tanned with syntans based on phenolsulphonic acids and aromatic oxysulfones (I.N.C.D.T.P. – Division: Leather and Footwear Research Institute, Bucharest, Romania) [12, 15];

- Woolen sheepskins (Merinos) treated during fatliquoring operation with products based on essential oils (mint, cajeput, eucalyptus);

- Product P-M based on mint essential oil: dry substance – 20-21%, pH (10% solution) – 4-4.5, density – 0.900-0.920 g/cm^3;

- Product P-C based on cajeput essential oil: dry substance – 19-20%, pH (10% solution) – 4-4.5, density – 0.890-0.900 g/cm^3;

- Product P-E based on eucalyptus essential oil: dry substance – 18-19%, pH (10% solution) – 4-4.5, density – 0.880-0.890 g/cm^3 [19].

Methods

Chemical and Physico-Mechanical Tests

Chemical characteristics of products based on essential oils were determined according to the following standards: dry substance (%) – SR EN ISO 4684:2006; pH – SR-EN ISO 4098: 2006.

Chemical and mechanical characteristics of furs were determined according to the following standards: volatile matter % – SR EN ISO 4684:2012, extractable substances % – SR EN ISO 4048:2002, ash % – SR EN ISO 4047:2002, shrinkage temperatures (°C) – SR EN ISO 3380:2003, the longitudinal and transverse tensile strength – SR EN ISO 3376:2012.

Antibacterial Evaluation

The antibacterial properties of the sheepskins were evaluated by the inhibition zone diameter method according to DIN EN ISO 20645-2005 [16].

Staphylococcus aureus (ATCC 653) and *Escherichia coli* (ATCC 10536) were placed into 5 ml of medium and shaken for 24 h in a constant temperature shaker, then the bacterial solution was diluted to a concentration of 1 × 105 CFU/ml with phosphate-buffered saline (PBS) buffer. Then Luria-Bertani (LB) broth powder (10 g/l peptone, 5 g/l yeast extract powder, 10 g/l sodium chloride) was added to 950 ml distilled water, then adjusted to pH 7.0-7.2 with 0.1 mol/l NaOH solution after entirely dissolving and stirring all contents, and then made up to a volume of 1000 ml with distilled water. Agar powder (1.5 g per 100 ml of the medium) was added to the medium, and then autoclaved for 30 min after heating and dissolving. The medium solution (20 ml) was poured into a culture dish at a temperature of 45°C and UV-sterilized for 30 min to prepare an agar medium plate. The alloy sample was placed in the center of the plate and 500 µl of the bacterial suspension was evenly spread on the surface of the agar medium with a pipette. At least five times duplicates were measured for statistical analysis. The leather

specimens (2 cm diameter) are placed on the surface of the nutrient medium and then incubated at 37°C for 24 h.

Inhibition zones were calculated according to the formula given by [16]:

$$H = \frac{D-d}{2} \quad (1)$$

where H is the inhibition zone in mm, *D* is the total diameter of the specimen and inhibition zone in mm, and *d* is the diameter of the specimen in mm. When H is equal to or larger than 1 mm and there is no growth of bacteria, the antibacterial property is good; when H is equal to 0 mm and there are regions with some bacteria, the antibacterial property is limited; and when H is equal to 0 mm and there are regions with many bacteria, there is no antibacterial property.

Absorption Test

This test method evaluates the antibacterial activity of footwear products treated with antibacterial finish by making use of the method in which the test bacterial suspension is inoculated directly on to samples. In this study, we measured antibacterial properties of the prepared samples with the ISO 16187 Absorption test [17]. We placed the target sample (50 mm × 50 mm × 1 mm) on the Petri dish, added 0.4 mL of bacterial solution containing the target bacterial species (*S. aureus*, *E. coli*), and attached the film from the top. After a cultivation of 24 h at 35°C, we washed out the bacteria in a dedicated medium (SCDLP) and counted the number of colonies [18].

The antibacterial effect of the sample was determined by using the antibacterial activity value.

Calculation of Antibacterial Activity Ratio

The bacteriostatic activity ratio was obtained according to the following formula:

$$R = \frac{C_t - T_t}{C_t} X100\% \quad (2)$$

R is the antibacterial activity ratio;

C_t is the average number of colonies of two control samples after 24 h or the specified incubation period, expressed as CFU/ml;

T_t is the average number of colonies of two test samples after 24 h or the specified incubation period, expressed as CFU/ml.

Obtaining Ecologic Medical Sheepskins

Ecologic medical sheepskins were obtained using the products based on sulphated fatty alcohols, oils based on sulphated and sulphonated natural and synthetic fatty substances and syntans based on phenol sulphonic acids and aromatic oxysulphones [12]. Sheep fur was tanned (non-metallic tanning) and was treated with the product based on essential oils with therapeutic properties (mint, cajeput, eucalyptus).

Woolen sheep skins (Merinos) were treated during fatliquoring operation with 20-30g products based on essential oils (mint – P-M, or cajeput – P-C, or eucalyptus – P-E) /1000g fur tanned weight:

- P-M-1 – Sheep fur treated with 20g product P-M/1000g fur tanned weight;
- P-M-2 – Sheep fur treated with 30g product P-M/1000g fur tanned weight;
- P-C-1 – Sheep fur treated with 20g product P-C/1000g fur tanned weight;
- P-C-2 – Sheep fur treated with 30g product P-C/1000g fur tanned weight;
- P-E-1 – Sheep fur treated with 20g product P-E/1000g fur tanned weight;
- P-E-2 – Sheep fur treated with 30g product P-E/1000g fur tanned weight.

The products based on essential oils contain 55-60% essential oil (mint – P-M, or cajeput – P-C, or eucalyptus – P-E), 10-15% ethyl alcohol, 8-10% lauric alcohol ethoxylate with seven moles of ethylene oxide, 8-10% polyethylene glycol 400 (non-ionogenic) and deionized water [19].

RESULTS AND DISCUSSIONS

Characterization of Furs by Physical-Chemical and Physical-Mechanical Analyses

The values of the physical-chemical characteristics of the medical furs are comparable to the values set by the standards for sheep furskins intended for clothing (volatile dermal matter 10.40-12.70% and volatile wool matter 9.60-12.30%, extractable dermal substances 9.20-12.20% and wool extracts 0.50-0.80%, ash 3.20-3.80%, pH of aqueous extract, 4-4.5.

Values of shrinkage temperatures for medical sheep furskins are lower (75°C) than those of sheep furs processed with basic chromium salts (approx. 80°C).

The longitudinal tensile strength tests resulted in a value of 210-280 N, compared to the standard for the sheep furskins tanned with chromium salts for clothing, which are of min. 110 N, and the transverse tensile strength values are 180-220 N, compared to the values given in the standard for sheep furskins tanned with chromium salts for clothing, which are of min. 80 N.

Antibacterial Activity

The natural furs for medical use were tested for microbial activity against two bacteria strains, including *Escherichia coli* and *Staphylococcus aureus* according to SR EN ISO 20645/2005—Control of the antibacterial activity. The evaluation of the samples is based on the absence or presence of bacterial multiplication in the contact area between the inoculum and the sample and on the appearance of a possible inhibition zone around the samples (Figure 1).

Images of Petri plates after 24h incubation are shown in Figure 1 and assessment of antibacterial activity is shown in Table 1.

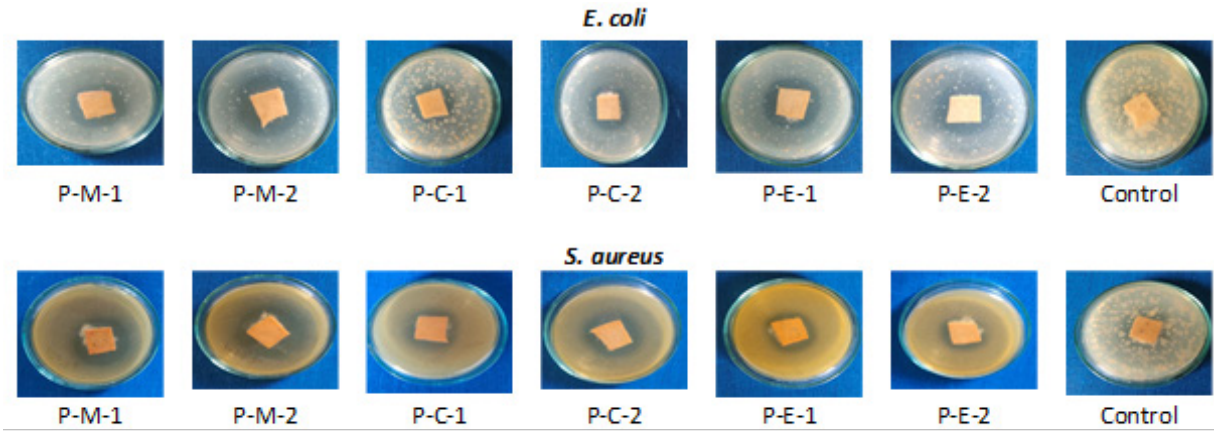

Figure 1. Images of Petri plates showing antibacterial effect after 24 h of incubation

The results summarized in Table 1 revealed that all samples treated with essential oil products presented microbiological activity and do not allow the development of aerobic germs for any of the bacteria tested.

Table 1: Evaluation of the antibacterial activity

	E. coli		*S. aureus*	
Code	Inhibition zone (mm)	Evaluation	Inhibition zone (mm)	Evaluation
P-M-1	+++++	Total inhibition zone	+++++	Total inhibition zone
P-M-2	+++++	Total inhibition zone	+++++	Total inhibition zone
P-C-1	+++++	Total inhibition zone	+++++	Total inhibition zone
P-C-2	+++++	Total inhibition zone	+++++	Total inhibition zone
P-E-1	+++++	Total inhibition zone	+++++	Total inhibition zone
P-E-2	+++++	Total inhibition zone	+++++	Total inhibition zone
Control	-	Unsatisfactory effect	-	Unsatisfactory effect

An insufficient effect was obtained for the control sample which did not present antimicrobial activity against the bacterial strains. The inhibition areas produced by all the formulations loaded with products based on essential oils showed diameters ranging between 5 and 11 mm when tested against *Staphylococcus aureus* and 2 and 6 mm against *Escherichia coli* after 24 h of incubation.

Absorption Test

Antibacterial performance of the functionalised natural furs for medical use was assessed quantitatively using a test method as described in the Absorption test [17]. Growth reduction rate R (%) was calculated and summarised in Tables 2 and 3. The formula describes the difference in the number of viable bacteria on the test samples compared to the control samples after incubation. The number of viable bacteria post incubation on the control samples should increase compared to time zero. If the test samples have antibacterial activity, the number of viable bacteria attached on the surface after incubation should be fewer than the number on the control.

Table 2: Growth reduction rate (R %) of the natural fur samples after 24 h contact time for *Staphylococcus aureus* ATCC 6538

Sample	Result	R%	Log_{10} red.
Inoculum concentration	T_0=1x10^{5}CFU/mL		
P-M-1	T_0=1x10^{5}CFU/mL T_{24}=10 UFC/mL	99.99%	4.00
P-M-2	T_0=1x10^{5}CFU/mL T_{24}=7 UFC/mL	99.99%	4.15
P-C-1	T_0=1x10^{5}CFU/mL T_{24}=0 UFC/mL	100%	5.00
P-C-2	T_0=1x10^{5}CFU/mL T_{24}=0 UFC/mL	100%	5.00
P-E-1	T_0=1x10^{5}CFU/mL T_{24}=0 UFC/mL	100%	5.00
P-E-2	T_0=1x10^{5}CFU/mL T_{24}=0UFC/mL	100%	5.00
Control	T_0=1x10^{5}CFU/mL T_{24}=4.5x10^{4}UFC/mL	55.00%	0.35

Table 3: Growth reduction rate (R %) of the natural fur samples after 24 h contact time for *Escherichia coli* ATCC 10536

Sample	Result	R%	Log_{10} red.
Inoculum concentration	T_0=1x10^{5}CFU/mL		
P-M-1	T_0=1x10^{5}CFU/mL T_{24}=6 UFC/mL	99.99%	4.22
P-M-2	T_0=1x10^{5}CFU/mL T_{24}=3 UFC/mL	100%	4.52
P-C-1	T_0=1x10^{5}CFU/mL T_{24}=0 UFC/mL	100%	5.00
P-C-2	T_0=1x10^{5}CFU/mL T_{24}=0 UFC/mL	100%	5.00
P-E-1	T_0=1x10^{5}CFU/mL T_{24}=0 UFC/mL	100%	5.00
P-E-2	T_0=1x10^{5}CFU/mL T_{24}=2UFC/mL	100%	4.70
Control	T_0=1x10^{5}CFU/mL T_{24}=5.5x10^{4}UFC/mL	45.00%	0.26

The results of antimicrobial tests against gram-negative, gram-positive are presented in Tables 2 and 3 and showed efficiency above 99-100% in all cases. As can be seen, natural furs without the addition of essential oils showed low antibacterial activities against the two bacterial species tested, with "R" values of 55.00 and 45.00 for *S. aureus* and *E. coli*, respectively.

Characterisation of Obtained Fur Assortments for Medical Use

The prepared products with therapeutic properties (analgesic, anti-inflammatory and relaxing) can be used for treatment of medical furs. Menthol, the ingredient in the composition of peppermint oil, stimulates receptors signalling the cold sensation and inhibits receptors reacting to pain stimuli, temporarily relieving muscle pain. Eucalyptol, the ingredient in the composition of cajeput and eucalyptus oils, with analgesic and disinfectant properties, is effective in the treatment of patients suffering from rheumatism, lumbar radiculopathy and cervical spondylosis, stimulating blood circulation and relieving rheumatic and joint pain.

Mint oil contains 40.04% menthol, 23.78% l-menthone, 14.51% i-menthone, 4.24% menthyl acetate etc. Cajeput oil contains 57.02% eucalyptol, 2.93% alpha-linalool, 2.93% alpha-linalool, 2.77% caryophyllene etc. Eucalyptus oil contains 73.23% eucalyptol, 14.99% d-limonene, 4.10% o-cymene, 2.82% gamma-terpinene etc [13, 14].

The results of the antimicrobial tests highlighted a strong antibacterial character of the sheep fur samples tested, having a "satisfying effect", because no bacterial multiplication was observed [16]. Sheep fur samples, treated with materials based on essential oils (mint, cajeput, eucalyptus) do not allow the development of aerobic germs for the tested bacteria, namely, *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). Untreated control materials have not shown microbial reduction.

The product based on essential oils can be used to treat the sheep furskins (free of

metals) for medical purposes and improve the quality of natural fur and fur articles (lumbar and cervical belts, knee pads, elbow pads etc.) used to prevent, relieve and treat rheumatic, muscular, circulatory disorders, complementing the medical treatment of patients suffering from these conditions, keeping the fur-covered area warm. Treatment with these products can be repeated at certain time intervals, on the fur surface or fur articles.

CONCLUSIONS

▪ Sheepskins were tanned with syntans based on phenolsulphonic acids and aromatic oxysulfones.

▪ The products based on essential oils (mint, cajeput, eucalyptus) with therapeutic properties (analgesic, anti-inflammatory and relaxing) can be used for treatment of medical furs.

▪ The results of the antimicrobial tests highlighted a strong antibacterial character of the sheep fur samples tested, having a "satisfying effect", because no bacterial multiplication was observed.

▪ Sheep fur samples, treated with materials based on essential oils (mint, cajeput, eucalyptus) do not allow the development of aerobic germs for the tested bacteria, namely, *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*).

▪ The product based on essential oils can be used to treat the sheep furskins (free of metals) for medical purposes and improve the quality of natural fur and fur articles (lumbar and cervical belts, knee pads, elbow pads etc.) used to prevent, relieve and treat rheumatic, muscular, circulatory disorders, complementing the medical treatment of patients suffering from these conditions, keeping the fur-covered area warm.

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PREPARATION OF ELASTIN MEMBRANES BASED ON SURFACTANTS AND SEPARATION MECHANISM

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PREPARATION OF ELASTIN MEMBRANES BASED ON SURFACTANTS AND SEPARATION MECHANISM

ABSTRACT. The influence of a classical surfactant – palmitoyl-glycylglycine and bola amphiphilic – demecarium bromide upon the elastin membrane preparation and separation mechanism of turmeric from aqueous solutions was studied by: UV-VIS spectroscopy, scanning electron microscopy, dynamic light scattering and separation rates. The tensile strength and hydrophobic property were improved by introducing a surfactant (classic or bola). In this research the influence of surfactants upon the microporous structure and retention of turmeric from aqueous solutions was studied. The biomembranes were produced by a casting-solvent evaporation technique. The elastin powder was dissolved in a water-acetic acid (70:30 v/v) solution with and without plasticizer: glycerol and surfactant (classic or bola), constant continuous stirring for 5-7 hrs. at 60°C, then degassed the solution for 2 hrs. The solution was poured and afterwards maintained in the oven at 45-55°C for 5-8 hrs. Ecological biomembranes are obtained from a biodegradable biopolymer – elastin, and can be used successfully in removing turmeric from wastewaters.

KEY WORDS: elastin biomembranes, surfactants (classical and bolaform), separation mechanisms of turmeric from aqueous solutions

PREPARAREA MEMBRANELOR DIN ELASTINĂ PE BAZĂ DE SURFACTANȚI ȘI UN MECANISM DE SEPARARE

REZUMAT. Influența unui surfactant clasic – palmitoil glicilglicină și a unei bolaamfifile – bromură de demecariu asupra preparării membranei din elastină și a mecanismului de separare a curcumei din soluții apoase a fost studiată prin: spectroscopie UV-VIS, microscopie electronică de scanare, împrăștierea dinamică a luminii și ratele de separare. Rezistența la tracțiune și capacitatea hidrofobă au fost îmbunătățite prin introducerea unui surfactant (clasic sau bola). În această cercetare a fost studiată influența surfactanților asupra structurii microporoase și a gradului de retenție a curcumei din soluții apoase. Biomembranele au fost produse printr-o tehnică de turnare-evaporare a solventului. Pulberea de elastină a fost dizolvată într-o soluție de apă-acid acetic (70:30 v/v) cu și fără plastifiant: glicerol și surfactant (clasic sau bola), agitare continuă constantă timp de 5-7 ore, la 60°C, apoi s-a degazat soluția timp de 2 ore. Soluția a fost turnată și apoi menținută în etuvă la 45-55°C timp de 5-8 ore. Biomembranele ecologice sunt obținute dintr-un biopolimer biodegradabil – elastină și pot fi utilizate cu succes la îndepărtarea curcumei din apele uzate.

CUVINTE CHEIE: biomembrane din elastină, agenți tensioactivi (clasici și bola), mecanisme de separare a curcumei din soluții apoase

PRÉPARATION DE MEMBRANES D'ÉLASTINE À BASE DE TENSIOACTIFS ET MÉCANISME DE SÉPARATION

RÉSUMÉ. L'influence d'un surfactant classique – palmitoyl-glycylglycine et une bola amphiphile – bromure de démécarium sur la préparation de la membrane d'élastine et le mécanisme de séparation du curcuma des solutions aqueuses a été étudiée par : spectroscopie UV-VIS, microscopie électronique à balayage, diffusion dynamique de la lumière et taux de séparation. La résistance à la traction et la propriété hydrophobe ont été améliorées par l'introduction d'un tensioactif (classique ou bola). Dans cette recherche, l'influence des tensioactifs sur la structure microporeuse et la rétention du curcuma des solutions aqueuses a été étudiée. Les biomembranes ont été produites par une technique de coulée/évaporation du solvant. La poudre d'élastine a été dissoute dans une solution eau-acide acétique (70 : 30 v/v) avec et sans plastifiant : glycérol et tensioactif (classique ou bola), agitation continue constante pendant 5-7 h. à 60°C, puis la solution a été dégazée pendant 2h. La solution a été versée et ensuite maintenue dans le four à 45-55°C pendant 5-8 heures. Les biomembranes écologiques sont obtenues à partir d'un biopolymère biodégradable – l'élastine et peuvent être utilisées avec succès pour éliminer le curcuma des eaux usées.

MOTS CLÉS : biomembranes d'élastine, tensioactifs (classiques et bolaformes), mécanismes de séparation du curcuma des solutions aqueuses

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INTRODUCTION

Sustainable biopolymers are favorable resources for improving innovative biomaterials with vast potential in various fields of application. Elastin is a protein such as collagen, keratin, etc [1-5]. Hydrolyzed elastin powder is extracted from pork tendons by biotechnology and is amphipathic, hydrophilic and lipophilic, which makes it compatible with most of the ingredients. It is a fiber protein made up of polypeptide subunits and one of the most important structural proteins in the human body.

Like other biopolymers, elastin is composed of simple amino acids, especially: leucine, glycine and proline.

The elastin powder was dissolved in a water-acetic acid (70:30 v/v) solution with and without plasticizer: glycerol and surfactant, constant continuous stirring for 5-7 hrs. at 60°C, then degassed the solution for 2 hrs. The solution was poured and afterwards maintained in the oven at 45-55°C for 5-8 hrs, Figure 1.

These conditions allow the elastin molecules from solution to be structured and to form intermolecular bonds without any cross-linking agent.

EXPERIMENTAL

Materials and Methods

In order to obtain elastin membranes, the following materials have been used: elastin and turmeric powder, palmitoyl-glycylglycine and acetic acid from Sigma-Aldrich; demecarium bromide and glycerol from SERVA Feinbiochemica GmbH & Co.

A new procedure was proposed in this research, for obtaining elastin membranes based on tensides, by a casting-solvent evaporation technology and is presented in Figure 1.

In this research elastin membranes are obtained by a uniform casting of the solution with: elastin powder/water-acetic acid/glycerol/ surfactant (classical or bolaform) on a glass plate. Elastin membranes were prepared using or not a plasticizer-glycerol and surfactant such as palmitoyl-glycylglycine or demecarium bromide.

The surfactants are involved in the membrane processes, influencing flow through polymeric porous media, cleaning of membranes during the process and after use or modifying the microstructure of the disperse system for separation. The influence of surfactants on the microporous structure and the mechanism retention of turmeric from aqueous solutions were studied.

The surfactant-turmeric mixed aqueous solutions were obtained by varying the turmeric and surfactant concentration and characterized by: UV-VIS spectroscopy, dynamic light scattering, and scanning electron microscopy.

The following equipment was used in this research:

- a “SEM QUANTA 200” equipment from FEI company, with EDAX coupled. The samples for SEM investigations were prepared by slow evaporation in clean atmosphere at room temperature;
- a Zetasizer-nano “MALVERN” equipment, with measuring range between 0.3 nm-60.0 microns and zeta potential determination with an accuracy of +/-2%;
- an UV-VIS spectrophotometer JASCO (model 918).

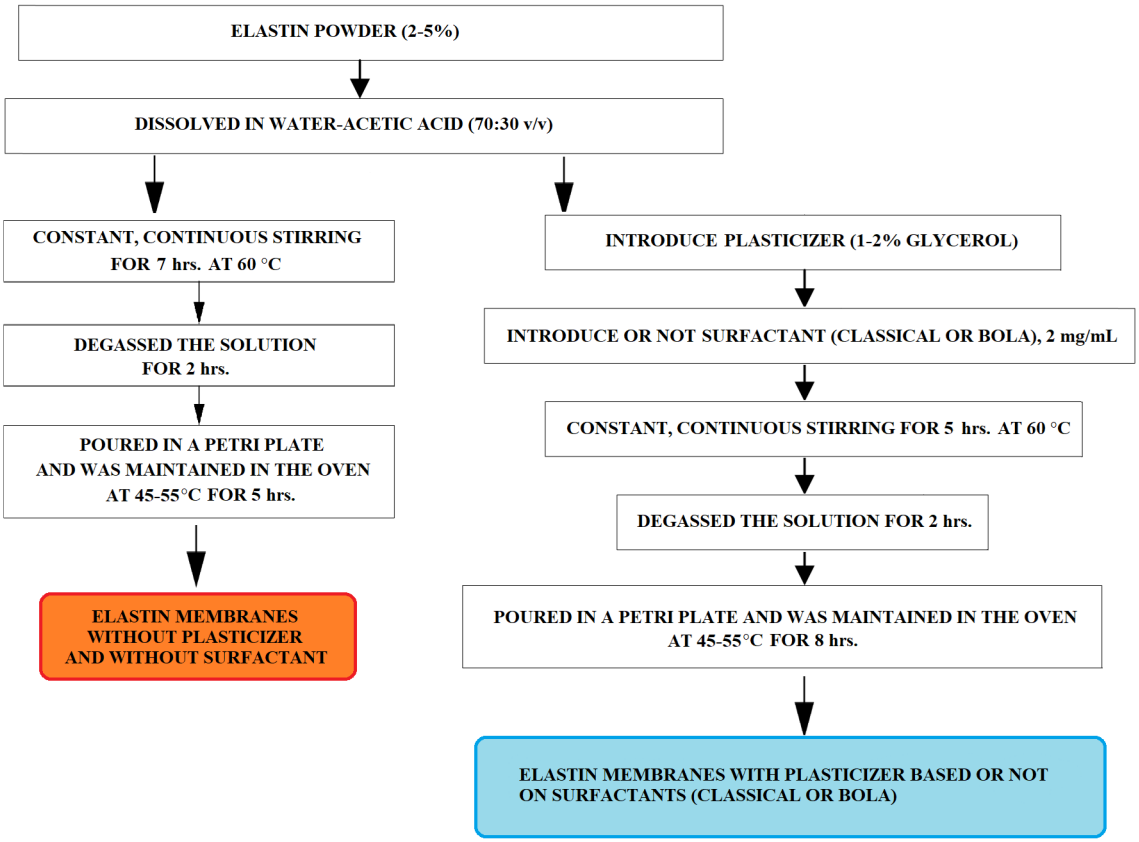
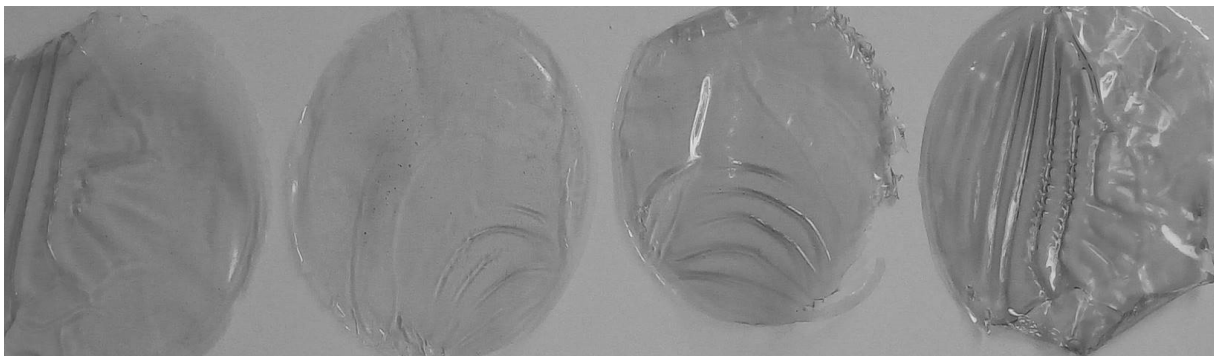


Figure 1. Technological flow for obtaining elastin membranes with and without plasticizer – glycerol-based or not for surfactants (classic or bola)

RESULTS AND DISCUSSIONS

Obtaining Biomembranes Based on Surfactants (Classic or Bola)

The images of elastin biomembranes obtained were shown in Figure 2.



a) b) c) d)

Figure 2. Images of: a) elastin membrane without plasticizer and surfactant; b) elastin membrane with plasticizer, c) elastin membrane with plasticizer and bola surfactant, d) elastin membrane with plasticizer and classic surfactant

This research focused on studying the separation mechanism of turmeric from aqueous solutions through the elastin membranes obtained based on surfactants (or not).

Characterization of Elastin Biomembranes Based or Not on Surfactants (Classic or Bola)

SEM images of the surface elastin membranes based on surfactants after retention of turmeric from aqueous solutions give information on the surface morphology of the membranes.

The surface of the elastin membranes based on surfactants consists of pores of varying sizes, as compared to classical membranes with uniform distribution of pores. Cross-sections of the membranes were prepared to assess the internal structure. Cross-sections were cut using a scalpel and fractured.

The compression of the structure is visible in Figure 3. Elastin membranes based on surfactants consist of a finger-like microsubstructure (Fig. 3. c, d).

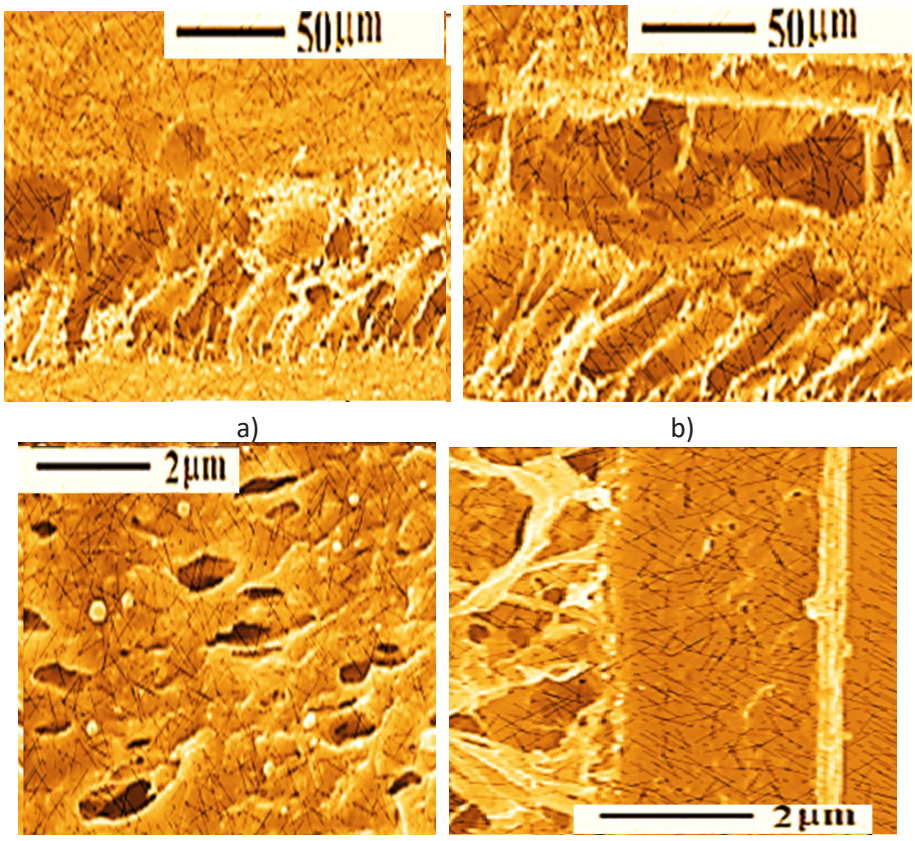


Figure 3. SEM images of cross-sections for elastin membranes after retention of turmeric from aqueous solutions for: a) elastin membrane without plasticizer and surfactant; b) elastin membrane with plasticizer; c) elastin membrane with plasticizer and bola surfactant; d) elastin membrane with plasticizer and classic surfactant

SEM image for turmeric from aqueous solution, retained on the elastin membrane with plasticizer and bola surfactant is shown in Figure 4.

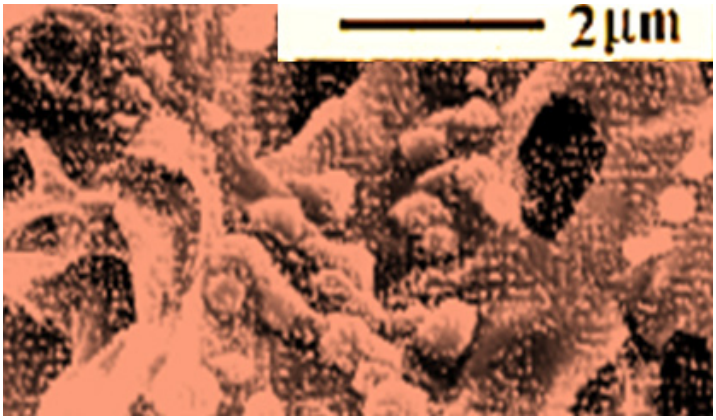


Figure 4. SEM image for turmeric from aqueous solution, retained on the elastin membrane with plasticizer and bola surfactant

The influence of surfactants upon the microporous structure and retention of turmeric from aqueous solutions from different concentrations was presented in Figure 5.

By UV-VIS spectroscopy at λ=420 nm, characteristic for fingerprint spectrum of turmeric in water, the dependence of the normalized flux - J/J_0 and retention - R of turmeric vs. concentration was determined.

The retention and normalized flux for turmeric solutions through membranes were calculated for elastin membrane with plasticizer and surfactants (classical or bola).

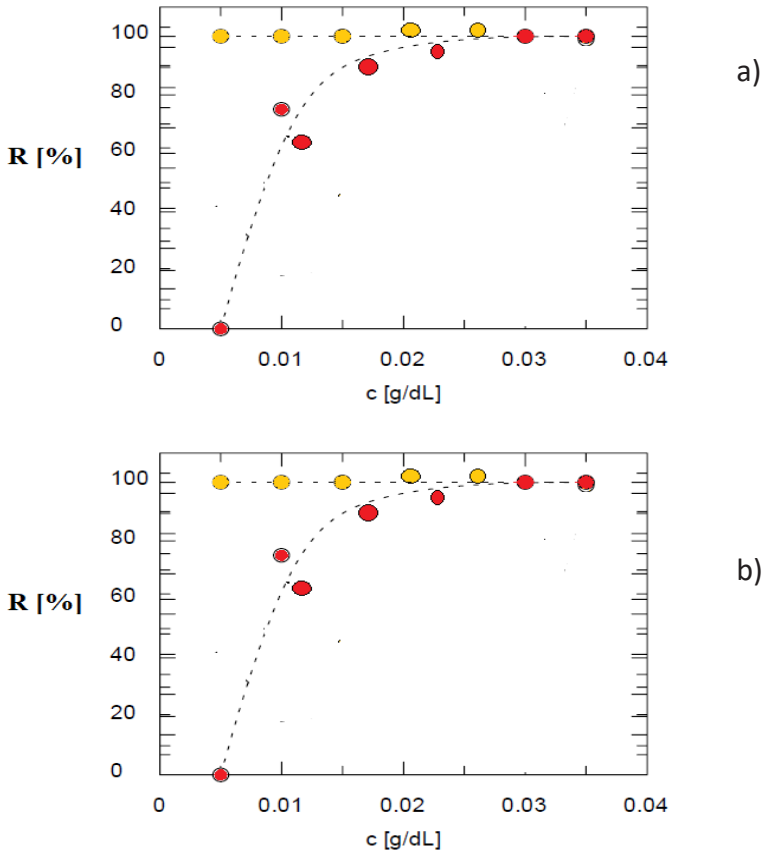


Figure 5. Dependence of retention (R ·····): a) of the normalized flux (J/J_0 —) b) of turmeric in water vs. concentration for: o – elastin membrane with plasticizer and bola surfactant and o – elastin membrane with plasticizer and classical surfactant

From Fig. 5 we observed for both membranes with surfactant the retention of turmeric of 100%. For elastin membrane with plasticizer and bola surfactant, we have a gradual increase and then a level of retention for turmeric and for the membrane with classical tenside is only a uniform retention around the value 100%.

The turmeric in aqueous solutions for different concentrations was characterized by dynamic light scattering. Dynamic light scattering test showed the 2 types of associates: nano and micro level The size, percentage of the particles, and Zeta potential were determined (indicating their stability).

The particles of turmeric in aqueous solutions for different concentrations, have sizes ranging between 50-80 nm and also aggregate at 2 µm-50 µm.

CONCLUSIONS

The conducted research has led to the following results:

- SEM microscopy examination showed unusual flat sheet elastin membranes based on surfactants (classical or bola).
- The presence of surfactants in the composition of the membranes formed was emphasized in order to maintain the ecology and membrane performances. Surfactants in the casting solution alter the size, as well as the density of pores and the roughness of the elastin membranes surface. The surfactants analyzed, yield membranes with small and dense pores and with smooth surface. Also, elastin membranes-based surfactants influenced the separation rates of the turmeric in aqueous solutions with different concentrations.
- Ecological membranes are obtained from a biodegradable biopolymer and can be successfully used in turmeric separation from water. The current European Community strategy related to the maintenance of the health of population, quality of life, and of the environment encourages the separation of organic pollutants through membranes.

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BIODEGRADABLE POLYMERIC COMPOSITES BASED ON NATURAL RUBBER AND FUNCTIONALIZED POST-CONSUMER LEATHER WASTE

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BIODEGRADABLE POLYMERIC COMPOSITES BASED ON NATURAL RUBBER AND FUNCTIONALIZED POST-CONSUMER LEATHER WASTE

ABSTRACT. This work presents the development and characterization of biodegradable polymeric composites based on natural rubber and protein waste from finished post-consumer leather. Protein waste is cryogenically ground to min. 500 nm, functionalized by a mechanical process at temperature with potassium oleate (5%) and mixed in the composite in various proportions (5, 10, 20, 30, 50%). This composite will be made into a low-density product, with low cost, recovery and reuse of waste, and last but not least, biodegradable. The methodology for making the new materials involves the following steps: sorting waste, grinding, functionalization and compounding. These operations are easy to manage and do not involve new equipment. Compounding, the most important operation, will be carried out on a roller and the mixtures will be processed into finished products by compression in an electric press. The tested biodegradable composites were structurally and physico-mechanically characterized. Waste transformation (ground and functionalized) into new value-added products will lead to remarkable improvements in the life cycle of raw materials and the sustainable use of this waste, contributing to sustainability, improving eco-efficiency and economic efficiency and reducing the "pressure" of waste on the environment.

KEY WORDS: protein waste, polymer composite, biodegradability

COMPOZITE POLIMERICE BIODEGRADABILE PE BAZĂ DE CAUCIUC NATURAL ȘI DEȘEURI DE PIELE POST-CONSUM FUNCȚIONALIZATE

REZUMAT. Această lucrare prezintă realizarea și caracterizarea unor compozite polimerice biodegradabile pe bază de cauciuc natural și deșeuri proteice de piele finită post-consum. Deșeurile proteice sunt măcinate criogenic la dimensiuni de min. 500 nm, funcționalitate prin procedeu mecanic la temperatură cu oleat de potasiu (5%) și amestecate în compozit în proporții variate (5, 10, 20, 30, 50%). Acest compozit va fi transformat într-un produs cu densitate scăzută, cu costuri reduse, valorificând și reutilizând deșeurile și, nu în ultimul rând, biodegradabil. Metodologia de realizare a noilor materiale implică următoarele etape: sortarea deșeurilor, măcinarea, funcționalizarea și amestecarea. Aceste operațiuni sunt ușor de gestionat și nu implică echipamente noi. Compoundarea, cea mai importantă operațiune, va fi realizată pe un valț și amestecurile vor fi procesate în produse finite prin compresie într-o presă electrică. Compozitele biodegradabile experimentate au fost caracterizate structural şi fizico-mecanic. Transformarea deșeurilor (măcinate și funcționalizate) în noi produse cu valoare adăugată va duce la îmbunătățiri remarcabile ale ciclului de viață al materiilor prime și la utilizarea durabilă a acestor deșeuri, contribuind la sustenabilitate, îmbunătățirea eco-eficienței și a eficienței economice, precum și la reducerea „presiunii" deșeurilor asupra mediului.

CUVINTE CHEIE: deșeu proteic, compozit polimeric, biodegradabilitate

COMPOSITES POLYMÈRES BIODÉGRADABLES À BASE DE CAOUTCHOUC NATUREL ET DE DÉCHETS DE CUIR POST-CONSOMMATION FONCTIONNALISÉS

RÉSUMÉ. Cet article présente la réalisation et la caractérisation de composites polymères biodégradables à base de caoutchouc naturel et de déchets protéiques provenant de cuirs finis post-consommation. Les déchets protéiques sont cryogéniquement broyés à min. 500 nm, fonctionnalisés par un procédé mécanique à température avec de l'oléate de potassium (5%) et mélangé au composite en différentes proportions (5, 10, 20, 30, 50%). Ce composite sera transformé en un produit à faible densité, à faible coût, en récupérant et en réutilisant des déchets, et enfin et surtout, biodégradable. La méthodologie de fabrication des nouveaux matériaux comprend les étapes suivantes : tri des déchets, broyage, fonctionnalisation et compoundage. Ces opérations sont faciles à gérer et n'impliquent pas de nouveaux équipements. Le compoundage, opération la plus importante, sera réalisé sur rouleau et les mélanges seront transformés en produits finis par compression dans une presse électrique. Les composites biodégradables testés ont été caractérisés structurellement et physico-mécaniquement. La transformation des déchets (broyés et fonctionnalisés) en nouveaux produits à valeur ajoutée conduira à des améliorations remarquables du cycle de vie des matières premières et à l'utilisation durable de ces déchets, contribuant à la durabilité, améliorant l'éco-efficacité et l'efficacité économique et réduisant la « pression » des déchets sur l'environnement.

MOTS CLÉS : déchets protéiques, composite polymère, biodégradabilité

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INTRODUCTION

The problem of waste polluting the environment has been addressed over the years through several methods: depollution (deposition on the ground, burial, composting, burning), recovery through reuse and/or energetic recycling (incineration) and/or mechanical and/or chemical recycling (pyrolysis, gasification, hydrolysis, etc.). In the integrated concept of waste management of natural fibers, vulcanized rubber and plastic materials, along with these methods, there is also the possibility of reducing quantities through the use of biodegradable polymer materials. If the re-introduction of these materials into the productive circuit is carried out without taking into account the influences of the content of non-polymeric impurities and those resulting from specific destruction processes, then the materials resulting from simple mechanical recycling have the mechanical properties that are all the lower the more the content of non-polymeric impurities is higher. For this reason, these polymers can be used for peripheral, low-performance applications [1-2]. It has been demonstrated that the residual properties can be brought to useful values by modification with a primary polymer and necessarily by subsequent homogenization from the melt, i.e., by mechanical recycling.

Composites represent a versatile and very valuable family of materials, which can solve a number of existing problems in various applications/industries, because they provide materials with new properties. Recycling and the use of renewable natural resources offer a new dimension in the discovery of new materials. Recently, special attention has been paid to the development of composites with polymer matrix reinforced with natural fibers instead of conventional composites reinforced with inorganic fibers (glass, carbon, etc.). The development of environmentally friendly "green" materials is due to the biodegradability of these natural materials (from various sources), low weight, low cost, high availability, high specific resistance compared to glass or carbon fibers, as well as due to the possibility of adapting existing equipment to processors from the field, to mass production [2-4]. Composites reinforced with natural fibers are used in a variety of structural applications such as aerospace, automotive components/parts, sports or recreational equipment, boats and office products, equipment, etc. The most common types of waste from renewable resources used for reinforcing polymer matrices are natural fibers from plants or ligno-cellulosic (flax, hemp, cotton), natural fibers from animals (leather fibers, wool, etc.), wood fibers – wood flour, sawdust (having as the majority component cellulose and lignocellulose, etc.) [5-7]. Leather is a natural polymer, derived from amino acid monomers, with the original fibrous structure more or less intact, tanned or treated to limit putrefaction. Leather is made up of millions of short fibers, having an average length, treated with numerous chemicals during the tanning process. It is known that the leather industry is one of the most polluting sectors on the environment, because it generates both organic and inorganic pollutants, which strongly affect the surroundings and the "bionetwork". The environment is under continuous pressure due to the solid and liquid waste that is generated by this industry. The footwear sector "consumes" most (60%) of the amount of leather produced worldwide. Logically, this industry also produces the largest amount of finished leather waste (~ 60% w). Tanned leather waste contains chromium (III) as a result of the tanning process. Chromium can exist in different oxidation states and its compounds behave differently. Chromium (VI) compounds are extremely toxic and are classified as MAK III A 2 carcinogens. Neutralization of hide waste particles (blocking the transformation of trivalent beneficial Cr into hexavalent harmful element) can be done by treatment with ammonia solution and formic acid [8]. Therefore, chromium-containing leather waste is considered toxic to

the environment and humans, and this has been an important environmental problem for the footwear industry in recent decades. Although in the past, a number of other procedures for using these wastes have been developed, only a few of them are applied in practice due to low financial viability [9-11]. Today, protein powder is either incinerated or bio-gasified [12]. The cost of incineration has increased in recent years by 300-400%. Eco-technologies are a result of multi-disciplinary and integrated research with huge potential for improving competitiveness and sustainable development in a wide range of industrial sectors. The benefits of using leather waste to obtain bio-composites with applications in construction are the following:

- Leather waste is a source of renewable natural materials;
- They are easy to recycle, eco-friendly;
- Leather fibers are self-extinguishing, do not sustain combustion and burn at high temperatures;
- in a relaxed state, they do not change their volume and do not lose their elasticity;
- they are very hygroscopic, up to 35% [8, 13].

Currently, there are several conventional methods for the management of solid waste generated from the leather processing industry, which include codification, thermal incineration and anaerobic digestion. These methods of elimination / treatment generally have several deficiencies, such as environmental pollution mainly due to being thrown in the landfill, risks to the health of people who handle this waste due to unhygienic conditions, as well as the possibility of conversion / transformation of trivalent chromium (non-toxic) to hexavalent chromium (toxic) during incineration. Trivalent chromium in the environment will have its own toxic effects when it comes into contact with living organisms [14]. Environmental pollution is a common problem in the vast majority of countries in the world, and unfortunately in some countries, this problem of solid waste is neglected, and thrown without any restriction into rivers, in open places, etc. Incineration of solid waste is one of the most welcome methods in many fields. There is no sorting of solid waste based on their properties and mixed solid waste is dumped in landfills, which confirms a negligible attention to waste at the moment. In the leather goods industry and the footwear manufacturing industry, enormous amounts of leather are thrown away as waste, and it is essential to pay more attention to this waste, because it currently represents a resource not fully exploited. The nature of the tanning industry and the negative effect of the waste, as well as the minimal attention paid to the practice of using and/or disposing of waste at this time require advanced scientific research [15]. In this regard, experiments regarding composites based on natural rubber with vulcanized rubber waste [16] and wood waste were conducted.

The aim of this paper is to study the properties of natural rubber reinforced composites with differential leather waste contents (10, 20, 30 and 50 wt%). Tensile strength, tear strength, elasticity, hardness, elongation of break, attrition and morphological study (FT-IR) of natural rubber/leather waste composites were examined.

EXPERIMENTAL

Materials and Methods

Materials

Materials used were: (1) natural rubber (NR rubber): purity 99%; Mooney viscosity (100%) – 32±3; density – 0.96 g/cm^3; (2) stearin: white flakes; moisture – 0.5% max.; (3) zinc oxide microparticles (ZnO): yellow powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g; (4) silicon dioxide (SiO_2): density – 1.9-4.29 g/cm^3, molar mass – 60.1 g/mol; (5) precipitated chalk: white powder, purity 99.09%; (6) leather waste – leather fibres functionalized with potassium oleate; (7) mineral oil; (8)

N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD 4010): density – 1.1 g/cm^3, solidification point over 76.5°C, flat granules coloured brown to dark purple); (9) sulphur (S): vulcanization agent, fine yellow powder, insoluble in water, melting point: 115°C, faint odor; (10) N-cyclohexylbenzothiazole-2-sulphenamide (Cz): curing agent, density – 1.26 g/cm^3, melting point 93-100°C; (11) diphenyl guanidine (D): curing agent, density – 1.34g/cm^3; (12) PEG – Polyethylene glycol: plasticizer, white pellets.

The functionalization of protein waste fibers (finished leather) was achieved by mixing with a stirrer with helical paddles, for 2 hours at a temperature of 80°C with slow dripping of potassium oleate and a speed of 40 rpm. Different percentages of functionalizing agent related to the amount of waste were experimented, but the percentage of 7% was selected, considered optimal due to the degree of absorption, the elimination of fiber agglomeration, the working method and the favorable influence on the physical-mechanical characteristics of the composite.

Preparation of Various Types of Biodegradable Polymer Composite

Table 1 presents the recipes for polymer composites based on natural rubber, with semi-active white mineral charge – ZnO and precipitated chalk, recipes based on the formulation for processing caps for antibiotic bottles for zootechnical use. In order to obtain polymer composites based on natural rubber and protein waste from finished post-consumer leather, the basic recipe was modified by adding protein waste functionalized with potassium oleate in different proportions, respectively 10, 20, 30, 50% waste relative to the amount of elastomer.

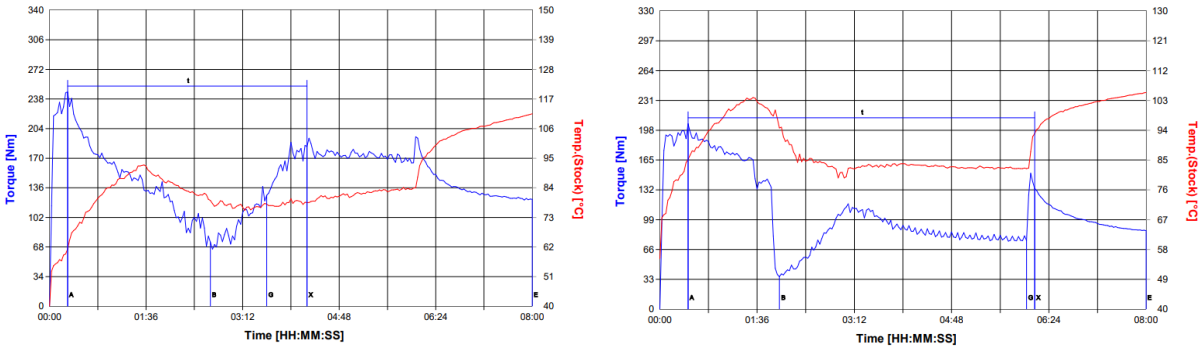
Table 1: Polymeric composites based on natural rubber compounded with protein waste functionalized with potassium oleate

Material	UM	N0	NP1	NP2	NP3	NP4
Processing on Brabender mixer						
Natural rubber	g	190	190	190	190	190
Stearic acid	g	3.8	3.8	3.8	3.8	3.8
Zinc oxide	g	9.5	9.5	9.5	9.5	9.5
Precipitated chalk	g	95	76	57	38	0
Protein waste	g	-	19	38	57	95
Mineral oil	g	4.5	5.7	5.7	5.7	5.7
IPPD antioxidant	g	4.5	5.7	5.7	5.7	5.7
PEG 4000	g	1.14	1.14	1.14	1.14	1.14
Processing on roller						
Sulfur	g	4.85	4.85	4.85	4.85	4.85
Cz accelerator	g	2.28	2.28	2.28	2.28	2.28
D accelerator	g	0.29	0.285	0.285	0.285	0.285

N0, NP1-NP4 composites were mechanically mixed in Brabender Plasti-Corder PLE 360 at 45°C and 80 rpm for 3 minutes and 2 min. at 23°C for homogenisation. The total time was 5 min.

According to the diagrams (Fig. 1-2), the following can be observed: in the first portion (A-B), the elastomer is introduced into the mixer and the torque increases. The first loading peak, A, corresponds to the introduction of elastomers. As the torque increases, so does the temperature due to friction. The torque starts to decrease until B, mainly due to the homogenization and plasticization of the elastomer, as well as due to the increase in temperature as a result of the shear forces. The other ingredients are introduced and the rotation speed is reduced to 20 rpm, and the mixer is kept open. Between point B and

point X, the torque starts to increase due to the inclusion of the ingredients. After incorporating the fillers and the other ingredients, the second loading peak, X, is observed, when a maximum torque appears. The torque begins to decrease, indicating the homogenization of the mixture. As a result, a maximum torque value is obtained due to the compaction and homogenization of the rubber mixture. This is generally followed by a decrease in the torque value, which indicates both the homogenization of the mixture and the increase in the temperature of the mixture due to friction at a higher rotational speed (60 rpm) with the mixer closed.



Mixture N0 Mixture NP4

Figure 1. Torque and temperature variation over time recorded on the Brabender Plasticorder while obtaining samples N0 and NP4

From the diagrams shown in Figure 1 it can be seen that the temperature in the mixing chamber increases, depending on the percentage of post-consumer protein waste introduced into the polymer composite (starting from 84°C to 105°C, it decreases approximately to 85°C, then increases to 107°C). Also, the mixing forces increase proportionally with the percentage of protein waste in the composite, starting at a temperature of 185°C and reaching a maximum at 30 seconds of mixing of 246 Nm for sample N0 and decreasing proportionally to 198 Nm for sample NP4. The maximum torque is reached when the natural rubber plasticizes, mixes with the ingredients (plasticizer, fillers, antioxidants, protein waste) and begins to disperse the waste particles. After reaching the maximum torque, it decreases uniformly (195 Nm), in the last minute decreasing uniformly to 66 Nm, which indicates the homogenization of the mixture. This decrease is due to the elastic behavior of the protein waste functionalized with potassium oleate, which also acts as a plasticizer. Table 2 shows the processing characteristics presented in the Brabender diagrams, for each processed composite. The data obtained from the Brabender diagrams are similar to those obtained when making composites based on natural rubber with elastomeric and functionalized wood waste, previously experimented [16].

Table 2: Characteristics presented in Brabender processing diagrams for polymeric composites – NP series

Characteristics	Sample code				
	N0	NP1	NP2	NP3	NP4
Temperature at peak load, °C	61	63	67	68	71
Temperature at the inflection point, °C	78	82	84	89	91
Maximum temperature, °C	112	109	112	108	97
Energy at the peak load, Nm	2.0	255.9	263.0	271.6	263.1
Maximum energy, Nm	183.5	171.4	169.6	159.1	128.2
Gelation zone energy, kNM	10.3	33.7	33.1	34.7	35.2
Specific energy, kNm/g	0.7	0.8	0.6	0.6	0.5
Gelation rate, Nm/min.	142.5	171.2	22.0	26.3	52.5

The mixtures made on the Brabender were added on the roll with the vulcanizing agents. The working method on the laboratory-scale electric roller for adding vulcanizing agents to the mixtures is as follows, mentioning the fact that the mixture is processed on the roller at a temperature of 23-30°C, roller friction 1:2 and with 50 revolutions/min:

- the composite is plasticized;
- the vulcanization agents are introduced and mixed for approximately 5-10 minutes;
- the mixture is homogenized on the roller for 1-2 minutes and taken out in the form of a 1-2 mm thick sheet.

The Monsanto 100S Rheometer was used to determine the vulcanization parameters of the tested composites, which describes their vulcanization and processing parameters. The analysis is carried out as follows: a sample is sealed in a cavity of the device, at a controlled and constant temperature (in the case of this work a temperature of 165°C was used), which surrounds a rotor with oscillations at a frequency of 1.67 Hz (100 cpm). The output correlates with the degree of vulcanization depending on vulcanization time.

From the experimental data (Table 3) it can be seen that by replacing the amount of precipitated chalk inactive filler with functionalized elastomeric waste, the rheological characteristics of the mixtures are changed as follows:

- the minimum torque (ML) decreases, the maximum torque (MH) has a value of about 4 dNm, and the torque variation (ΔM = MH-ML) increases as the amount of rubber powder increases compared to quantities of silicon dioxide; this indicates a stiffness of the mixtures in the unvulcanized state which may be due to the agglomeration of the rubber powder or its larger dimensions compared to the sizes of the silicon dioxide particles, but in the vulcanized state, the mixtures show a similar stiffness.
- the scorching time (t_{s2}) shows very good values, over 2', and the optimal vulcanization time (t_{90}) is over 20' and increases with the replacement of the silicon dioxide active filler with the elastomeric filler (indicating a decrease in crosslinking density as a result of reducing the amount of active reinforcing filler).

Table 3: Rheological characteristics of mixtures – NP series

Rheological characteristics at 165°C	Sample code				
	N0	NP1	NP2	NP3	NP4
ML (dNm)	8	16.5	19.3	16.5	18.5
MH (dNm)	54.3	74	74	74.1	74.2
ΔM = MH-ML (dNm)	46.3	57.5	54.7	57.6	55.7
Mf - Reversion (dNm)	47	2.47	2	2.4	2.86
t_{s2} (min)	1.2	10.01	9.28	11.15	6.91
t_{50} (min)	1.67	25.76	25.16	28.03	11.05
t_{90} (min)	2.54	16.5	19.3	16.5	18.5

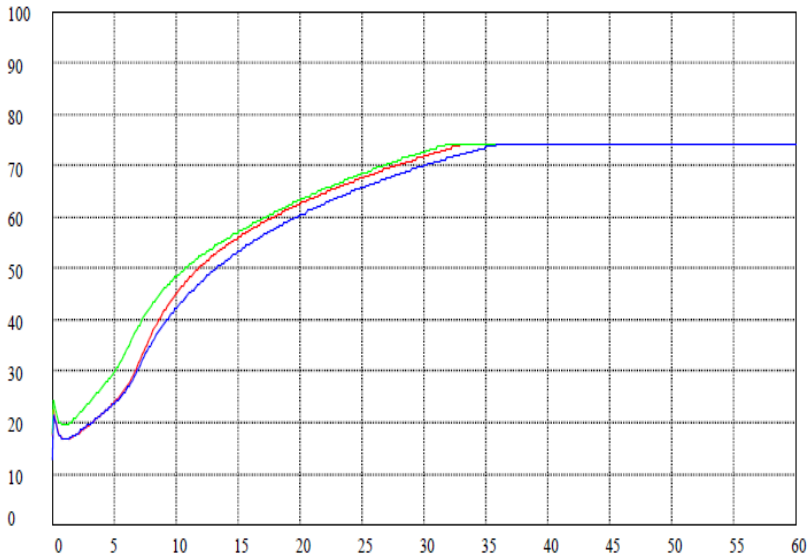


Figure 2. Torque variation expressed in dNm (OY axis) depending on time expressed in minutes (OX axis) for mixtures based on natural rubber: NP1 (red), NP2 (green) and NP3 (blue)

The vulcanization parameters presented in Table 4 were set according to the data from the rheograms.

The compounds were then compression-molded (using an electrically heated laboratory press) to obtain a sheet of about 2 mm thick. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Table 4: Vulcanization parameters for making samples by vulcanization in the press for mixtures based on natural rubber and elastomeric waste – NP series

Vulcanization parameters	Sample code				
	N0	NP1	NP2	NP3	NP4
Vulcanization temperature	165°C	165°C	165°C	165°C	165°C
Vulcanization time - T_{90}	4 min	4 min	4 min	4 min	4 min
Pressing force	300 kN	300 kN	300 kN	300 kN	300 kN
Cooling temperature	45°C	45°C	45°C	45°C	45°C
Cooling time	10’	10’	10’	10’	10’
Pressing force	300 kN	300 kN	300 kN	300 kN	300 kN

Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore “A” Durometer according to SR ISO 7619-1:2011.

Abrasion resistance was carried out according to ISO 4649/2010, the cylinder method, using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Repeated flexions – Ross Flex – SR ISO 132/2018 is the test that determines the resistance of the specimens to the appearance

and propagation of cracks when they are subjected to repeated flexions at an angle of 90°C, on a mandrel with a diameter of 10mm, up to 30,000 cycles or until the crack appears or the material breaks.

FT-IR spectroscopy was performed using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range 2000-530 cm^{-1}.

RESULTS AND DISCUSSIONS

Physical-mechanical tests were carried out in the Investigation laboratory from INCDTP - Division ICPI, accredited by RENAR, and materialized in the determination of hardness, elasticity, tensile and tear strength, attrition, residual elongation and elongation at break for thermo-oxidative aging (168h x 100°C) and normal state (Table 5).

Table 5: Physical-mechanical characteristics of mixtures – NC series

Physical-mechanical characteristics	Sample code				
	N0	NP1	NP2	NP3	NP4
Normal state					
Hardness, °Sh A	44	45	42	38	34
Elasticity, %	32	24	26	28	24
100% modulus, N/mm^2	1.0	0.51	0.05	0.046	0.046
300% modulus, N/mm^2	2.0	1.04	0.64	0,87	1.11
500% modulus, N/mm^2	4.52	3.21	1,76	1.97	2.88
Tensile strength, N/mm^2	14.23	10.46	6.2	3.17	5.31
Elongation at break, %	740	820	740	700	560
Residual elongation, %	28	38	32	28	22
Tear strength, N/mm	24.39	19.23	16.9	15	13
Specific weight, g/cm^3	1.2	1.12	1.10	1.08	1.06
Attrition, mm^3	123.45	320	280	265.36	231.71
Rossflex repeated flexions SR ISO 132/2018	Resist up to 150.000 cycles			100.000 cycles crack appear, resist up to 128.000 cycles	
After accelerated ageing for 168 hours at 70°C					
Hardness, °Sh A	51	40	39	37	38
Elasticity, %	34	38	32	34	28
100% modulus, N/mm^2	1.22	1.0	0.84	0.06	0.06
300% modulus, N/mm^2	2.8	1.5	1.0	1.3	1.28
Tensile strength, N/mm^2	11.3	6.6	5.4	4.7	4.3
Elongation at break, %	620	660	780	580	620
Residual elongation, %	32	28	30	24	20
Tear strength, N/mm	29.2	25.6	21.4	20.7	16.1

The hardness decreases by 9-14 °ShA, from 45 °ShA in the control sample to 34 °ShA in the composite based on natural rubber with functionalized post-consumer finished leather waste in a proportion of 30-50%. The decrease in hardness is due to the increase in plasticizer from the rubber waste functionalization process and its low density. After accelerated aging, the hardness increases due to the loss of plasticizer when the samples are kept at a temperature of 70°C for 168 h.

- Elasticity decreases by 25-38%, but the variations are uneven.

- The modulus, tensile strength and tear strength values decrease as the precipitated chalk inactive filler is replaced by the elastomeric waste. When the precipitated chalk is completely replaced with rubber powder, an increase in

these characteristics is observed, but without exceeding the values of the control sample.

- Elongation at break shows good values, over 620%.
- Attrition increases in samples with elastomeric waste.
- The density of the mixtures decreases as the amount of powder increases and the amount of precipitated chalk decreases, because the density of elastomeric waste is lower than that of chalk.
- Repeated flexions – Ross Flex – The footwear standards in force specify values of 100,000 cycles for vulcanized rubber shoe soles when determining repeated flexions. The values presented in Table 5 show that only the NP3 and NP4 composites with rubber waste content of 30%, and 50%, respectively, do not fall within this value (after 90,000 cycles crack appears, resist up to 128,000 cycles). The others have values higher than 150,000 cycles, higher than the values imposed by the standard.
- IR spectrum represents the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 µm. IR domain for usual organic chemistry is between 2.5 and 25 µm. The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm^{-1}, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid-state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the natural rubber and rubber waste elastomeric spectrum. The FTIR spectra of the analyzed materials are presented in Figure 5. In the spectrum recorded for the unvulcanized natural rubber, the most important bands that allow its qualitative and quantitative identification can be highlighted. The band at 2960.79 and 2851.81 cm^{-1} can be attributed to asymmetric (ν_{as}) and symmetric (ν_s) stretching of $-CH_3$ bond, and the one at 1375.58 cm^{-1} represents the in-plane deformation vibration, namely the shear (δ^s) of $-CH_3$ bond, the band at 841.97cm^{-1} represents the out-of-plane deformation vibration (γ) of -CH-CH bond originating from cis-1,4 units. The band at 1444.82 cm^{-1} is associated with deformation bonds of CH_2 groups, the band at 1375.58 cm^{-1} comes from the shear vibration of $-CH_3$ bonds and the one at 1663.01 cm^{-1} represents the stretching vibration of C=C bond [15].

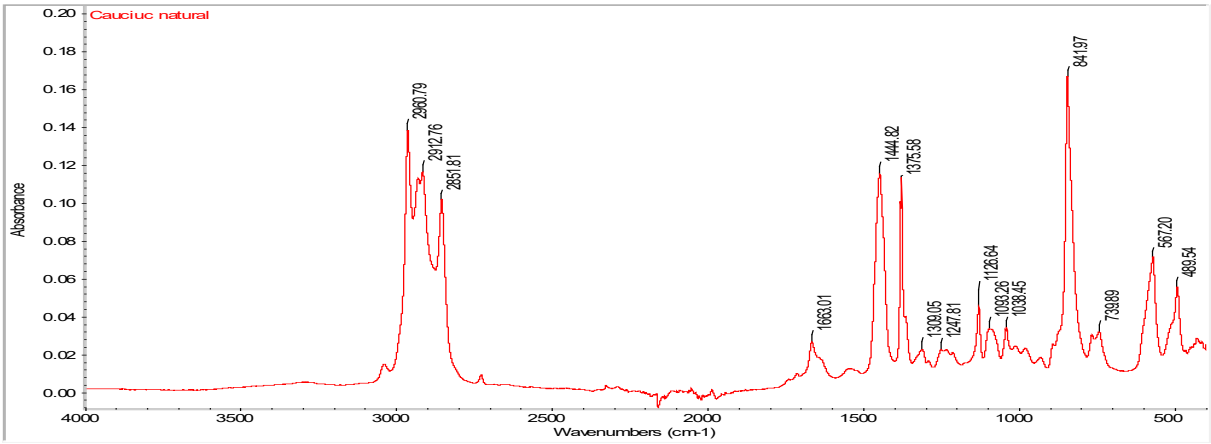


Figure 3. FTIR spectrum of unvulcanized natural rubber

In the case of the elastomeric waste used as filler in the tested composites, both the bands characteristic of SBR rubber and bands originating from other specific processing additives can be identified. Thus, in the spectrum recorded for the unmodified elastomeric waste, the bands characteristic of the functional groups in SBR can be highlighted. Thus, the band at 962.41 cm^{-1} is attributed to 1,4 groups from trans-butadiene and the one at 907.46 cm^{-1} is attributed to 1,2 units from butadiene. The bands at 2914.39 and 2847.55 cm^{-1} correspond to CH bond deformations originating from the aromatic styrenic ring.

In the case of the elastomeric waste modified on the surface with potassium oleate, the appearance of peaks at 1560.84 and at 1413.25 cm^{-1} are characteristic of the mode of asymmetric and symmetric stretching of COO^- bond. The band at 1463.59 cm^{-1} comes from the CH_2 bond vibration. The band at 719.08 cm^{-1} is due to - $(CH_2)_n$ – bond deformations.

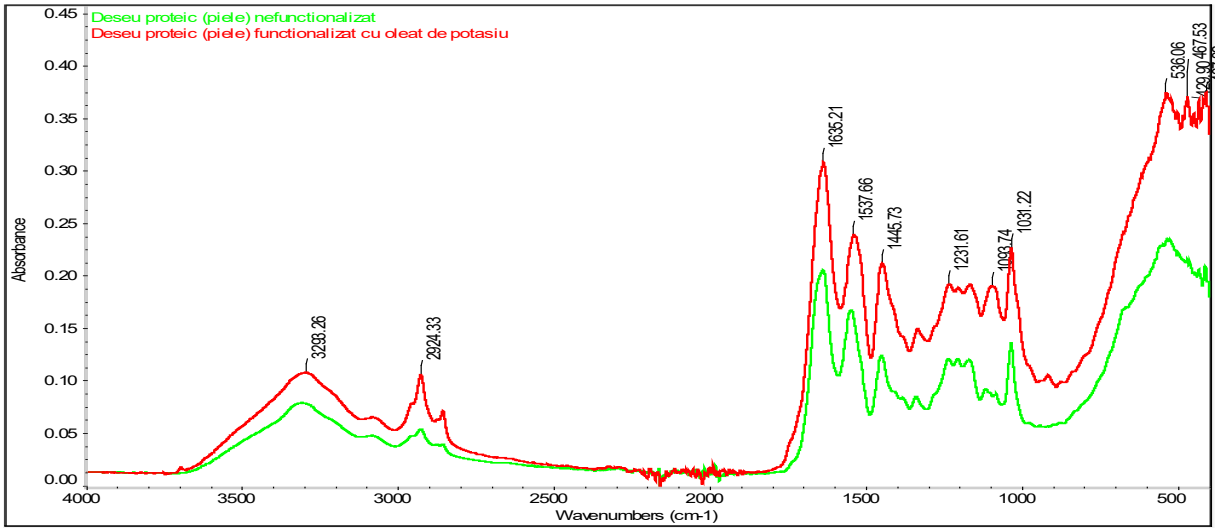


Figure 4. FTIR spectra of protein waste non-functionalized (green) / functionalized with potassium oleate (red)

The spectra obtained for the protein waste non-functionalized/functionalized with potassium oleate highlight the characteristic bands originating from leather, namely: the band at 3293.26 cm^{-1} can be associated with N-H stretching bonds, the band at 1635.21 cm^{-1} (Amide I – associated with the stretching vibration of C=O bond originating from the protein structure). The band at 1537.66 cm^{-1}, known as Amide II, can be associated with the bending vibration of N-H bond and the stretching vibration of C-H bond. The band at 1231.61 cm^{-1} – Amide III – represents the stretching vibration of C-N bond, respectively the in-plane bending vibration of N-H bond from the amide bond, the vibration of CH_2 groups originating from glycine and proline (cyclic secondary amine), respectively. The presence of potassium oleate could not be visualized in the spectrum, most likely due to the fact that it was adsorbed inside the leather fibers.

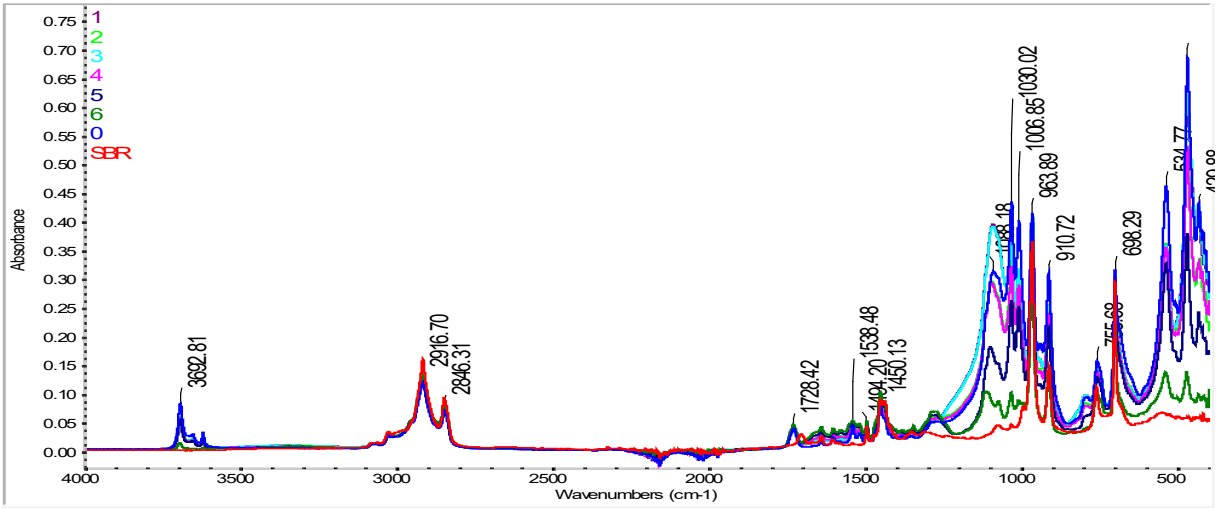


Figure 5. FTIR spectra of mixtures based on natural rubber reinforced with varying percentages of protein waste modified with potassium oleate

In the case of the N0 mixture (control sample without elastomeric waste), besides the bands characteristic of natural rubber, the presence of very intense bands due to the groups originating from calcium carbonate at 1424.82, 873.75 and 712.6 cm^{-1} can be highlighted. The intensity of these bands is directly proportional to the amount of calcium carbonate introduced into the mixtures. Thus, the control mixture N0 contains the highest amount of calcium carbonate, following that in the mixtures NP1-NP3 the amount of carbonate is gradually replaced by the elastomeric waste modified with oleate. Instead, in the case of the NP4 mixture, the calcium carbonate was completely replaced by the protein waste, which led to the disappearance of the bands associated with $CaCO_3$. The characteristic bands of the protein residue modified with oleate, and in particular the band at ~1537 cm^{-1} (due to the bending vibration of N-H bond and the stretching vibration of C-H bond) and 1621 cm^{-1} (the stretching vibration of C=O bond from oleate) can be visualized in all processed mixtures NP1-NP4, the greater the amount of rubber waste modified with oleate, the greater their intensity. In the case of vulcanized mixtures, it can be observed that the band at 1663.01 cm^{-1} associated with the stretching vibration of C=C bond (clearly detectable in the spectrum obtained on the unvulcanized natural rubber) is consumed during the sulfur vulcanization process, its relative intensity decreasing.

CONCLUSIONS

The recipe based on natural rubber used in the processing of stoppers for bottles of antibiotics for zootechnical use was modified by replacing the inactive filler (precipitated calcium carbonate) with cryogenically ground post-consumer protein waste with a particle size of 500 nm and functionalized with potassium oleate. These polymer composites were processed on a Brabender mixer and laboratory roller using elastomeric waste with different proportions (10, 20, 30 and 50%). The polymeric composite samples with percentages of 10 and 20% post-consumer protein waste presented the best physical-mechanical performance compared to those with higher percentages of elastomeric waste (30 and 50%), characteristics that fall within the specific values for the control sample without waste. Properties such as elongation at break and elasticity showed a slight reduction compared to the control sample – N0, and the hardness decreased by 9-14 units. The tensile strength of the composition decreased to about half that of N0. Although the values are lower, the NP1-NP3 composites, with a percentage of

10-30% functionalized elastomeric waste, fall within the standardized physical-mechanical values. The physical-mechanical values obtained after accelerated aging are slightly modified, corresponding to the standardized ones. The experimental data in the case of composites based on natural rubber and protein waste are similar to those obtained when making composites based on natural rubber with functionalized elastomeric and wood waste, previously experimented [16].

Acknowledgements

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DISCLAIMER

LIFEGREENSHOES 4 ALL, (LIFE17ENV/PT/000337) project is been co-funded with support from the European Commission under the LIFE- programme. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

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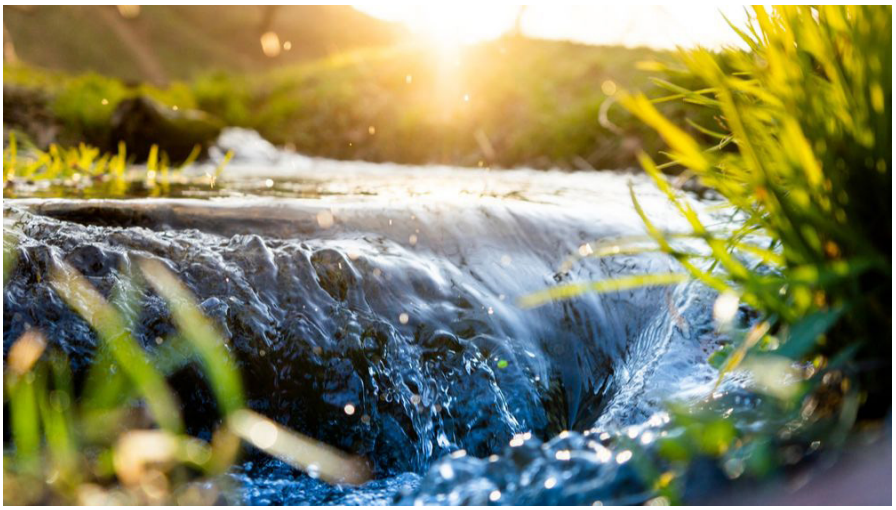
EUROPEAN RESEARCH AREA

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 2019-2021 issues of *Leather and Footwear Journal*. Newsletter 6 of 2022 is given below.

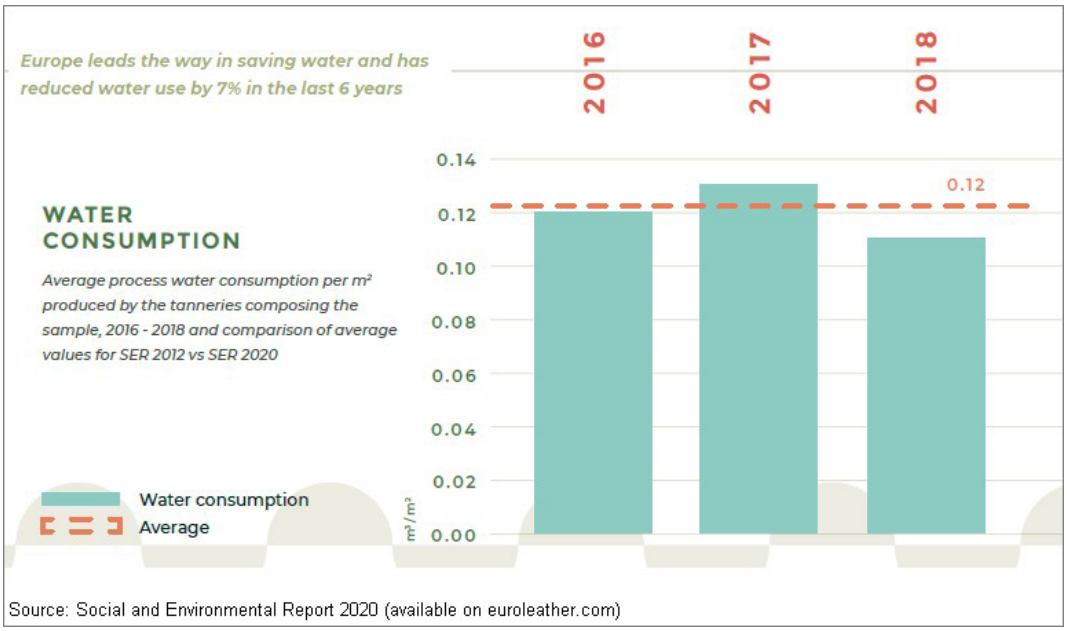
NEWS 6/2022

Tanners Take Care of the Water They Borrow to Produce Leather



We are all aware that water is a scarce commodity and that good management is essential to ensure that it is used sustainably. The European tanning industry, which requires water to produce leather, takes this issue very seriously.

The tanning process borrows a certain volume of water and purifies it after use before returning it to nature. First the hides are rinsed and, once they are clean, free from mud, dung and hair, are tanned and dyed. It is necessary to optimize the use of water and guarantee its adequate treatment after each of these processes.



Thanks to the European tanning industry's sound environmental practices, accredited by well-known audits and guidelines for progress in the treatment of wastewater, the quality of the water returned to the environment is constantly increasing, and is always at least compliant with the legal requirements for discharge to the environment.

In Europe, wastewater from tanneries is treated to very high standards. Its common effluent treatment plants (CETP) showcase technical excellence.

For instance, Italy, with CETP in the tannery clusters of Tuscany, Veneto or Campania, has become an international reference for the management and treatment of water in industrial districts of tanneries.

Another example is the Portuguese tanning district of Alcanena which separately collects the tanning baths from associated tanneries to recycle any residual tanning agents.

A Spanish example is the treatment plant Igualadina Depuració i Recuperació S.L. (IDR). IDR (picture above) treats waters from 28 tanning companies of Igualada (associated with the Spanish Leather Association, ACEXPIEL, and the Leather Cluster Barcelona), as well as part of the local urban wastewater and that from other industries. At the end of the innovative biological system, it leaves the water in conditions comparable to domestic wastewaters, which are, in a following step, sent to a municipal wastewater plant, guaranteeing an adequate return to the environment.

Due to its unique characteristics, this CETP has been the subject of international recognition, as a case study in a seminar by UNEP, organised for advisors of Ministries of the Environment, and the focus of a report of by Global Water Intelligence, a reference for the water industry.

Perfectly aligned with the United Nations' sixth Sustainable Development Goal – clean water and sanitation – European tanners are moving decisively towards higher sustainability standards.

edited by COTANCE

in collaboration with CURTIDORES ESPAÑOLES SPANISH TANNERS

News Release from the IULTCS

26 July 2022

Registration for AICLST Conference in New Zealand Underway

The 12th Asia International Conference on Leather Science and Technology (AICLST) will be taking place in a hybrid format from 18–20 October at Massey University's Sport and Rugby Institute, situated in Palmerston North on the North Island of New Zealand.

Conference organiser and Director of New Zealand Leather and Shoe Research Association, Mr Geoff Holmes, welcomes abstracts from potential presenters and registration for delegates wishing to attend in person or virtually. He highlighted some of the key benefits of attending the conference saying "The 12th AICLST Conference will provide a 3-day programme that seeks to stimulate discussion and bring together the wider leather community of scientists, leather manufacturing companies

and chemical and equipment suppliers. It will showcase the latest advances in leather science and technology, promoting science excellence and impact in support of the drive towards more sustainable leather production.

The Gala Dinner for AICLST will be held at Massey University's Refectory. The 3-day event costs $250 NZD per person or just $75 NZD for those joining remotely."

Full details can be found on the conference website: https://www.aiclst.org

There will be 7 main themes covering a wide range of topics to appeal to anyone involved in leather science or manufacturing:

1. Advances in Basic Leather Science
2. Raw stock improvement
3. Cleaner leather production and closed-loop processing
4. Value-added uses for waste streams and by-products
5. Environmental protection and impact assessment
6. Industry 4.0. Detection and traceability
7. Advances in machinery used in the leather processing Industry

The AICLST conference also offers the opportunity for sponsorship.

Mr Holmes ends by saying "While celebrating our 75th year of incorporation we invite scientists and industry chemists from across the globe to join us for this joyous occasion, to foster international communication and collaboration across the leather community and to boost advancement in leather science and related manufacturing technology."

News Release from the IULTCS

28 July 2022

III IULTCS EuroCongress Scientific Programme Announced

The organising committee of the III IULTCS EuroCongress are pleased to announce that the scientific programme has been finalised and participants are now able to register to attend (closing date for registration 05 September 2022).

The congress will be held in Vicenza, Italy from 18-20 September 2022 at the Vicenza Convention Centre with a full package of events included in addition to the extensive scientific presentations. The highlight will be the exclusive Gala Dinner which will be held in Bevilacqua Castle, a medieval construction dating back to 1300, situated in the town of Bevilacqua (Verona).

For further information visit www.iultcs2022italy.org
www.iultcs2022italy.org/programm
https://www.iultcs2022italy.org/registration/

News Release from the IULTCS

09 August 2022

IULTCS Welcomes New Korean Members

The IULTCS is pleased to announce that two organisations from the Republic of Korea have joined the IULTCS family. Representing leather industry companies 'Korea Tanners' Association' has joined as an Associate Member and also leather producer Whanam Leather Ind Co Ltd has joined as a Supporting Member.

IULTCS President, Jean-Pierre Gualino, welcomed the new member organisations saying "On behalf of the Executive Committee I am pleased to welcome South Korea to IULTCS thorough the memberships of Korea Tanners' Association and Whanam Leather Ind Co Ltd the scientific community becomes stronger with their participation and we look forward to their active involvement in IULTCS activities".

News Release from the IULTCS

02 September 2022

IULTCS Asks EU Legislators to Reconsider Proposed Restrictions

Members of IULTCS have collaborated with industry scientists from FILK, Stahl and TFL to prepare a document that was submitted to DG Grow (the European Commission Directorate-General department responsible for EU policy on the single market, industry, entrepreneurship and small businesses) and DG ENV (The Directorate-General for Environment department responsible for EU policy on the environment).

The purpose of preparing the document was to address proposed EU restrictions on the presence of Chrome VI and Bisphenols in leather. It is considered that the new proposed REACH restrictions could seriously impact the leather industry, particularly in the European Union.

The IULTCS document asks the EU for a proper assessment of the impact of these measures on the environment, people and leather manufacture. IULTCS President Jean-Pierre Gualino and Executive Secretary Dr Luis Zugno stated "Our call is for a more detailed study of data and testing methodology relating to Chrome VI and more time to implement the proposed Bisphenol restrictions".

News Release from the IULTCS

01 October 2022

IULTCS Young Leather Scientist Grant Programme 2023 Announced

The Executive Committee of the IULTCS is pleased to announce the 2023 grants to be awarded to three young scientists, under the age of 35, for research projects in the categories: Basic Leather Research, Machinery / Testing and Sustainability / Environment – to be conducted at a recognised institution in 2023.

As in previous years Leather Naturally will again sponsor the Dr Mike Redwood Sustainability/ Environment grant with the monetary sum of €1,000 sponsorship and Erretre will similarly sponsor the Machinery / Testing grant also with a sum of €1,000. In addition, IULTCS is delighted to receive the support of a new sponsor, Tyson Foods, who will provide a €1,500 Basic Leather Research grant for research on the topics such as innovative leather processing, new chemicals for leather processing, analytical method development, hide/skin preservation, environmental studies applied to the tanneries, tannery waste treatment and basic research in collagen and leather.

2023 will be the ninth year of the grant and Professor Michael Meyer, Chairman of the International Union Research Commission (IUR) of IULTCS and Research Director at Freiberg (Germany) based FILK Freiberg Leather Institute expressed his appreciation of the continued engagement: "We are very happy to announce the award for the 9th year. The detailed project results of previous winners are presented in their reports on the IULTCS web site. It is worthwhile reviewing these substantial and significant investigations. We very much value the contribution of all sponsors to our YLSG programme. It is a vital instrument to encourage young leather scientists to acquire awareness and become more connected to the established research community of our industry. We have seen the programme growing stronger over the past years. Last year´s awards resulted in numerous, ambitious applications with innovative ideas and sustainable technologies."

Application submissions for the 2023 YLSG programme open on 01 October 2022 and Luis Zugno, immediate past President and now secretary of IULTCS, asks young research talents of the industry to file innovative and thought-provoking project ideas before the **30 November 2022** deadline.

Details of the eligibility requirements are available on the IULTCS website YSLG_application_rules_and_procedure_2023.pdf (iultcs.org). The IULTCS requests that readers of this announcement forward the information to those institutions and individuals who could benefit from the award.

Chinese Embassy in Romania Launches CHINACTIV Electronic Newsletter

On August 15, 2022, the Chinese Embassy in Romania officially released the first issue of *Chinactiv* electronic journal and Ambassador Han Chunlin delivered the opening speech for the journal. The journal includes columns on Politics and Diplomacy, Economy and People's livelihood, In-depth Focus and Romania-China relations, aiming to introduce the latest situation of China's politics, economy, diplomacy, culture, science and technology and Romania-China relations in a comprehensive and in-depth manner and enhance the understanding of China and Romania-China relations from all walks of life in Romania.

The language of the journal is Romanian and it is published every two months.

The newsletter is available on the website of the Embassy, on Facebook and other platforms. For subscription, please send an e-mail to newsletterul.ambasadachinei@gmail.com.

More information: https://www.facebook.com/AmbasadaChineiinRomania

LIFE GreenShoes4All, (LIFE17 ENV/PT/000337)

Nowadays, there is a proliferation of so called 'eco' labels or schemes, and misleading 'green' claims. Consumers find this confusing and footwear manufacturers that want to produce 'green products' find it hard to differentiate their products from these and need the right tools to do. Life Cycle Assessment (LCA) standards may be too flexible to ensure comparability of results. In this respect, Product Environmental Footprint (PEF) could play an important role.

The LIFE GreenShoes4All project is designed to support the implementation of a Product Environmental Footprint evaluation methodology, to help companies involved in the footwear business to measure the environmental performance of their products.

The PEF methodology introduces several important improvements compared to other life cycle analysis (LCA) methods including, among others, clear identification of the potential environmental impact categories to be looked at to perform a comprehensive LCA, setting minimum data quality requirements and clearer technical instructions for addressing some critical aspects of a LCA study.

PEF results are quantitative and enable companies to assess the full life-cycle impact of a final product, compare different product's environmental impacts and identify what life-cycle stages or production processes contribute the most impact.

LIFE GreenShoes4All teams conducted PEF studies in footwear models ranging from fashion to safety footwear, with uppers in leather, textiles and/or manmade materials, midsoles in polyurethane (PU) or ethyl vinyl acetate (EVA), soles in rubber, PU, thermoplastics, EVA and others. The results indicate that climate change and resource use impact categories each represent on average, around or over 30% of the total impact.

To reduce products PEF is important to namely to design footwear to reduce the number of different materials used, use recyclable and recycled materials, use materials that at lightweight and durable, and conceive shoes that are easy to disassemble and recycle.

To this end, LIFE GreenShoes4All project and metrics also encompasses supply chain activities from materials and products industrial production tunning through the product use and waste management.

The project proposes more tangible targets on raw materials selection, products ecodesign and manufacturing, waste polymers recycling (rubber, thermoplastic and EVA), and measures to reduce greenhouse gas emissions.

LIFEGreenShoes4All was developed by 9 partners: AMF, APICCAPS, ATLANTA, CEC, CTCP (coordinator), EVATHINK, ICPI, INESCOP, FICE and PESTOS, that thank the support of the European project LIFE GreenShoel4All (LIFE17 ENV/PT/000337, https://www.greenshoes4all.eu/).

The main project outcomes include:

- Methods to measure and reduce materials, soles and shoes products environmental footprint between 10 % and 30 %.

- Practical ecodesign guidelines for shoes design, distribution, and use phase.
- New recycling routes to obtain high quality recycled thermoplastics, EVA and vulcanised rubber incorporating between 60 % up to 100 % of discarded material thus reducing the virgin materials needed and wastes.
- Innovative sustainable fashion and safety green shoes based in new design approaches, recycled materials and manufacturing methodologies.
- Contribute to the Single Market for Green Products and Green Deal Package by demonstrating the great added value of the European Product Environmental Footprint methodology, Ecodesign and Circular Business Models.

DISCLAIMER

LIFEGREENSHOES4ALL (LIFE17 ENV/PT/000337) project is been co-funded with support from the European Commission under the LIFE + programme. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

PARTNERS:

NATIONAL AND INTERNATIONAL EVENTS

SUSTAINABILITY THROUGH SCIENCE AND TECHNOLOGY (SIPS 2022)
27 NOVEMBER – 1 DECEMBER 2022, PHUKET, THAILAND

SIPS 2022 is a yearly event that is deeply science-focused and technology & engineering-oriented, organized since 2003 by the not-for-profit corporation FLOGEN Stars Outreach (www.flogen.org), which is dedicated to achieving sustainability through science and technology. It incorporates summit plenary lectures from well-known speakers that address the link between scientific, technology and engineering domains in the pursuit of sustainable development, as well as specific science, technology and engineering symposia that feature technical presentations with the same goals in mind. Due to COVID-19 restrictions in 2020, this year's summit is for 2020, 2021 and 2022.

Based on the FLOGEN Sustainability Framework given in the right side and following the rich tradition of previous years, the summit will cover 3 sustainability pillars: (1) Science, Technology & Industry, (2) Governance & Management and (3) Education & Civil Society.

Prof. Ferid Murad, Nobel Laureate in Medicine

SIPS 2022 is entirely dedicated to and bears the name of **Prof. Ferid Murad**, Nobel Laureate in Medicine and the SYMBOL of Unified Science. Prof Murad is a pioneer in discovering the positive role of Nitric Oxide in human organism. Nitric Oxide is an inorganic compound considered to be a very dangerous polluter in the atmosphere. However, Prof. Murad discovered and proved that Nitric Oxide inside the human organism has a very positive role in various directions. With his discovery, Prof. Murad became a symbol of a unified inorganic and organic world, and all related science and technology fields.

The summit simultaneously incorporates numerous International Symposia covering the fields of: oxidative stress; medical innovations; green chemistry and polymers; physical chemistry; solid state chemistry; solution chemistry; electrochemistry; molten salt and ionic liquids; advanced materials; advanced manufacturing; advanced technologies; iron and steel making; aluminum; batteries; bio-extraction; cement; coal; coatings; composites; ceramics; ecosystems; education; energy production; environment; ferro-alloys; mathematics; metallic systems; metals and alloys; minerals; mining; multiscale materials; nanomaterials; non-ferrous smelting and hydro/electrochemical processing; quasi-crystals; rare earth and platinum group metals; recycling; and rotary kiln operations. The topics within each symposium span across scientific, technological, environmental, health, legal, management, financial, policy, taxation, social, and pedagogical issues.

Important Dates

Full Manuscript Submission Deadline:	2022/09/30
Notification of acceptance for Oral Presentations:	5 days after submission
Revised Final Submission after Review (if necessary):	2022/10/30
Early Bird Registration Deadline:	2022/09/20
Announcement of the Preliminary List of Abstracts:	2022/10/15
Announcement of the Advance Program/Preliminary Schedule:	2022/11/01
Discounted Registration Deadline:	2022/09/15
Advanced Registration Deadline:	2022/10/30
Presentation File Submission Deadline:	2022/11/01
Announcement of the Final Program:	2022/11/01

More information: www.flogen.org

8TH WORLD CONGRESS ON RECENT ADVANCES IN NANOTECHNOLOGY (RAN'23)
23-25 MARCH 2023, LISBON, PORTUGAL

The 8th World Congress on Recent Advances in Nanotechnology (RAN'23) will be delivered in-person in Lisbon, Portugal and virtually, providing the opportunity of online presentation for the people who can not travel for any reason. Attendees will be able to connect with researchers from across the globe and network in-person or virtually. The registration fee for virtual participation is reduced.

The congress proceedings will be indexed by Scopus and Google Scholar.

RAN is aimed to become one of the leading international annual congresses in the field of nanotechnology. The congress is composed of 2 conferences. While each conference consists of an individual and separate theme, the 2 conferences share considerable overlap, which prompted the organization of this congress.

- **ICNNFC'23** - 8th International Conference on Nanomaterials, Nanodevices, Fabrication and Characterization
- **NDDTE'23** - 8th International Conference on Nanomedicine, Drug Delivery, and Tissue Engineering

This congress will provide excellent opportunities to the scientists, researchers, industrial engineers, and university students to present their research achievements and to develop new collaborations and partnerships with experts in the field.

Important Dates

SUBMISSION DEADLINES	Extended Paper Submission Deadlines	October 7, 2022
	Extended Notification to Authors	November 4, 2022
	Extended Final Version of Accepted Submissions	November 30, 2022
	Extended Early-Bird Registration	November 30, 2022
REGISTRATION DEADLINES	Extended Regular Registration	December 23, 2022
	Late Registration	After December 23, 2022

More information: https://rancongress.com/

THE LONDON 2023 CONFERENCES
03-11 AUGUST 2023, LONDON, UNITED KINGDOM

The London conferences invite university scholars, scientists and researchers for submission of their papers in the form of extended abstracts, short papers, and full manuscripts. The extended submission deadline for the conferences is **January 6, 2023,** and the early bird registration ends on **March 10, 2023.**

The aim of these conferences is to provide opportunities to university professors, students, scientists, researchers, and industrial engineers to present their research acquirements and to develop new collaborations and partnerships with highly experienced professionals in the field.

The 5th International Conference on Statistics: Theory and Applications (ICSTA'23) aims to become the leading annual conference in fields related to Statistics: Theory and Applications. The goal of this statistics conference 2023 is to gather scholars from all over the world to present advances in the relevant fields and to foster an environment conducive to exchanging ideas and information. This conference will also provide an ideal environment to develop new collaborations and meet experts on the fundamentals, applications, and products of the mentioned fields.

The 9th World Congress on Electrical Engineering and Computer Systems and Science (EECSS'23) is aimed to become one of the leading international annual congresses in the fields of electrical engineering and computer systems and science. The congress is composed of 5 conferences. While

each conference consists of an individual and separate theme, the 5 conferences share considerable overlap, which prompted the organization of this congress.

- **CIST'23** - 8th International Conference on Computer and Information Science and Technology
- **MHCI'23** - 10th International Conference on Multimedia and Human-Computer Interaction
- **MVML'23** - 9th International Conference on Machine Vision and Machine Learning
- **ICBES'23** - 10th International Conference on Biomedical Engineering and Systems
- **EEE'23** - 9th International Conference on Electrical Engineering and Electronics

The 9th World Congress on Mechanical, Chemical, and Material Engineering (MCM'23) is aimed to become one of the leading international annual congresses in the fields of mechanical, chemical, and material engineering. The congress is composed of 4 conferences. While each conference consists of an individual and separate theme, the 4 conferences share considerable overlap, which prompted the organization of this congress.

- **HTFF'23** - 10th International Conference on Heat Transfer and Fluid Flow
- **ICMIE'23** - 12th International Conference on Mechanics and Industrial Engineering
- **MMME'23** - 11th International Conference on Mining, Material and Metallurgical Engineering
- **ICCPE'23** - 09th International Conference on Chemical and Polymer Engineering

The 9th World Congress on New Technologies (NewTech'23) is aimed to become one of the leading international annual congresses in the fields of new technologies. The congress is composed of 4 conferences. While each conference consists of an individual and separate theme, the conferences share considerable overlap, which prompted the organization of this congress.

- **ICNFA'23** - 14th International Conference on Nanotechnology: Fundamentals and Applications
- **ICEPR'23** - 13th International Conference on Environmental Pollution and Remediation
- **ICBB'23** - 9th International Conference on Biotechnology and Bioengineering
- **ICERT'23** - 7th International Conference on Energy Research and Technology

More information: https://icsta.net/; https://eecss.org/; https://mcmcongress.com/; https://newtechcongress.com/

INSTRUCTIONS FOR AUTHORS

Publication Ethics and Malpractice Statement

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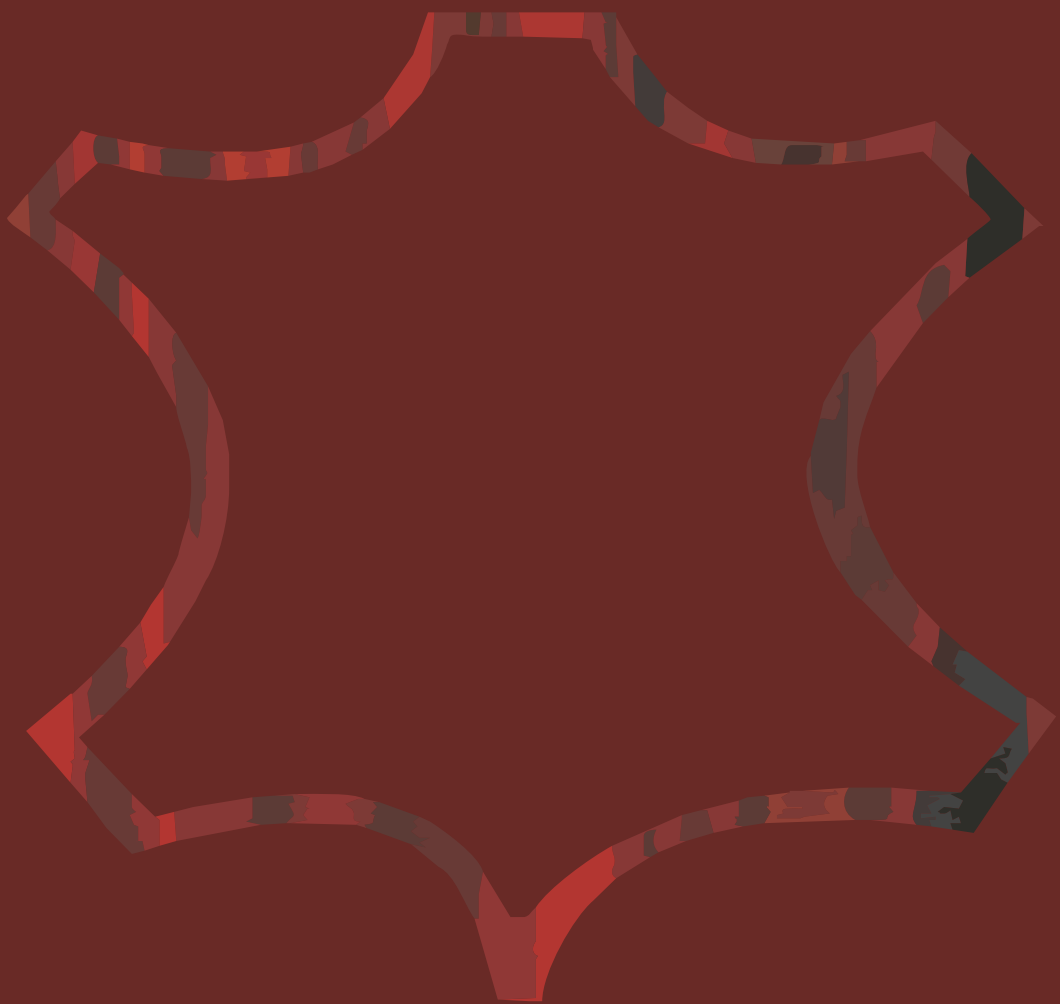

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