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ABLATION METHOD OF GRINDING A LEATHER SPLIT UNDER THE INFLUENCE OF LASER RADIATION

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ABLATION METHOD OF GRINDING A LEATHER SPLIT UNDER THE INFLUENCE OF LASER RADIATION

ABSTRACT. Using scanning electron microscopy, the surface morphology of a split leather sample was studied under the action of laser radiation from the front and backsides. It has been established that the effect of laser skin resurfacing is achieved in the range of input energies of 40 J and exposure times of 40 sec. It was found that laser exposure from the front and backsides leads to polishing of splits. Skin resurfacing from the front and leather split starts at different input energies from the front side from the split, which is associated with a looser structure of the leather from the split and its lower absorption of radiation.

KEY WORDS: leather tissue, pigment concentrate, protein, acrylic aldehyde, copolymer emulsion of butyl acrylate, methyl methacrylate and acrylic acid, coating dyes, laser radiation, diffusion, split leather surface structure, collagen fibers, elemental analysis, hygroscopicity, moisture return

METODĂ DE ŞLEFUIRE A ŞPALTULUI DE PIELE UTILIZÂND ABLAȚIA LASER

REZUMAT. S-a studiat morfologia suprafeței unei probe de șpalt de piele sub acțiunea radiației laser pe ambele părți folosind microscopia electronică cu scanare. S-a stabilit că efectul de remodelare a suprafeței pielii cu laser are loc la o energie inițială de 40 J și la un timp de expunere de 40 de secunde. S-a descoperit că expunerea pielii la laser pe ambele părți conduce la șlefuirea suprafeței șpaltului. Procesul de remodelare a suprafeței șpaltului începe la energii inițiale diferite pe fața șpaltului, care este asociată cu o structură mai slabă a șpaltului și cu o absorbție mai scăzută a radiațiilor.

CUVINTE CHEIE: țesut de piele, pigment concentrat, proteine, aldehidă acrilică, emulsie de copolimer de acrilat de butil, metacrilat de metil și acid acrilic, coloranți de acoperire, radiații laser, difuzie, structura suprafeței șpaltului, fibre de colagen, analiză elementară, higroscopicitate, retur de umiditate

MÉTHODE DE POLISSAGE DE LA CROÛTE DE CUIR À L›AIDE D›UNE ABLATION AU LASER

RÉSUMÉ. La morphologie de surface d'un échantillon de croûte de cuir sous l'action d'un rayonnement laser des deux côtés a été étudiée par microscopie électronique à balayage. On a déterminé que l'effet de remodelage de la surface du cuir au laser se produit à une énergie initiale de 40 J et un temps d'exposition de 40 secondes. L'exposition du cuir au laser des deux côtés s'est avérée lisser la surface de la croûte. Le processus de remodelage de la surface de la croûte commence à différentes énergies initiales sur la face de la croûte, ce qui est associé à une structure de la croûte plus faible et à une absorption de rayonnement plus faible.

MOTS CLÉS : tissu de la peau, pigment concentré, protéine, aldéhyde acrylique, émulsion de copolymère d'acrylate de butyle, de méthacrylate de méthyle et d'acide acrylique, colorants de revêtement, rayonnement laser, diffusion, structure de surface de la croûte, fibres de collagène, analyse élémentaire, hygroscopicité, retour d'humidité

INTRODUCTION

The structural miracle of collagen makes natural skins. The skin matrix is superior to other synthetic matrices [1-3].

A technology has been developed for plasma-chemical finishing of natural leathers based on the use of silver nanoparticles and high-frequency low-pressure plasma radiation [4]. An induction high-frequency plasma torch has been developed for processing materials with nanoparticles under the conditions of an inductive discharge. It has been established that the use of this technology can significantly improve the quality of natural leathers, in particular, significantly improve their physical and mechanical properties.

In previous works [5-7] it was shown that the introduction of plasma treatment before liquid processes in the leather industry makes it possible to achieve results in improving the consumer properties of leather and intensifying liquid processes. However, the processing of leather material with a moisture content of more than 20% requires a long pumping time to create a pressure of the order of 1.33 Pa, in addition, constant monitoring of the moisture content of the processed material is necessary, because at a humidity of more than 50%, ice crystals form between the structural elements of the dermis.

The effect of plasma treatment and nano-finishing on the properties of leather was studied. O_2 and N_2 gases were used to activate the skin surface, on which thin layers of hexamethyldisiloxane and tetraethyloxysilanes were deposited [8]. The process of finishing with nanoparticles was carried out using a TiO_2-SiO_2 nanocomposite solution.

The surface properties of the treated leathers were characterized by scanning electron and atomic force microscopy. The results showed that the hydrophobicity of the skin was clearly improved after the treatment with hexamethyldisiloxane, while the treatment with tetraethyloxysilane increased its hydrophilic properties. In addition, the strength properties and water vapor permeability of the skin have been improved.

The structure and composition of titanium and hafnium nitride coatings on orthopedic skin, obtained by condensation from the vapor-plasma phase under ion bombardment, were studied by scanning electron microscopy and X-ray fluorescence analysis. The rate of condensation of combined coatings was calculated. The micro- and nanostructure of condensates was fixed, and the stages of formation of a multilayer nitride coating on the skin were shown [9].

With laser exposure in a two-pulse mode, the effect of laser polishing of a leather split is observed. There is an understanding that for each type of laser there is a certain energy and time area for optimal efficient processing of split leather.

For ablative resurfacing of split skin, lasers with a short pulse duration are most suitable. Such laser devices with a short pulse duration at a certain power density are able to effectively remove the surface layer of the derma structure split (up to 100 µm).

The mechanism and modes of exposure are determined by the properties of the splits, the characteristics of the radiation (irradiation mode: continuous or pulsed, wavelength, laser power, energy in the pulse, the absorption coefficient of this radiation by natural skin and its individual components. Thus, it is possible to remove its defects from the surface of the leather split: scars, etc. Scars on the skin of animals significantly change the overall relief of the skin. In the dermis, elastic fibers disappear, and collagen fibers grow.

This paper presents the results on the use of laser radiation for skin resurfacing from the front and a split sample.

The purpose of the work is to establish the features of laser modification (polishing) of the skin surface from the front and split in the dual pulse mode.

EXPERIMENTAL

Materials and Methods

Laser Radiation

In this work, we used laser processing in the regime of double pulses of a sample of genuine leather. An LS-2134D yttrium-aluminum grenade 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). The sample was treated with laser radiation in the energy range 5–40 J at exposure times of 5–40 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 [10].

Tensile strength [11] is defined as the load at break of the skin or leather tissue of the fur, which falls on the unit cross-sectional area of the sample. This indicator to a greater extent characterizes the mechanical properties of the skin, the leather tissue of the fur and is normalized by state standards.

The tensile strength is determined on the scale of the loads of the tensile machine at the moment of destruction of the sample. Since the test specimen may have uneven thickness in the test area, the cross-sectional area at the rupture site is taken into account [11].

Tensile strength σr, Pa, is calculated by the formula:

$$\sigma p = \frac{P}{S} \quad (1)$$

where:

P is the load at break, N; S is the cross-sectional area of the specimen at the point of fracture, m^2.

The total elongation of the skin and leather tissue of the fur is set at a load at the moment of sample rupture or at a certain load per unit of cross section and is determined as a percentage of the initial length of the sample.

Relative elongation at break εp, %, is determined by the formula:

$$\varepsilon p = 100\frac{\Delta \mathrm{lp}}{I} \quad (2)$$

where:

is elongation at break of the sample, mm; lp is the absolute length of the sample at the moment of rupture, mm; l is the initial length of the sample, mm.

Hygroscopicity (G) [12] as a percentage is calculated by the formula:

$$G = \frac{m_1 - m}{m \times 100} \quad (3)$$

where:

m_1 is the mass of an elementary sample after moisture absorption, g;

m is the mass of the elementary sample before moisture absorption, g.

Moisture return (W) [13] as a percentage is calculated by the formula:

$$W = \frac{m_1 - m_2}{m \times 100} \quad (4)$$

where:

m is the mass of an elementary sample before moisture absorption, g;

m_1 is the mass of the elementary sample after moisture absorption, g;

m_2 is the mass of the elementary sample after moisture release, g.

Adhesion: The force required to lift a coating layer from the skin, applied evenly at an angle of about 90° to a solid bonding plate to which the finished skin is adhered [14]. The finished surface of the leather strip is glued to the bonding plate with a thermosetting adhesive. A force is applied to the free end of the skin strip to peel off the coating from it over a predetermined length. In this case, the coating remains on the bonding plate along with the adhesive layer. The force required to pull off is measured and recorded as the adhesion of the coating to the skin. The tests are carried out under conditions of normal relative humidity and temperature. If necessary, pre-moistened samples can be tested.

RESULTS AND DISCUSSION

In this work, we used laser processing of a split leather sample in the dual pulse mode. We used an LS-2134D yttrium aluminum garnet laser (LOTIS, Belarus) with a wavelength of 1064 nm, generating in a two-pulse mode (pulses separated by a time interval of 3 µs, pulse duration 10 ns). The sample was treated with laser radiation in the energy range of 40 J at exposure times of 40 sec. from front and back.

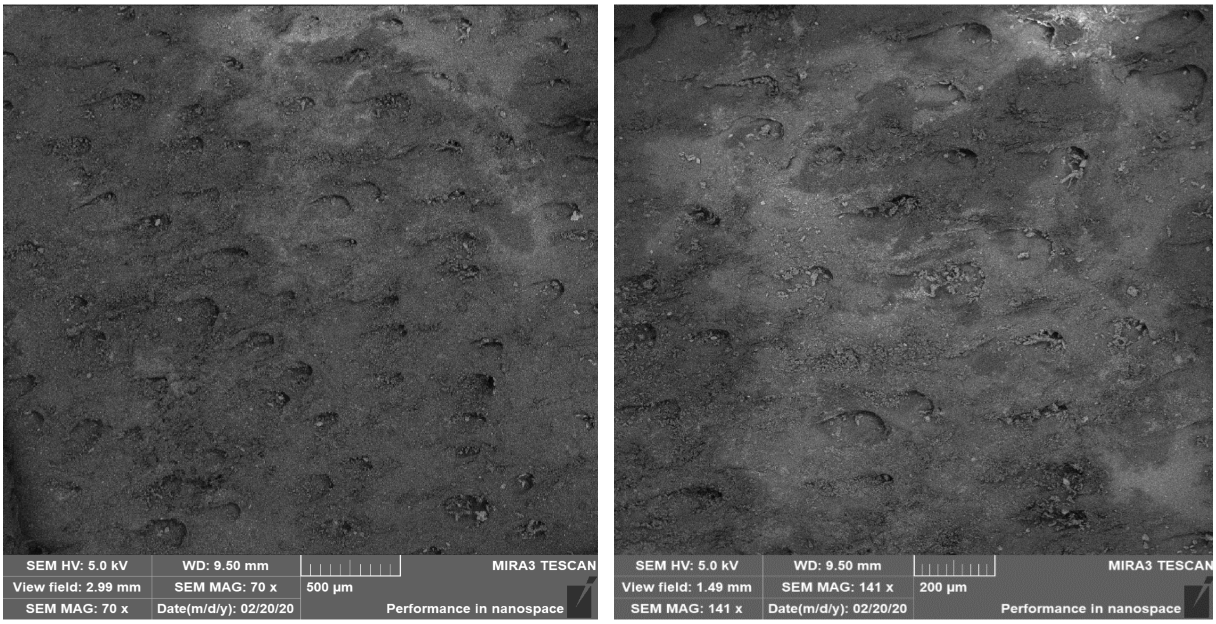
The study of the surface morphology of the leather split was carried out using a scanning electron microscope MIRA-3 (Czech Republic) with a system of microanalyzers from Oxford Instruments (Great Britain). The device allows you to simultaneously study the morphology of the surface of the material, determine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

The leather split leather of chrome tanning (produced in Uzbekistan) was studied, unpainted chrome waste leather was used, with the following physical and chemical parameters. In %: humidity - 52.4; total ash - 4.8; fatty substances - 3.2; naked substance 76.83; chromium oxide - 5.2; and hydrothermal destruction 92.0 °C, the front side of the sample of leather splits, ~ 1.2 mm thick, was treated with laser radiation.

According to [15–16], 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 [15]. The processes of nonequilibrium heating, melting, and ablation of a substance under the action of nanosecond pulses were studied in [15], however, the final stage of the ablation process, associated with the formation of the surface morphology of the coated polymer, has not been studied enough. It is known [15–18] that, under the action of a series of nanosecond pulses, the main mechanism of substance removal is thermomechanical ablation, which leads to the removal of the surface layer.

When exposed to IR laser radiation, energy is absorbed on the surface of the material, the layer depth can be from fractions to tens of micrometers. The nature of light erosion is determined to a large extent by the characteristics of the material itself: optical, thermophysical properties and structural inhomogeneities, etc.

Figure 1 a) and b) shows the morphology of the surface of the front side of a natural leather sample before and after laser resurfacing.

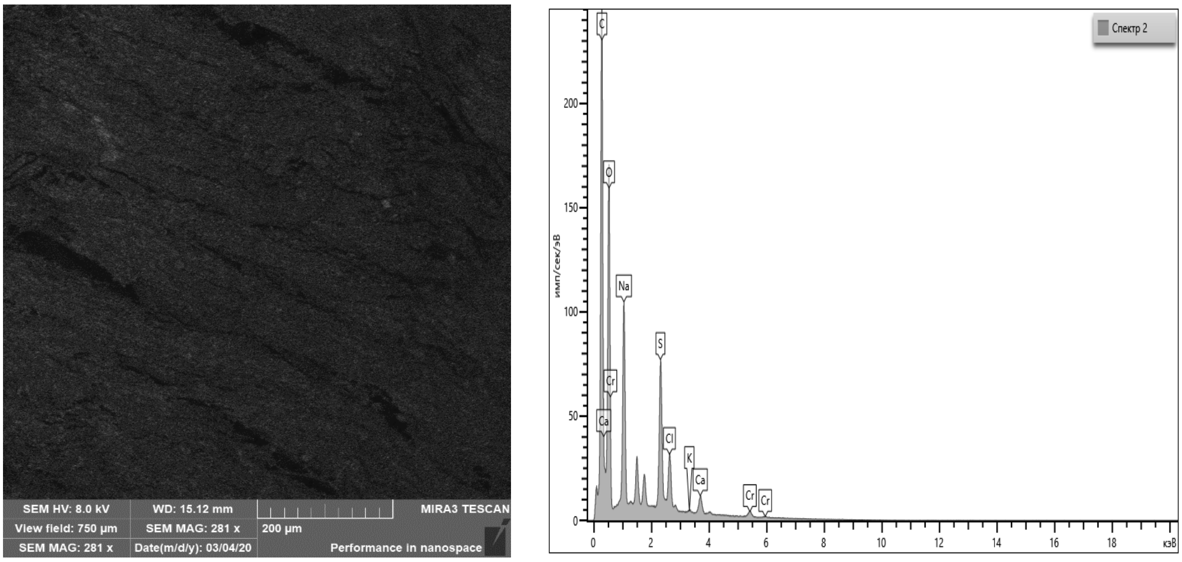


a) b)

Figure 1. Morphology of the surface of the front side of the skin before and after laser exposure: a) without exposure, b) after exposure (energy input 40 J, exposure time 40 sec)

Analysis of Figure 1 shows that in the process of laser ablation, the leather split is polished, the surface morphology of the leather split is changed, and the relief is smoothed out.

Figure 2 shows the morphology and elemental composition of the split leather before laser ablation.



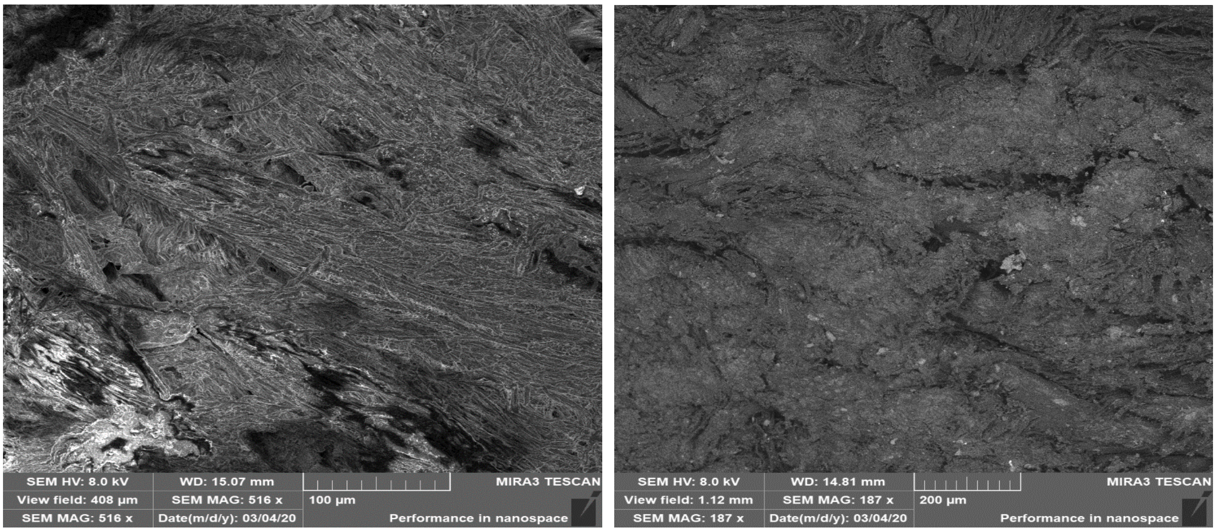
a) b)

Figure 2. Surface morphology of split leather before laser exposure

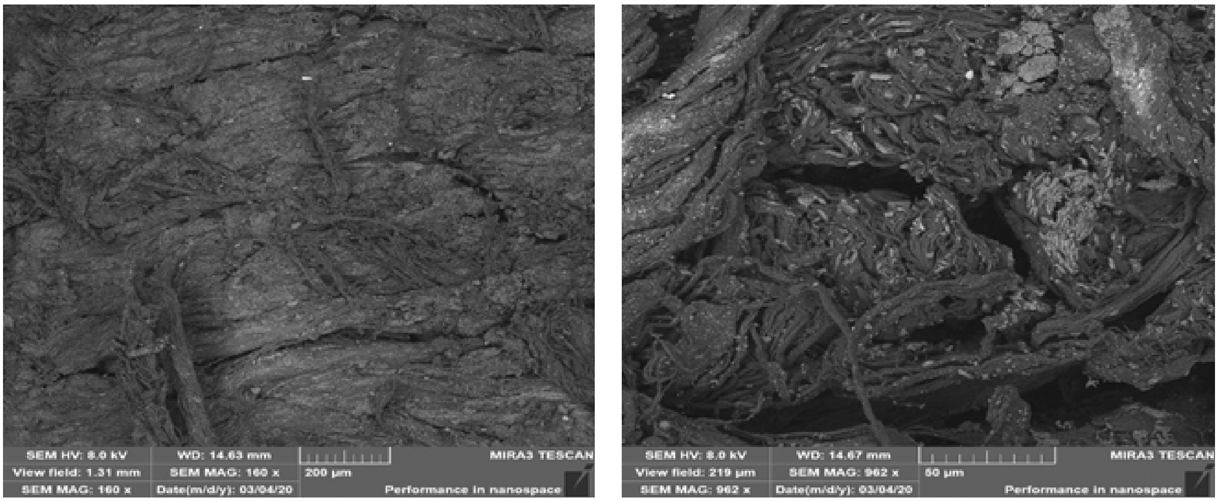
It should be noted (Figure 2) that the surface of the leather split is characterized by a heterogeneous structure and a loose structure.

Figure 3 shows the surface morphology of a leather split after laser exposure at various input energies and exposure times.

It should be noted that, in contrast to the front side, the laser exposure energy required to start the grinding process from a split leather sample increases. From the comparison of Figures 3 a), b), c), d) it follows that with an increase in the invested energy and exposure time, the surface relief of the skin splits is smoothed out, the skin structure appears better, on its surface (Figure 3 c), d)) are clearly visible separate collagen fibers with a thickness of 1-2 microns, the connections of these collagen fibers form bundles of fibers with a thickness of 30-50 microns, intertwining in different directions form a complex tissue of the dermis. Figure 3a) also clearly shows individual fibrils (thickness ~ 0.5 μm). It should be noted that the skin tissue on the reverse side of the sample has a fairly developed inner surface and has many empty spaces of various shapes, the sizes of which vary in a wide range from 7 to 40 μm.



a) b)



c) d)

Figure 3. Morphology of the surface of a leather split under various processing modes: a) input energy 25 J, exposure time 40 sec; b) input energy 30 J, exposure time 40 sec; c) input energy 35 J, exposure time 40 sec; d) input energy 40 J, exposure time 40 sec.

When obtaining and studying the properties of coating dyes, the problem of improving the physical and mechanical properties during long-term operation of products was solved. The non-pigmented primer contains 20% liquid rubber, a penetrator and water. The top coat contains a pigment concentrate, protein, aldehydes, a copolymer emulsion of butyl acrylate, methyl methacrylate and acrylic acid (in a ratio of 35.37:46.68:17.95, respectively) and water.

A distinctive feature of the new coating dyes is the use of the process of protein crosslinking with aldehyde, as well as the use of the product of emulsion copolymerization of butyl acrylate, methyl methacrylate and acrylic acid.

Laser processing of leather split, both with dense and loose coated structures, allows you to simultaneously modify the nanostructure of the leather tissue and the structure of the coating, as a result of which the area of mutual penetration of the two contacting polymers increases, leading to an improvement in the adhesion of the coating to the leather tissue up to 4 times, in addition, all physical and mechanical parameters are increased, as well as the hygienic properties of the composite material. Based on the results of this work, four pilot batches of leather fabric with a dense structure, 24 pieces each, and four pilot batches of leather with a loose structure, 16 pieces each, were produced, two batches of leather fabric with dense and loose structures were subjected to laser processing in the selected modes. The pigment concentrates included in the coating compositions were preliminarily modified. The results of changes in the physical and mechanical properties of batches of leather splits of dense and loose structures are presented in Table 1.

Table 1: Physical and mechanical properties of batches of coated leather split leather

№	Physical and mechanical indicators	Control	Experienced
	Dense structure		
1	Hygroscopicity, %	14,2	17,8
2	Moisture return, %	17,5	21,7
3	Tensile Strength, MPa	11,4	13,7
4	Elongation at stress 10 MPa, %	33,0	37,0
5	Coating resistance to repeated bending, points	3,0	5,0
6	Coating resistance to abrasion, revolutions	35,0	45,0
7	Coating adhesion to dry skin, N/m	570	1720

№	Physical and mechanical indicators	Control	Experienced
	Loose structure		
1	Hygroscopicity, %	16,3	20,1
2	Moisture yield, %	20,4	25,6
3	Tensile strength, MPa	8,8	10,9
4	Elongation at stress 10 MPa, %	36,0	41,0
5	Coating resistance to repeated bending, points	3,0	4,0
6	Coating resistance to abrasion, revolutions	32,0	40,0
7	Coating adhesion to dry skin, N/m	540	1640

As can be seen from the values given in the table, the leather split of a dense and loose structure with a coating, obtained using the developed technologies, improves the following indicators: hygroscopicity by 25.35 %; moisture return - 25.50%; skin strength by 20.17%; elongation by 12.12%; resistance of the coating to repeated bending by 33-66%; coating resistance to abrasion by 28.57%; adhesion of the coating to the skin up to 3 times.

CONCLUSIONS

For the first time, laser modification of a leather split surface sample from the front side was carried out using a laser generating in a two-pulse mode (pulses separated by a time interval of 3 µs, pulse duration 10 ns) with a wavelength of 1064 nm at an input energy of 40 J and an exposure time in the range of 40 sec.

It was found that laser exposure from the front and back sides leads to skin resurfacing. It is shown that resurfacing of the skin from the front and leather split starts at different input energies from the front side, from the split, which is associated with a looser structure of the skin from the split and its lower absorption of radiation.

The use of this technology for finishing split leather allows for high-quality sorting of finished products, i.e., if the coating is applied with large deviations, then the laser treatment after the final finishing increases the defectiveness of the coating.

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THE INFLUENCE OF PROTEIN AND ELASTOMER WASTE MIXTURE ON THE NBR-BASED ELASTOMER COMPOUND

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THE INFLUENCE OF PROTEIN AND ELASTOMER WASTE MIXTURE ON THE NBR-BASED ELASTOMER COMPOUND

ABSTRACT. The paper presents the influence of a mixture of elastomeric and protein waste from the footwear industry on the properties of elastomeric compounds based on NBR (butadiene-co-acrylonitrile) rubber, as well as their obtaining and characterization. The mixture of leather and rubber waste was cryogenically ground, in three grinding cycles, and the selected size was 0.35 mm, and the rotation speed of 14,000 rpm. After grinding, the leather and rubber waste mixture was functionalized with potassium oleate at a temperature of 60°C. The polymer compounds based on butadiene-co-acrylonitrile rubber (NBR) and the mixture of protein and elastomeric waste (in the ratio of 15, 20, 40, 50%) from the footwear industry were processed by mixing on an internal Brabender mixer, tested from a rheological, physical and mechanical point of view (hardness, elasticity and tensile strength) after conditioning for 24 h at room temperature according to the standards in force, but also by FT-IR spectroscopy performed with a double beam IR molecular absorption spectrometer, in the range 4000-400 cm^{-1}, using the FT-IR Thermo Nicolet iS 50, equipped with ATR with diamond crystal. Following characterisation, it can be said that they present optimal values that fall within the standards for the footwear industry.
KEY WORDS: elastomer, protein and elastomeric waste, composite, vulcanisate, compound

INFLUENȚA DEȘEULUI PROTEIC ȘI ELASTOMERIC ÎN AMESTEC ASUPRA PROPRIETĂȚILOR COMPOUNDULUI ELASTOMERIC PE BAZĂ DE NBR

REZUMAT. Lucrarea prezintă influența deșeului elastomeric și proteic în amestec, deșeu provenit din industria de încălțăminte, asupra proprietăților compoundurilor elastomerice pe bază de cauciuc NBR (butadien-co-acrilonitrilic) și, de asemenea, obținerea și caracterizarea acestora. Deșeul de piele și cauciuc în amestec a fost măcinat criogenic, în trei cicluri de măcinare, iar dimensiunea selectată a fost cea de 0,35 mm, viteza de rotație fiind de 14.000 rot/min. Deșeul de piele și cauciuc în amestec după măcinare a fost funcționalizat cu oleat de potasiu la temperatura de 60°C. Compoundurile polimerice pe bază de cauciuc butadien-co-acrilonitric (NBR) și deșeu proteic și elastomeric în amestec (în proporție de 15, 20, 40, 50 %), deșeu provenit din industria de încălțăminte, au fost prelucrate prin tehnica amestecării pe un amestecător Brabender intern, testate din punct de vedere reologic, fizico-mecanic (duritate, elasticitate și rezistență la rupere) după condiționare timp de 24 h la temperatura camerei conform standardelor în vigoare, dar și prin spectroscopie FT-IR realizată cu un spectrometru de absorbție moleculară IR cu fascicul dublu, în intervalul 4000-400 cm^{-1}, folosind FT-IR Thermo Nicolet iS 50, dotat cu ATR cu cristal de diamant. În urma caracterizărilor aferente putem spune că acestea prezintă valori optime ce se încadrează în standardele aferente pentru industria de încălțăminte.
CUVINTE CHEIE: elastomer, deșeu proteic și elastomeric, compozit, vulcanizat, compound

L'INFLUENCE DES DÉCHETS PROTÉIQUES ET ÉLASTOMÈRES EN MÉLANGE SUR LES PROPRIÉTÉS DES COMPOSÉS ÉLASTOMÈRES À BASE DE NBR

RÉSUMÉ. L'article présente l'influence des déchets mixtes élastomères et protéiques de l'industrie de la chaussure sur les propriétés des composés élastomères à base de caoutchouc NBR (butadiène-co-acrylonitrile), ainsi que leur obtention et leur caractérisation. Les déchets de cuir et de caoutchouc dans le mélange ont été cryobroyés, en trois cycles de broyage, la taille choisie était de 0,35 mm, et la vitesse de rotation de 14.000 tr/min. Les déchets de cuir et de caoutchouc en mélange après broyage ont été fonctionnalisés avec de l'oléate de potassium à une température de 60°C. Les composés polymères à base de caoutchouc butadiène-co-acrylonitrile (NBR) et de déchets mixtes élastomères et protéiques (dans un rapport de 15, 20, 40, 50%) de l'industrie de la chaussure ont été traités par la technique de mélange sur un mélangeur interne Brabender, testé d'un point de vue rhéologique, physique et mécanique (dureté, élasticité et résistance à la traction) après conditionnement pendant 24h à température ambiante selon les normes en vigueur, mais aussi par spectroscopie FT-IR réalisée avec un spectromètre d'absorption moléculaire IR à double faisceau, dans la gamme 4000-400 cm^{-1}, utilisant le FT-IR Thermo Nicolet iS 50, équipé d'ATR en cristal diamant. En suivant les caractérisations, on peut dire qu'ils présentent des valeurs optimales qui rentrent dans les standards de l'industrie de la chaussure.
MOTS-CLÉS : élastomère, déchets élastomères et protéiques, vulcanisé, composé

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INTRODUCTION

In the last decade, waste management has gained momentum not just at the European level, but at the global level. That is why rubber waste, especially used waste (from the footwear industry and not only) was perceived as a potential source of very valuable raw materials [1]. Recycling and reusing it (reintroducing up to 5 reuse cycles) can contribute to environmental protection – Directive 2008/98/EC [2], and protection of human health by eliminating emissions during the burning of this type of waste, as well as to increasing the turnover of specialized economic agents [3] and at the same time with the help of advanced technologies it is possible to contribute to the improvement of product quality [4]. Also, in December 2015 the European Commission adopted a set of measures related to the Circular Economy in order to achieve the transition to an economy in which resources are used sustainably [3, 5]. At the same time, our country issued a series of regulations and decisions related to waste management. An important Governmental Decision is GD no. 85/2002 – "Introduction of the waste management record and the European waste catalog": "Also, waste means a material that appeared as a result of a biological or technological process and that can no longer be used as such" [6]. Waste recycled, reused and processed by cryogenic grinding to micro or even nanometer sizes can be used, with the help of new advanced technologies, in the industry of processing elastomers, as well as plastomers, in the presence of new materials, which when used can restore predetermined properties [7, 8]. Butadiene-co-acrylonitrile (NBR) elastomers are easy to process due to properties such as high abrasion resistance, high temperature stability from -40 to +108°C (-40 to +226°F) [9-13]. The vulcanisates based on NBR, fillers, plasticizers and other ingredients specific to elastomers also show good resistance to mineral oils, petroleum products, resistance to aging (by adding accelerators and activators) and low gas permeability [14]. Some fillers can be successfully replaced (totally) by cryogenically ground waste (leather and rubber waste mixture from the footwear industry) [12].

The polymer compounds based on butadiene-co-acrylonitrile rubber (NBR) and protein and elastomeric waste from the footwear industry in a mixture of 15, 20, 40, 50% were processed by the mixing technique, tested in terms of rheological, physical and mechanical properties according to the standards in force, but also by FT-IR spectroscopy. Following characterisation, it can be said that they present optimal values that fall within the standards for the footwear industry [15].

EXPERIMENTAL

Materials

The materials used to obtain elastomeric compound (based on butadiene-co-acrylonitrile and protein and elastomer waste in mixture) were:

1) NBR rubber – butadiene-co-acrylonitrile rubber: content in acrylonitrile – 34%; Mooney viscosity (100%) – 32±3; density – 0.98 g/cm^3; 2) Stearin: white flakes; moisture – 0.5% max; ash – 0.025% max; 3) Zinc oxide microparticles (ZnO): white 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) Kaolin: white powder, molecular weight 100.09; 6) Leather and rubber waste mixture; 7) Leather and rubber waste mixture: ground waste functionalized with potassium oleate; 8) Mineral oil; 9) N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD 4010): density – 1.1 g/cm^3, solidification point above 76.5°C, flat granules coloured brown to dark violet; 10) Sulphur (S): vulcanization agent, fine yellow powder, insoluble in water, melting point: 115°C, faint odor; 11) Tetramethylthiuram disulfide (Th): curing agent, density – 1.40g/cm^3, melting point <146°C, an ultrafast curing accelerator, 12) Diphenylguanidine (D): curing agent, density 1.19 d/cm, Tt>145.

Methods

Preparation of Elastomeric Compounds Based on NBR Rubber and Functionalized Protein and SBR Rubber Waste in Mixture

The vulcanized polymer compounds with the mixture of protein and elastomeric waste were processed by mixing on an internal Brabender mixer, with the possibility to adjust the mixing speed and working temperature, respecting the order of introduction of the ingredients. After processing, the formulations (Table 1) are tested from a rheological and physical-mechanical point of view [15] (normal state and accelerated aging), in terms of biodegradation [16] and FT-IR spectroscopy [6]. Before being introduced into the formulations, the mixture of leather and rubber waste (15, 20, 40, 50%) was ground using a Retsch ZM 200 cryogenic mill, in three cycles, to different sizes (1 mm initially at 12,000 rpm, then to 0.5 mm at 12,000 rpm), and the selected size was 0.35 mm, at a rate of 14,000 rpm [17]. After grinding, the waste was functionalized with potassium oleate (in a proportion of 25%) at a temperature of 60°C [18].

The initial working temperature on the Brabender mixer is set at 45°C. The NBR elastomer (butadiene-co-acrylonitrile) is introduced for plasticization for 2’, at 45 rpm. After plasticizing the NBR, the rest of the ingredients are added and mixed for 4’ according to the working recipe, keeping the initial temperature, at 30 rpm. Mixing is continued for 2’ for homogenization at temperatures between 80-100°C, 100 rpm. After being obtained in the Brabender mixer, the polymer composites based on NBR rubber and leather and rubber waste in a mixture were rheologically tested, at 165°C, for 24’, on a Monsanto Rheometer. Rheological testing is done to determine the optimal vulcanization times by pressing in an electric press (in molds specific to elastomers), where standardized samples (15x15x2 mm) are obtained. Pressing to obtain the samples in standardized molds is done by the compression method between the plates of the electric press at optimal parameters, as follows: pressing temperature – 165°C, 6 minutes pressing time, 10 minutes cooling time and pressure – 300 kN. After that, the samples are left to rest for 24 h at ambient temperature, and then they are subjected to related characterizations according to the standards in force: physical-mechanical testing (normal state and accelerated aging at 70°C, 168 h) and FT-IR spectroscopy analysis [15-19].

Table 1: Polymer composite based on NBR (butadiene-co-acrylonitrile rubber) compounded with non-functionalized/functionalized protein and elastomer waste mixture

Symbol	MU [%]	B_0 (control)	BCB_0	BCB_1	BCB_2	BCB_3	BCB_4
Butadiene-co-acrylonitrile	%	100	100	100	100	100	100
Stearin	%	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	%	6	6	6	6	6	6
Silicon dioxide	%	30	-	20	10	-	-
Kaolin	%	30	30	30	30	30	30
Protein and elastomer waste functionalized with potassium oleate	%	-	-	15	20	40	50
Non-functionalized protein and elastomer waste	%	-	10	-	-	-	-
Mineral oil	%	3	3	3	3	3	3
IPPD 4010	%	1	1	1	1	1	1
Sulfur (S)	%	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethylthiuram disulfide (Th)	%	0.9	1.5	0.9	0.9	0.9	0.9
Diphenyguanidine (D)	%	0.5	0.5	0.5	0.5	0.5	0.5

B_0 – composite without waste

Characterization of Polymeric Compounds

The polymeric compounds were tested in terms of physical-mechanical properties like: hardness, °ShA – ISO 48-4:2018; elasticity %, ISO 4662:2017; tensile strength, N/mm^2 – SR ISO 37-2020, normal condition and accelerating ageing at 70°C and 168 h.

Physical-mechanical characterization was performed and then followed by spectrometric characterization. FT-IR spectral determinations were performed with a double beam IR molecular absorption spectrometer, in the range 4000-400 cm^{-1}, using the FT-IR Thermo Nicolet iS 50, equipped with ATR with diamond crystal.

RESULTS AND DISCUSSIONS

Rheological Characterization of Polymeric Compounds Based on NBR Elastomer and Protein and Elastomer Waste in Mixture

Through rheological testing, the optimal times of vulcanization in the electric press are established in order to obtain the samples that are subjected to physical-mechanical testing and FT-IR spectrometry.

In Table 2 are shown the arheological characteristics of mixtures based on NBR rubber compounded with protein and elastomer waste mixture non-functionalized and functionalized with potassium oleate.

Table 2: Rheological characteristics of mixtures based on NBR rubber compounded with protein and elastomer waste mixture

Rheological characteristics at 165°C	B_0 (control)	BCB_0	BCB_1	BCB_2	BCB_3	BCB_4
ML (dNm)	17.3	15.3	19.7	18.1	12.8	15.1
MH (dNm)	46.9	41	45.2	45	34.7	36.8
ΔM = MH-ML (dNm)	29.6	25.7	25.5	26.9	21.9	21.7
t_{s2} (min)	2.91	2.43	2.59	2.38	2.03	1.55
t_{50} (min)	6.38	3.12	3.44	3.18	2.54	2.03
t_{90} (min)	18.61	5.02	5.07	4.67	5.18	4.94

From the recorded rheological characteristics, Figure 1, it can be seen that by replacing the silicon dioxide (active filler) with leather and rubber waste in a non-functionalized/functionalized mixture (with potassium oleate 25% at a temperature of 60°C), the rheological characteristics are:

1. The maximum and minimum torque, ML and MH, decrease with the increase in the amount of protein waste and rubber in the non-functionalized/functionalized mixture (in different proportions from 15-50%);
2. ΔM = MH-ML – the torque variation decreases with the increase in the percentage of leather and rubber waste in the mixture, which indicates a stiffening of the samples, due to the agglomeration of protein waste fibers;
3. Due to the vulcanization (with vulcanization accelerators), a degradation of the samples is observed by some cross-linking bonds breaking, and the reversion phenomenon that is specific to vulcanized samples is also observed;
4. The optimal vulcanization time (t_{90}) decreases due to the replacement of the active filler with the mixture of protein and elastomeric waste;
5. the scorching time (t_{s2}) also decreases with the decrease in the percentage of leather and rubber waste mixture, or by the total replacement of silicon dioxide with waste functionalized with potassium oleate.

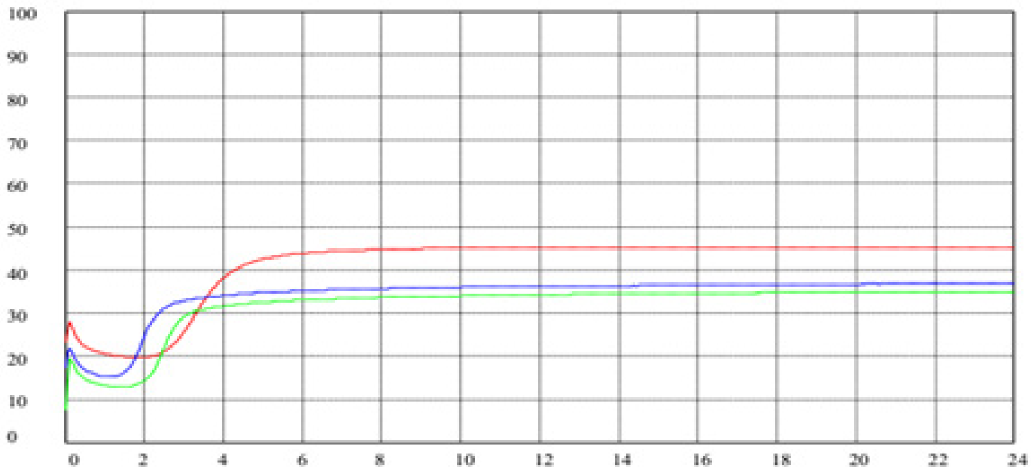

Figure 1. Torque variation expressed in dNm (OY axis) over time expressed in minutes (OX axis) for leather waste samples functionalized with potassium oleate: BCB_1 (red) – 15% waste; BCB_3 (green) – 40% waste; BCB_4 (blue) – 50% waste

Physical-Mechanical Characterization of Polymeric Compounds Based on NBR elastomer and Protein and Elastomer Waste in Mixture

Table 3: Physical-mechanical characterization of polymeric compounds based on NBR elastomer and protein and elastomer waste in mixture non-functionalized/functionalized with potassium oleate

Sample	B_0 (control)	BCB_0	BCB_1	BCB_2	BCB_3	BCB_4
Physical-mechanical characteristics: Normal State						
Hardness, °Sh A	61	62	61	59	58	57
Elasticity, %	18	20	24	24	25	25
Tensile strength, N/mm^2	11.3	5.1	9.5	8.85	3.16	2.67
Physical-mechanical characterization: Accelerated aging at 70°C and 168 h						
Hardness, °Sh A	66	64	63	62	61	60
Elasticity, %	24	22	22	23	24	26
Tensile strength, N/mm^2	14.47	5.6	13.75	8.77	3.25	2.75

Physical-mechanical characterisation was carried out according to standards in force.

As a result of physical-mechanical characterisation, Table 3, it follows that:

1. the hardness of polymeric compounds based on NBR rubber compounded with leather and rubber waste in mixture non-functionalized/functionalized with potassium oleate decreases proportionally with the amount of waste added to the mixture, especially for samples BCB_3 (40% functionalized waste, without active filler) and BCB_4 (the active filler is totally replaced with 50% functionalized waste) by maximum 6-7°Sh A;
2. the elasticity increases in different proportions, between 11-38% compared to the control sample B_0, with the increase in the percentage of non-functionalized/ functionalized waste and with the total replacement of the active filler (SiO_2), especially for the samples in which SiO_2 is totally replaced with protein and rubber waste in functionalized mixture (BCB_3 and BCB_4), indicating that the protein and elastomeric waste reduces the stiffness of the samples;
3. the tensile strength also decreases compared to the control sample (B_0),

especially for sample BCB_4 (compound with 50% waste functionalized with potassium oleate), the sample in which the silicon dioxide is replaced with leather and rubber waste mixture. Tensile strength decreases by approximately 78% compared to sample B_0;

4. after accelerated aging for 168 h at 70°C, hardness increases by 2-3°ShA for samples with 15-20% functionalized waste, as well as for samples in which the active filler is totally replaced with 40-50% waste (samples BCB_3 and BCB_4). In the case of elasticity after the accelerated aging process, a proportional increase by 4-8% compared to the control sample is observed.

Fourier Transformed Infrared Spectroscopy (FT-IR)

The stretching vibration bands of the polymer compounds based on NBR and protein and elastomeric waste in a functionalized mixture with potassium oleate are based on the bands in the reference spectrum of the NBR (butadiene-co-acrylonitrile) elastomer, Figure 2.

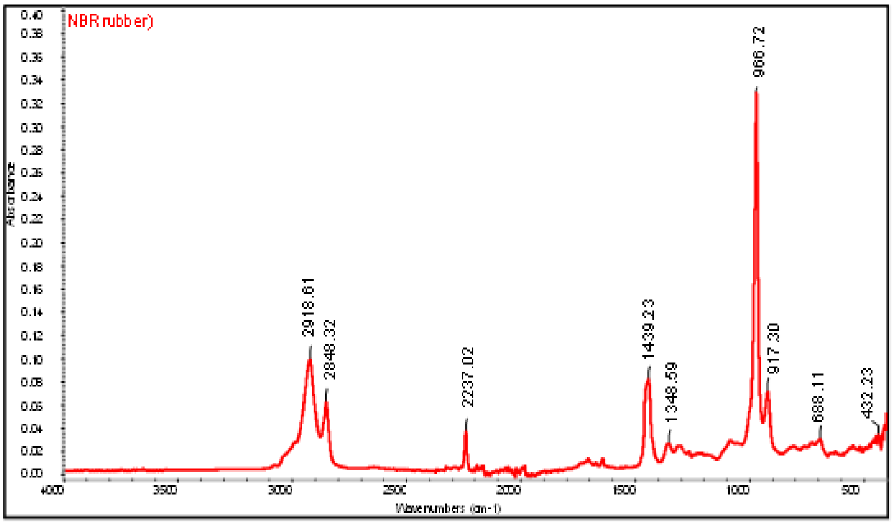

Figure 2. FT-IR spectrum for NBR rubber

The FT-IR spectrum (Figure 2) recorded for butadiene-co-acrylonitrile rubber (NBR) highlights the characteristic bands originating from the nitrile bond as well as the butadiene functional groups. Thus, the band at 2237.02 cm^{-1} confirms the presence of stretching groups of -CN bonds from nitrile as well as the stretching vibration of double bonds from butadiene =C-H at 966.72 cm^{-} [15, 19].

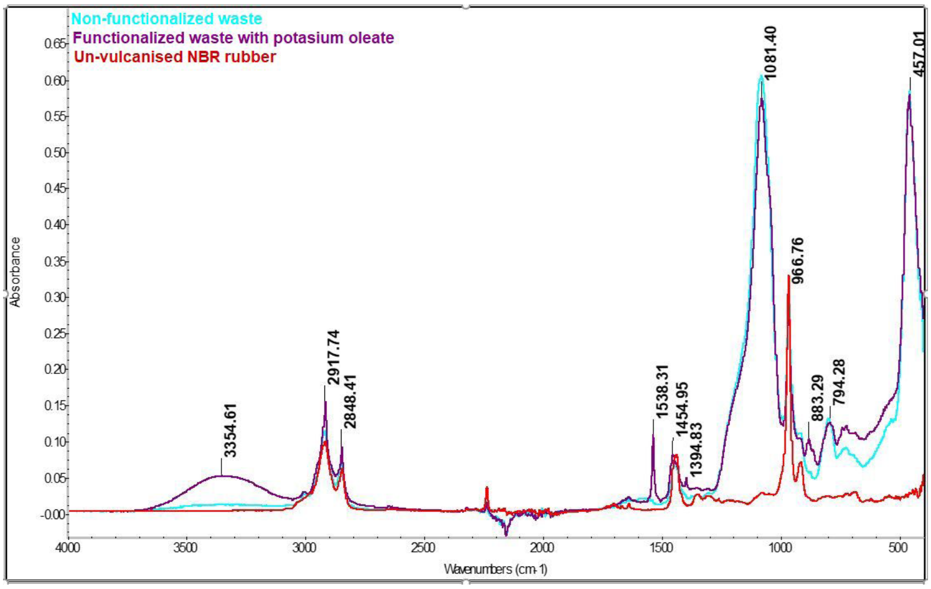

Figure 3. FT-IR spectra from non-functionalized/functionalized waste and un-vulcanized NBR elastomer

In the FTIR spectrum recorded for the butadiene-co-acrylonitrile elastomer (NBR) and unfunctionalized waste and functionalized with potassium oleate, Figure 3, the bands originating from the NBR rubber can be visualized at 2917.74, 2848.41, 1454.95, 966.76 cm^{-1}, and the presence of the silicon dioxide/kaolin at 1081.4, 794.28 and 457.01 cm^{-1}.

The bands showing the presence of potassium oleate can be observed at 1538.31 cm^{-1} and 1394.83 cm^{-1} respectively (associated with the asymmetric and symmetric stretching vibration of COO^- bonds).

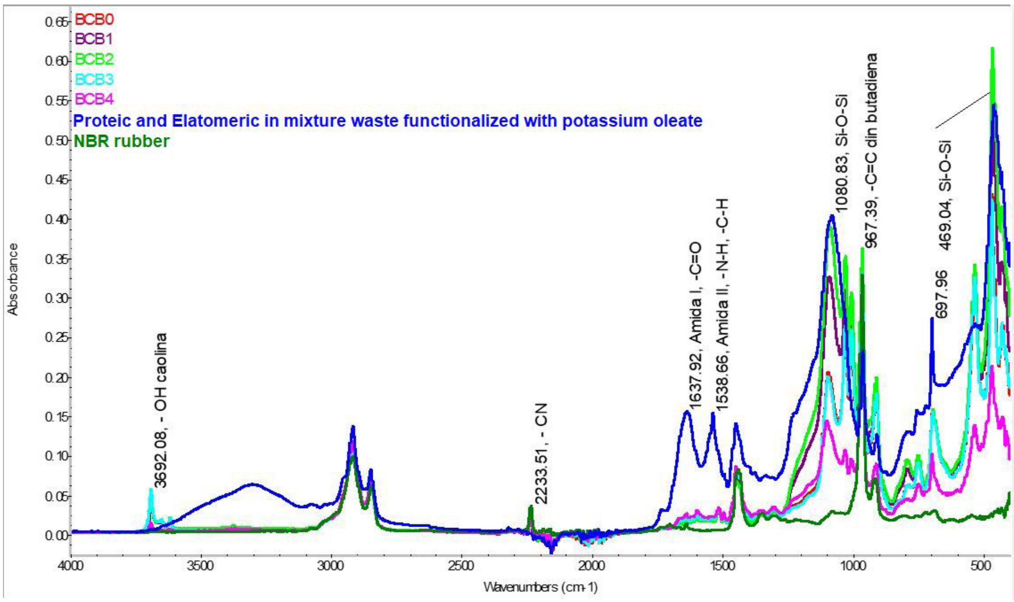

Figure 4. FTIR spectra of composites based on NBR rubber compounded with different amounts of leather and rubber waste non-functionalized/functionalized with potassium oleate

For sample BCB_0 (compound based on NBR rubber compounded with 10% non-functionalized leather and rubber waste) and BCB_1-BCB_4 (samples based on NBR rubber compounded with 15, 20, 40 and 50% protein and elastomeric waste functionalized with oleate potassium), the recorded FT-IR spectra highlight the characteristic bands of the individual components of butadiene-co-acrylonitrile rubber – 966.39 cm^{-1}, leather fibers, kaolin and silicon dioxide – 1080.83 cm^{-1} and 469.04 cm^{-1}. The intensity of the bands originating from the protein fibers is lower because, in addition to the leather fibers, the waste also contains high amounts of elastomer, which decreases the intensity of the bands known as Amide I – 1637.92 cm^{-1} and Amide II – 1538.66 cm^{-1}. For samples BCB_1 and BCB_2, the intensity of the bands obtained from silicon biooxide is higher than in the case of samples BCB_3 and BCB_4. From the recorded spectra it can be seen that the intensity of the bands coming from silicon dioxide and kaolin decreases as SiO_2 is replaced with protein and elastomeric waste in a mixture functionalized with potassium oleate.

CONCLUSION

The polymer compounds based on butadiene-co-acrylonitrile rubber (NBR) and protein and elastomeric waste from the footwear industry in a mixture of 15, 20, 40, 50% were processed by the mixing technique in an internal Brabender mixer, tested from a rheological point of view to establish the optimal vulcanization times for pressing in the electric press at controlled times, temperatures and pressures, to obtain products with characteristics necessary for use in the footwear industry: plates for soles for general use, but also in the food industry, technical plates, insoles, etc.

The bands of the stretching vibrations of the polymer compounds based on NBR and protein and elastomeric waste in a mixture functionalized with potassium oleate are based on the bands in the reference spectrum of the NBR elastomer. The presence of potassium oleate can be observed at 1538.31 cm^{-1} and 1394.83 cm^{-1}, respectively, associated with the asymmetric and symmetric stretching vibration of COO^- bonds. The recorded FT-IR spectra highlight the characteristic bands of the individual components of the NBR elastomer – 966.39 cm^{-1}, kaolin and silicon dioxide – 1080.83 cm^{-1} and 469.04 cm^{-1}. The intensity of the bands originating from the protein fibers is lower because the waste also contains high amounts of elastomer, which decreases the intensity of the bands known as Amide I – 1637.92 cm^{-1} and Amide II – 1538.66 cm^{-1}.

The physico-mechanical characterisations, normal state and accelerated aging were carried out according to the standards in force for testing elastomers in the footwear industry. Following the physico-mechanical characterisations, it is found that they are strongly influenced by the percentage of leather and rubber waste mixture, especially in the case of samples in which the active filler (silicon dioxide) is totally replaced by the waste (ground in three cycles up to size of 0.35 mm at a rate of 14,000 rpm) functionalized with potassium oleate, 25%, at 60°C, samples BCB_3 and BCB_4 presenting optimal values that fall within the related standards for the footwear industry.

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CITRIC ACID AS AN EFFECTIVE AND SAFE FIXING AGENT IN VEGETABLE TANNING PROCESS OF GOATSKIN

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CITRIC ACID AS AN EFFECTIVE AND SAFE FIXING AGENT IN VEGETABLE TANNING PROCESS OF GOATSKIN

ABSTRACT. Formic acid is known as a fixing agent in vegetable tanning process but this material is corrosive and irritant. Citric acid has the potential to be developed as an alternative fixing agent. This research aims to study the ability of citric acid as an alternative fixing agent in the tanning process, especially vegetable tanning of goatskin. The tanning process was carried out by the drum method. Pickled goatskins were tanned with mimosa and then fixed with citric acid. The concentration of citric acid varied from 1%; 1.5%; 2%; 2.5%; to 3%, to determine the optimum concentration. A fixing agent of 2% formic acid was used as a control. The results show that the control skin had similar characteristics to the treated skin. Physical properties of T4 have met the standard of SNI 0253-2009. It can be concluded that the optimal concentration of citric acid that can be used as an alternative fixing agent in vegetable tanning process of goatskin is 2.5%.
KEY WORDS: tanning, skin, fixing agent, citric acid

UTILIZAREA ACIDULUI CITRIC CA AGENT DE FIXARE EFICIENT ȘI SIGUR ÎN TABĂCIREA VEGETALĂ A PIEILOR DE CAPRĂ

REZUMAT. Acidul formic este cunoscut ca agent de fixare în procesul de tăbăcire vegetală, însă acest material este coroziv și iritant. Acidul citric are potențialul de a fi utilizat ca agent de fixare alternativ. Această lucrare de cercetare își propune să studieze capacitatea acidului citric ca agent alternativ de fixare în procesul de tăbăcire, în special la tăbăcirea vegetală a pielii de capră. Tăbăcirea s-a realizat în butoi. Pieile de capră piclate au fost tăbăcite cu mimosa și apoi fixate cu acid citric. Concentrația acidului citric a variat de la 1%; 1,5%; 2%; 2,5%; la 3%, pentru a determina concentrația optimă. S-a utilizat ca martor un agent de fixare pe bază de acid formic 2%. Rezultatele arată că pielea martor a avut caracteristici similare cu pielea tratată. Proprietățile fizice ale T4 au îndeplinit cerințele standardului SNI 0253-2009. În concluzie, concentrația optimă de acid citric care poate fi utilizată ca agent de fixare alternativ în procesul de tăbăcire vegetală a pieilor de capră este de 2,5%.
CUVINTE CHEIE: tăbăcire, piele, agent de fixare, acid citric

L'UTILISATION DE L'ACIDE CITRIQUE COMME AGENT DE FIXATION EFFICACE ET SÛR DANS LE PROCESSUS DE TANNAGE VÉGÉTAL DE LA PEAU DE CHÈVRE

RÉSUMÉ. L'acide formique est connu comme agent de fixation dans le processus de tannage végétal, mais ce matériau est corrosif et irritant. L'acide citrique a le potentiel d'être développé comme agent de fixation alternatif. Cette recherche vise à étudier la capacité de l'acide citrique comme agent fixant alternatif dans le processus de tannage, en particulier dans le tannage végétal des peaux de chèvre. Le processus de tannage a été effectué par la méthode du tambour. Les peaux de chèvre picklées ont été tannées au mimosa puis fixées à l'acide citrique. La concentration en acide citrique a été variée de 1 % ; 1,5 % ; 2 % ; 2,5 % ; à 3 %, pour déterminer la concentration optimale. Un agent de fixation à base d'acide formique à 2% a été utilisé comme témoin. Les résultats montrent que la peau témoin avait des caractéristiques similaires à la peau traitée. Les propriétés physiques du T4 ont satisfait à la norme SNI 0253-2009. On peut conclure que la concentration optimale d'acide citrique qui peut être utilisée comme agent de fixation alternatif dans le processus de tannage végétal de la peau de chèvre est de 2,5 %.
MOTS CLÉS : tannage, peau, agent de fixation, acide citrique

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INTRODUCTION

Nowadays, environmental factors have become a big issue in leather tanning process. Even the leather tanning industry needs to have an eco-green technology label which shows that the industry is environmentally friendly [1]. The tanning process cannot be separated from the fixation stage which affects the formation of the bond between skin collagen and tanning agent. This stage needs a chemical as a fixing agent that can arrange the charge of skin so that the bond can be formed. Various fixing agents are used depending on the material that will bind to skin protein. Chromium(III) and polyamines can be used as fixing agents for dyes, while polyacrylate is used as a fixing agent for chromium(III) [2]. This is due to its ability to form complexes through carboxylate groups. Sodium edate, tetrasodium edate, and trisodium citrate have also been reported to be used as fixing agents for fabric dyeing agents, where the fabric has functional groups similar to that of skin [3-4]. Formic acid is known as a fixing agent that is often used in the tanning process, especially in vegetable tanning process [5-9]. Formic acid combined with mineral acid as a fixing agent during the post-tanning operation also has been reported in a previous study [10]. Formic acid produces hydrogen ions (H^+) in the solution, resulting in the breaking of the salt bridges in skin protein. From a health perspective, formic acid is a corrosive and irritant chemical that also may cause severe skin burns. This has led some regions to apply occupational exposure limit values as a precaution. In addition, formic acid is expensive from an economical perspective [10]. Therefore, a safer and more effective fixing agent in the tanning process is needed.

One acid material that is easily found is citric acid. Citric acid is a weak acid that can be produced synthetically or naturally from fruits and vegetables, especially citric fruits [11]. It also has properties that are safe for the human body so there is no tendency to burn or irritate the skin. The presence of H^+ ions in the citric acid causes this acid to be used as a fixing agent in the tanning process. Therefore, identification of the ability of citric acid as a fixing agent was carried out in this study.

EXPERIMENTAL

Materials and Methods

Materials

The materials used were 6 sheets of pickled goatskins, mimosa (Mimosa ME produced by SODA), mimosa sulphited (produced by SODA), naphthalene sulphonates (Coralon OT produced by STAHL), sulphited oil (Derminol OCS produced by STAHL), citric acid (PT Golden Sinar Sakti) and sodium bicarbonate ($NaHCO_3$).

Methods

The pickled goatskins were processed through vegetable tanning using the drum method. The formulation of the tanning process is shown in Table 1. Variation of fixing agent in this study was divided into 5 treatments: treatment 1 (T1; 1% citric acid), treatment 2 (T2; 1.5% citric acid), treatment 3 (T3; 2% citric acid), treatment 4 (T4; 2.5% citric acid), and treatment 5 (T5; 3% citric acid). Control (T0; 2% formic acid) was used as a comparison. The vegetable-tanned skins were then characterized, including FT-IR analysis, shrinkage temperature, tensile strength, elongation, and tear strength. Treatment skin with the best physical properties was then analyzed using SEM (Scanning Electron Microscope) and compared to control skin.

RESULTS AND DISCUSSIONS

Tanning Process

Fixation stage has a major role in the tanning process because it determines the skin charge that results in interaction with the tanning agent. In general, fixation in vegetable tanning process involves acid as a fixing agent. This acid donates hydrogen ions to the collagen skin so that the charge becomes positive. In addition, the acid will lower the pH of the system.

Vegetable tanning process conducted in this study was carried out using citric acid as a fixing agent. Citric acid lowers the pH of the solution so that the pH at fixation stage is below the isoelectric point of the skin. The pH at

Table 1: The stages of vegetable tanning process of goatskin

Stage Process	Chemical	Time (min)
pH Adjustment	200% Water	
	2.5% $NaHCO_3$	90
Pretanning	200% Water	
	4% Coralon OT	45
Tanning	10% Mimosa sulphited	60
	3% Derminol OCS	45
	15% Mimosa	120
	4% Coralon OT	15
Fixation	1; 1,5; 2; 2,5; 3% Citric acid or 2% Formic acid	30

fixation stage in this study is presented in Table 2. It describes the fixation done at a pH of 3.5 when using formic acid and in the pH range of 4.2 to 4.5 in the use of citric acid. It is proved in previous studies that the skin proteins have strong internal cross-links in the isoelectric point range of skin, which is around pH of 5 to 7 [12-13]. This is due to the opposite charge of the protein being at its maximum. In addition, the spatial conditions of the protein chains are interconnected to form strong internal links, both from salt bridges and coordinate cross-links of hydrogen bonds. The addition of acid can decrease the pH of the system so that some of the salt bridges are broken due to the protonation of the carboxyl ion (Figure 1). This also causes the breaking of hydrogen bonds as a result of further crosslinked groups. Therefore, a new coordination group is formed that can react with the tanning agent [13].

Table 2: pH value of solution in fixation stage

Materials	pH of solution
T0	3.5
T1	4.5
T2	4.5
T3	4.2
T4	4.2
T5	4.2

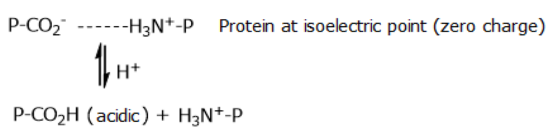


Figure 1. The effect of acid addition on the breaking of salt bridges in skin protein

Formic acid has a different pKa than citric acid. Formic acid in aqueous solution undergoes one stage of ionization (pKa = 3.74), while citric acid undergoes three stages of ionization (pK_{a1} = 3.13; pK_{a2} = 4.77; pK_{a3} = 6.40) [14]. According to Table 2, it is known that the fixation using citric acid was carried out at a pH below the pKa of formic acid for the control skin and below the pKa_2 of citric acid for the treated skin. This explains that fixation occurs with the help of H^+ ions resulting from the ionization of formic acid and citric acid. This phenomenon is in accordance with Gustavson's (1954) explanation above which states that the addition of acid can cause the skin to react with tanning agents [13]. Therefore, citric acid can also be used as a fixing agent in vegetable tanning process.

Mimosa is a condensed vegetable tanning material. This type of tanning material can react with collagen through hydrogen bonds and quinoid species to produce covalent bonds [2]. Therefore, a model of the structure of vegetable-tanned skin that is possible to form is shown in Figure 2.

The optimum concentration of citric acid that can react with the protein of the skin is 2% (Figure 3). An increase in the amount of reacted citric acid was observed at concentrations of 1% to 2%. This phenomenon states that the number of H^+ ions required for the fixation reaction is not sufficient at a concentration of 1%. Meanwhile, the amount of citric acid that reacts with the skin tends to be constant if the concentration of citric acid used is greater than 2%. This can happen because the number of H^+ ions needed has reached the saturation point. Therefore, the addition of citric acid concentration did not significantly affect the fixation reaction.

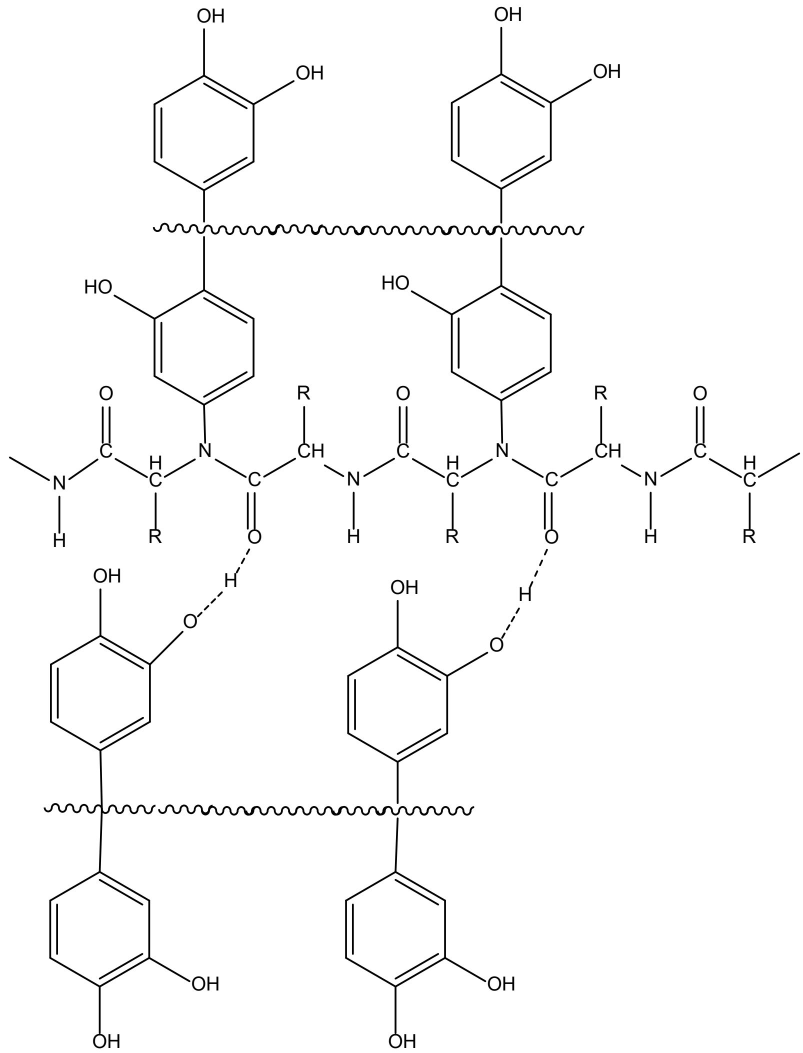


Figure 2. Hypothetical structure of vegetable-tanned skin

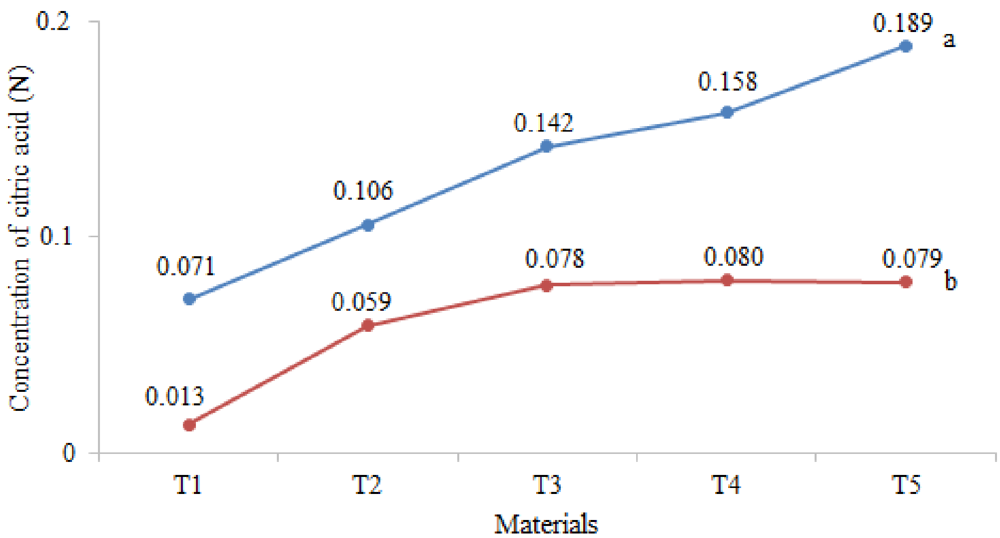


Figure 3. The concentration of citric acid (N): (a) added in the fixation stage and (b) reacts with collagen skin

Functional Groups

The vegetable-tanned skin is then characterized by FTIR spectrophotometer to identify the functional groups in the product. The result of infrared absorbance shows that the vegetable-tanned skin exhibits the characteristic absorbances of hydroxyl, methylene, and amide (Figure 4). The stretching vibrations of O-H are observed at 3398 cm^{-1} and 563 cm^{-1} [15]. Those bands are abroad due to the presence of hydrogen bonding. The vibration band at 2932 cm^{-1} comes from the asymmetric stretching vibration of C-H. Furthermore, the methylene group is detected at 1335 cm^{-1} [16-17]. Containing collagen, the absorbance of amide is observed at 1636 cm^{-1} from the stretching vibration of carbonyl collagen of amide I. The bending vibration of -OH also occurs at this wavenumber range, resulting in overlapping bands. Characteristic absorption of amide II is shown at 1543 cm^{-1} coming from stretching vibration of C-N and overlapping with N-H bending vibration band [15, 18-20]. Moreover, absorption of C-N is also detected at 1450 cm^{-1}. The absorption band at 1234 cm^{-1} proves the presence of amide III [19]. Whereas stretching vibration of C-O-C is observed at a wavenumber range of 1034-1111 cm^{-1} [16].

The use of formic acid as a fixing agent in control leather does not significantly affect the absorption band pattern of the skin. Likewise, for the use of citric acid in sample leather, the absorption bands resulted show that the leather has the same functional groups as skin. This is due to the fixing agents, both formic acid in control leather and citric acid in the sample, do not change the functional groups of the leather. The intensity of the absorption band of sample T1 is lower than that of other samples. This should be due to the fact that the amount of citric acid is not sufficient so that the mimosa could not be maximally fixed into the skin.

If the citric group is attached to the material, it will result in the absorption of asymmetric stretching of COO^-, symmetric stretching of COO^- and stretching of CH, respectively at 1629 cm^{-1}, 1383 $cm^{-1,}$ and 1054 cm^{-1} [21]. The presence of these absorption bands is difficult to observe due to the overlapping band of other functional groups. However, the similarity of the absorption bands between unfixed tanned leather and fixed tanned leather, indicates that the citric group is not bound to the skin. This confirms that only the H^+ ion of acid is involved in the fixation stage.

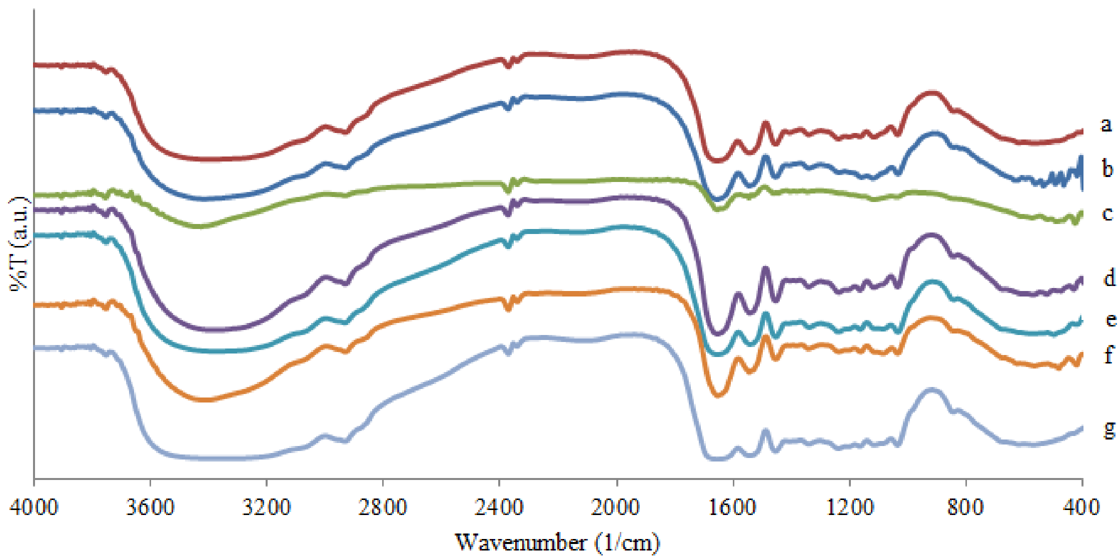


Figure 4. Infrared spectra of goatskins: (a) before fixation, (b) T0, (c) T1, (d) T2, (e) T3, (f) T4, (g) T5

Shrinkage Temperature

Shrinkage temperature is the temperature when the collagen structure of the skin begins to shrink by heating in a water medium [22]. Shrinkage temperature of the skin was measured to identify its stability to heat. Because of the same fixation reaction mechanism in the control skin as in the treated skin, there is no significant difference between the two (Table 3). The difference in shrinkage temperature shows the difference in the strength of the interaction between collagen and mimosa. This is following the statement of Covington (2009) that the difference in shrinkage temperature is influenced by the different types of reactions that occur [2]. Based on the structural model in Figure 2, it is known that collagen can bind to mimosa in two ways. The first way is the formation of hydrogen bonds, while the second is the formation of covalent bonds. The stronger covalent bond than the hydrogen bond causes the sample that has more covalent bonds to have a higher shrinkage temperature. This happens because it takes higher energy to break the covalent bond. The optimum shrinkage temperature is obtained when using 1.5% citric acid. This concentration is smaller than the required formic acid concentration (2%). This is possible because citric acid is a triprotic acid so it has a higher number of H^+ ions that can be donated than formic acid. Meanwhile, the number of cross-links also depends on the size of the polyphenolic molecule and the number of -OH groups of tannin molecules present [23].

Table 3: Shrinkage temperature of vegetable-tanned skins

Materials	Shrinkage temperature (°C)
T0	79
T1	76
T2	82.3
T3	76
T4	77
T5	80

In order to tan using vegetable extracts, the hides must be in contact with the extracts for a considerable time. The reason for this is that vegetable extracts are not simple products; they are composed of organic molecules of different molecular sizes [24]. It may be possible that the number of -OH groups of tannin molecules present in T2 is greater than others. This explains the different shrinkage temperatures even in similar fixation pH.

Tensile Strength, Elongation, and Tear Strength

Physical properties of tanned goatskin including tensile strength, elongation, and tear strength were tested. Tensile strength is the amount of load needed to pull tanned goatskin until the collagen fibers are broken. Meanwhile, elongation is a measure of the stretch characteristics of tanned goatskin produced by a tensile load. The tear strength indicates the maximum limit of the skin to be torn. The results are presented in Table 4.

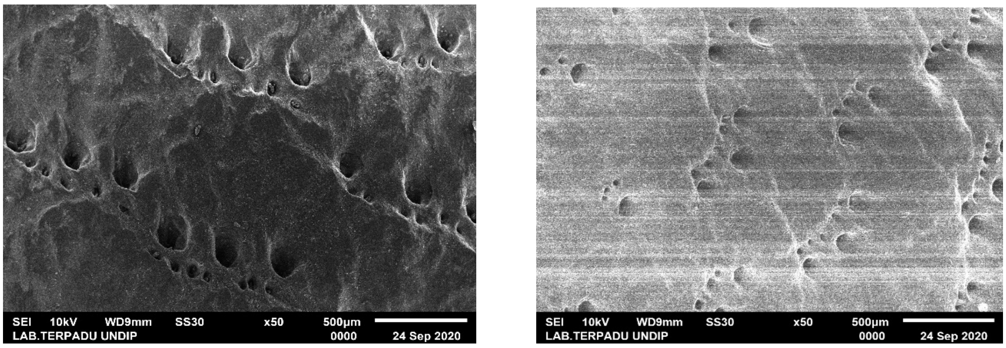
Table 4: Physical properties of vegetable-tanned skins

Materials	Tensile strength (N/cm^2)	Elongation (%)	Tear strength (N/cm)
T0	2163.23	30.42	112.03
T1	1257.52	40.12	94.56
T2	1521.2	25.78	81.3
T3	2402.12	26.92	111.9
T4	1604.97	48.44	167.44
T5	1787.94	26.20	91.66

The test result in Table 4 shows that there is no definite trend between the difference in the amount of citric acid and the physical properties. In addition, it is also known that the physical property values of the sample revolve around its control, indicating similar strength interaction on skin. When compared to SNI 0253-2009 [25], not every skin meets the standard. This indicates that the skins need to be further processed in post-tanning to obtain the appropriate properties. Among these skins, the skin that has met the SNI 0253-2009 standard is T4.

Surface Morphology

SEM analysis was employed to observe the surface morphologies of the control and sample (T4). The results are shown in Figure 5. It can be seen that the grain surface of the sample is flatter and fuller compared to the control. This is possible due to the filling effect resulting from the interaction of collagen and citric acid. Citric acid, which is a triprotic acid, provides a higher pH value in the system than formic acid. This allows the reaction between collagen and mimosa to be slower, resulting in a more flat and fuller tanned skin.



(a) (b)

Figure 5. Surface morphology of vegetable-tanned skins: (a) T0 and (b) T4

CONCLUSIONS

Citric acid can be used as an alternative fixing agent to substitute formic acid in vegetable tanning process. The control skin had similar characteristics to the treated skin. The optimal concentration of citric acid as a fixing agent is 2.5%, which has met the standard of SNI 0253-2009.

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TESTING OF MEDICAL SHEEP FUR WITH ANTIMICROBIAL PROPERTIES – PART 2

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TESTING OF MEDICAL SHEEP FUR WITH ANTIMICROBIAL PROPERTIES – PART 2

ABSTRACT. There are a number of people with rheumatic, joint and muscle diseases, and the medical treatment of patients suffering from these diseases requires an improvement through alternative methods. Pain is the main symptom of rheumatic diseases and chronic pain affects the physical and mental condition, lowering quality of life and ability to work. Natural products derived from plants with antimicrobial, anti-inflammatory, antioxidant, and chemo-preventive properties have been used for many generations in traditional medicine. 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 (daphne, ginger, basil), which can be used to treat the surface of tanned sheep fur for medical purposes. Ecological requirements 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. 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, bootees, etc.). They can improve rheumatic, muscular and circulatory conditions, complementing the medical treatment of patients suffering from these conditions. Heat can relieve rheumatic pains (transmitted through the application of natural fur). 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 – A DOUA PARTE

REZUMAT. Există o serie de persoane cu afecțiuni reumatismale, articulare și musculare, iar tratamentul medical al pacienților care suferă de aceste boli necesită o îmbunătățire prin metode alternative. Durerea este principalul simptom al afecțiunilor reumatismale, iar durerea cronică afectează starea fizică și psihică și astfel scade calitatea vieții și capacitatea de muncă. Produsele naturale derivate din plante cu proprietăți antimicrobiene, antiinflamatorii, antioxidante și chimiopreventive au fost folosite de multe generații în medicina tradițională. 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 (dafin, ghimbir, busuioc), care pot fi utilizate pentru tratarea suprafeței blănurilor de oaie tăbăcite în scopuri medicale. Cerințele ecologice au dus la dezvoltarea unor noi tehnologii de prelucrare a blănurilor, cum ar fi tăbăcirea wet-white pentru a elimina sau reduce cantitatea de săruri complexe de crom trivalent. 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, botoși etc.). Acestea pot ameliora afecțiunile reumatismale, musculare, circulatorii, completând tratamentul medical al pacienților care suferă de aceste afecțiuni. Căldura poate ameliora durerile reumatice (transmise prin aplicarea blănii naturale). 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 – DEUXIÈME PARTIE

RÉSUMÉ. Il existe un nombre de personnes atteintes de maladies rhumatismales, articulaires et musculaires, et le traitement médical des patients souffrant de ces maladies nécessite une amélioration par des méthodes alternatives. La douleur est le principal symptôme des affections rhumatismales et la douleur chronique affecte l'état physique et mental et diminue ainsi la qualité de vie et la capacité de travailler. Les produits naturels issus de plantes aux propriétés antimicrobiennes, anti-inflammatoires, antioxydantes et chimiopréventives sont utilisés depuis de nombreuses générations en médecine traditionnelle. 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 (laurier, gingembre, basilic), qui peuvent être utilisées pour traiter la surface de la fourrure de mouton tannée à des fins médicales. Les exigences écologiques ont conduit au développement de nouvelles technologies de transformation de la fourrure, comme le tannage wet-white pour éliminer ou réduire la quantité de sels complexes de chrome trivalent. Les fourrures 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, botillons, etc.). Ils peuvent améliorer les affections rhumatismales, musculaires et circulatoires, en complément du traitement médical des patients souffrant de ces affections. La chaleur peut soulager les douleurs rhumatismales (transmises par l'utilisation de fourrure naturelle). L'article présente la caractérisation chimique, physico-mécanique et microbiologique des fourrures naturelles à usage médical.

MOTS CLÉS : fourrures médicales, huiles essentielles, propriétés antimicrobiennes

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INTRODUCTION

Ecological requirements as well as requirements related to fur assortment characteristics have led to the development of new fur processing technologies, such as, sanitation of natural fur by binding some therapeutic species of plants to the dermis and/or the hair. 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. Natural products derived from plants with antimicrobial, anti-inflammatory, antioxidant, and chemo-preventive properties have been used for many generations in traditional 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. Essential oils contain terpene compounds, which can be acyclical (hydrocarbons, alcohols, carbonyl compounds) and cyclical (hydrocarbons, alcohols and ethers, carbonyl compounds and esters) [6-11].

Eugenol (the principal component of daphne essential oil) is characterized by a high antimicrobial action against a variety of microorganisms.

Linalool and eucalyptol are the principal components of basil essential oil and play a major role in the anti-inflammatory activity provided by the essential oils containing them.

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, bootees etc.) [12-15]. The antibacterial properties of the sheepskins were evaluated by standardized methods [16-18]. Products have been made based on essential oils with therapeutic properties (daphne, ginger, basil), which can be used to treat the surface of tanned sheep fur for medical purposes [19].

The medical treatment of patients with rheumatic, joint and muscle diseases can be improved by alternative methods. Pain is the main symptom of rheumatic diseases and chronic pain affects the physical and mental condition and thus lowers the quality of life and ability to work. For these diseases are recommended herbal plant species with antiallergic, anti-inflammatory effects, etc. The medical fur articles can improve rheumatic, muscular and circulatory conditions, complementing the medical treatment of patients suffering from these conditions. Heat can relieve rheumatic pains (transmitted through the application of natural fur).

EXPERIMENTAL

Materials

- Sheepskins tanned with syntans based on phenolsulfonic acids and aromatic oxysulfones (I.N.C.D.T.P. – Division Leather and Footwear Research Institute Bucharest, Romania) [12, 15];
- Woolen Sheep skins (Merinos) treated during fatliquoring operation with products based on essential oils (daphne, ginger, basil);
- Product P-D based on daphne essential oil: dry substance – 18-19%, pH (10% solution) – 4-4.5, density – 0.880-0.890 g/cm^3;
- Product P-G based on ginger essential oil: dry substance – 20-21%, pH (10% solution) – 4-4.5, density – 0.920-0.930 g/cm^3;
- Product P-B based on basil essential oil: dry substance – 17-18%, pH (10% solution) – 4-4.5, density – 0.870-0.880 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 1×10^5 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]:

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

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:

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

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 phenolsulfonic acids and aromatic oxysulfones [12]. Sheep fur was tanned (free of metals) and was treated with the product based on essential oils with therapeutic properties (daphne, ginger, basil).

Woolen sheep skins (Merinos) were treated during fatliquoring operation with 20-30g products based on essential oils (daphne – P-D, or ginger – P-G, or basil – P-B) /1000g fur tanned weight:

- P-D-1 – Sheep fur treated with 20g product P-D/1000g fur tanned weight;

- P-D-2 – Sheep fur treated with 30g product P-D/1000g fur tanned weight;
- P-G-1 – Sheep fur treated with 20g product P-G/1000g fur tanned weight;
- P-G-2 – Sheep fur treated with 30g product P-G/1000g fur tanned weight;
- P-B-1 – Sheep fur treated with 20g product P-B/1000g fur tanned weight;
- P-B-2 – Sheep fur treated with 30g product P-B/1000g fur tanned weight.

The products based on essential oils contain 55-60% essential oil (daphne – P-D, or ginger – P-G, or basil – P-B), 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, 20].

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 11.20-13.50% and volatile wool matter 9.10-11.80%, extractable dermal substances 10.30-14.40% and wool extracts 0.70-0.90%, ash 3.60-3.90%, 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 250-270 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 170-210N, 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

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

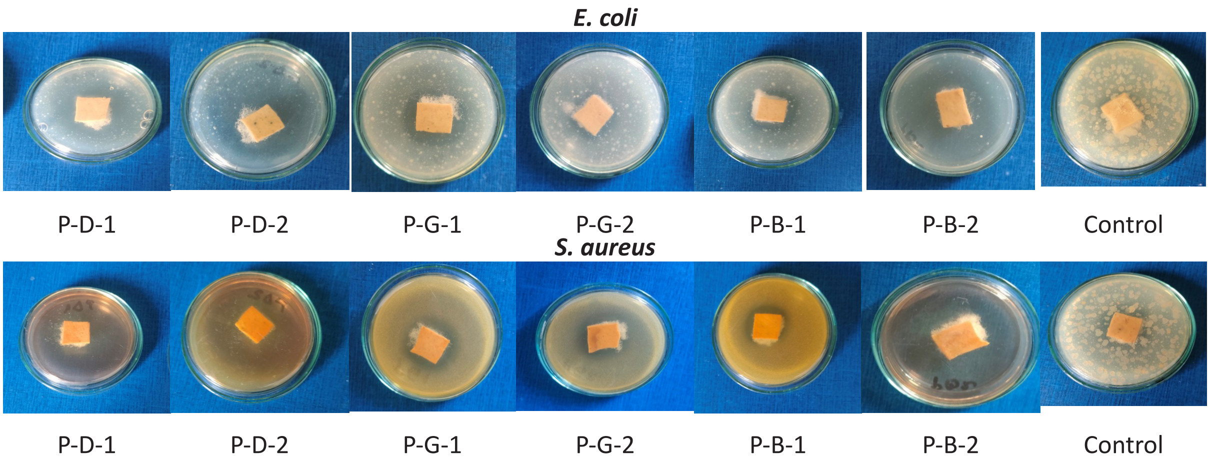

Figure 1. Images of Petri plates showing antibacterial effect after 24 h of incubation

The results of antimicrobial activity of natural fur samples against *Staphylococcus aureus* and *Escherichia coli* according to EN ISO 20645:2004 expressed as inhibition zone (H) are presented in Table 1.

Table 1: Evaluation of the antibacterial activity

	E. coli (ATCC 10536)		*S. aureus* (ATCC 6538)	
Code	Inhibition zone (mm)	Evaluation	Inhibition zone (mm)	Evaluation
P-D-1	11.5	Satisfactory effect	25	Satisfactory effect
P-D-2	20	Satisfactory effect	25	Satisfactory effect
P-G-1	5	Satisfactory effect	9	Satisfactory effect
P-G-2	2.5	Satisfactory effect	7	Satisfactory effect
P-B-1	3.5	Satisfactory effect	5	Satisfactory effect
P-B-2	25	Satisfactory effect	25	Satisfactory effect
Control	-	Unsatisfactory effect	-	Unsatisfactory effect

According to the standard, excellent antimicrobial protection is for H ≥ 1. The results of antimicrobial activity shown in Table 1 indicate that all antimicrobial treatments regardless of applied agents resulted in antimicrobial protection. Antiseptic treatments and essential oils resulted in a high degree of antimicrobial protection to both bacteria – Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*. Nevertheless, taking into account the extremely high value of inhibition zone, essential oils are indispensable for antibacterial protection.

Absorption Test

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=1x10^5CFU/mL		
P-D-1	T_0=1x10^5CFU/mL T_{24}=4 CFU/mL	100%	4.40
P-D-2	T_0=1x10^5CFU/mL T_{24}=0 CFU/mL	100%	5.00
P-G-1	T_0=1x10^5CFU/mL T_{24}=8 CFU/mL	99.99%	4.10
P-G-2	T_0=1x10^5CFU/mL T_{24}=5 CFU/mL	100%	4.30
P-B-1	T_0=1x10^5CFU/mL T_{24}=10 CFU/mL	99.99%	4.00
P-B-2	T_0=1x10^5CFU/ml T_{24}=7 CFU/mL	99.99%	4.15
Control	T_0=1x10^5CFU/mL T_{24}=4.5x10^4 CFU/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=1x10^5CFU/mL		
P-D-1	T_0=1x10^5CFU/mL T_{24}=2 CFU/mL	100%	4.70
P-D-2	T_0=1x10^5CFU/mL T_{24}=4 CFU/mL	100%	4.40
P-G-1	T_0=1x10^5CFU/mL T_{24}=4 CFU/mL	100%	4.40
P-G-2	T_0=1x10^5CFU/mL T_{24}=1 CFU/mL	100%	4.90
P-B-1	T_0=1x10^5CFU/mL T_{24}=6 CFU/mL	99.99%	4.22
P-B-2	T_0=1x10^5CFU/mL T_{24}=3 CFU/mL	100%	4.52
Control	T_0=1x10^5CFU/mL T_{24}=5.5x10^4CFU/mL	45.00%	0.26

This antimicrobial activity assay was performed for both target bacteria and the results are expressed as mean values of three biological replicates. The antibacterial activity value was calculated according to ISO 16187 Absorption test. Using this method all the samples showed strong efficacy against both bacteria.

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. Eugenol is characterized by a high antimicrobial action against a variety of microorganisms. Eugenol, d-limonene, linalool, eucalyptol – the ingredients in the composition of daphne, basil and ginger oils, with analgesic and disinfectant properties, are effective in the treatment of patients suffering from rheumatism, lumbar radiculopathy and cervical spondylosis, stimulating blood circulation and relieving rheumatic and joint pain.

Daphne oil contains 46.95% eugenol, 43.37% d-limonene, 7.14% alpha terpinolene, 0.93% alpha terpinene etc. Ginger oil contains d-limonene 21.88%, camphene 21.47%, alpha-pinene 11.29%, cineole 10.46%, zingiberene 9.32% etc. Basil oil contains 65.88% linalool, 5.37% eucalyptol, 3.87% p-allyl anisole, 3.23% alpha-cadinene, 0.79% eugenol etc. [13, 14].

The results of the antimicrobial tests highlighted a strong antibacterial character of the sheep fur samples tested, having a "satisfactory effect", because no bacterial multiplication was observed [16]. Sheep fur samples treated with materials based on essential oils (daphne, ginger, basil) 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, bootees, 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 phenolsulfonic acids and aromatic oxysulfones.

▪ The products based essential oils (daphne, ginger, basil) 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 "satisfactory effect", because no bacterial multiplication was observed.

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

▪ Samples P-D-1, P-D-2 and P-G-2 had maximum antimicrobial activity, 100%, against *S. aureus* and *E. coli*.

▪ Eugenol, d-limonene, linalool, eucalyptol the ingredients in the composition of daphne, basil and ginger 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.

▪ The product based 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, bootees 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, as heat can relieve rheumatic pains (transmitted through the application of natural fur).

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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*. Newsletters 7 and 8 of 2022 are given below.

NEWS 7/2022

Dying for Leather?

This kind of rhetoric is often heard when people talk about desirable bags, shoes, saddles, jackets, sofas... They must own them, they "can't live without them", but of course nobody would actually die for them.

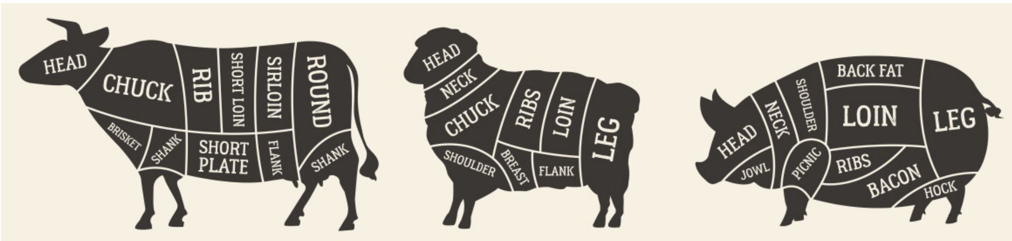
Now, whether people "live or die" for leather or not, certain activist groups claim that "every year a billion animals are killed for leather". Can this be true? The answer is clearly, NO!

But where does that statement come from? Who knows… But the intention behind it is clear; to undermine the good reputation of leather in the belief that it will hurt the meat industry.

However, let's look at the facts. The vast majority of leathers comes from hides and skins of cattle, sheep, goats and pigs (as people can find out by searching on the Internet). These farm animals are kept because they provide milk and meat for human consumption, and they often graze on land that is not suitable for crops (e.g. steppe, grassland). However, these animals are killed for meat for human nutrition, not for the production of leather. The hide or the skin is just a by-product and thank to their processing into leather, they do not become waste.

Since cattle are larger than sheep and goats, most leather comes from cattle. According to the WWF, there are 1.6 billion cattle on the planet, and according to the FAO 293 million were slaughtered in 2020.

Still not sure? Cattle weighs anything between 200 to over a 1000 kg. The hide is only 7% of the weight and 1% of the value. What do think happens to the rest of the animal. Does anyone believe that 100s of kg of meat, bones, and offal are thrown away while only the hide is kept for leather? Imagine the waste mountain.



If we want to make the world a better place, we need reliable information. That is information on which we can build an opinion. One thing is irrefutable; Hides & skins are by-products of milk and meat production and it is better to use them as leather than to turn them into waste.

edited by

COTANCE

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VDL

Verband der Deutschen Lederindustrie e.V.

NEWS 8/2022

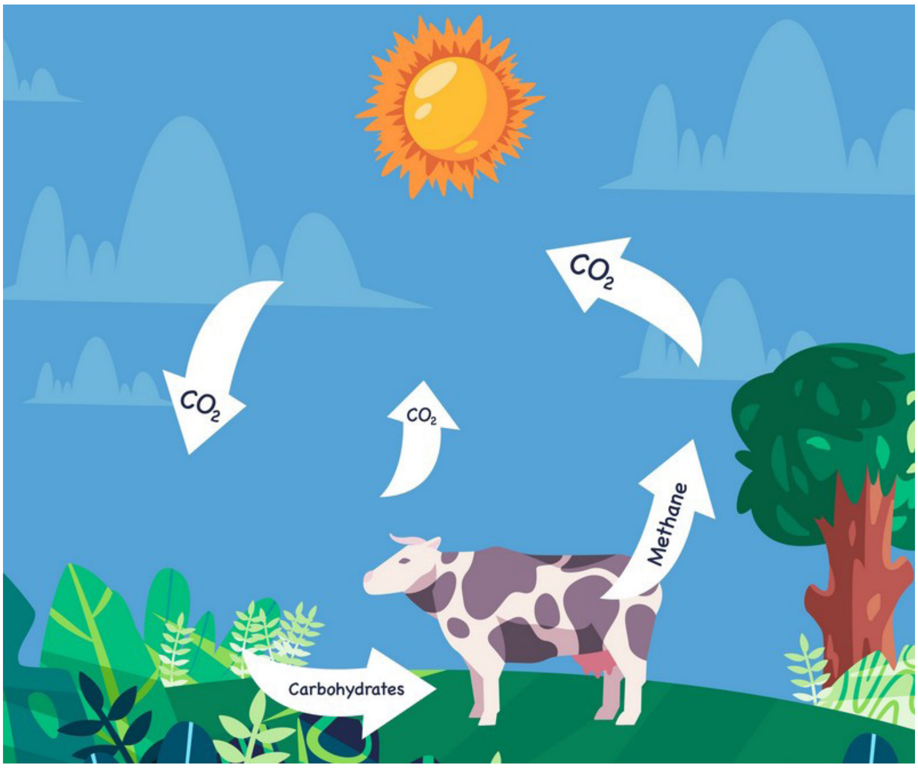
Leather for Christmas? Of course!

The hides and skins of cattle, sheep and goats are processed only because they are a by-product of the dairy and meat industries and because they can be used to make a wonderful material: Leather. This upcycling is not new, people have been doing it for almost as long as they have been around.

But aren't "vast amounts of food" necessary to raise these animals? Cattle, sheep and goats are ruminants that can digest cellulose, which humans cannot. That is why these animals can be kept on grassland, i.e. land on which plants cannot be grown for human food because it is too steep, too wet, too dry or the soil quality is too poor. The animals "improve" these areas by their "tramp", their dung and keeping the areas free by grazing. This highly effective symbiosis between grazing land and animals has developed over millions of years.

Hold on, not all cattle are fed only grass or graze on grassland! The cultivation of every kilogram of plant food produces three to five kilograms of biomass not suitable for human consumption. One example: cereals. We use the grains as food, the rest of the plant is not digestible for us humans.

Prof. Windisch of the Technical University of Munich speaks of "circular economy" when ruminants turn the inedible biomass into edible food in the form of milk and meat and, quite incidentally, fertiliser for plants is produced in the form of slurry and manure.



Well, there is still the matter of methane. Ruminants produce methane through their digestion, which is released into the atmosphere and is considered harmful to the climate. However, methane has a fairly short life span and constant numbers of livestock do not increase the methane concentration.

What would be the alternatives? Let the biomass rot in the fields or process it in biogas plants? That also causes emissions, but we produce less food.

Nature has developed perfect cycles, nothing remains unused. Let us reflect on this!
Shall we use leather? Of course!

edited by COTANCE

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Title. Title (Centered, 12 pt. TNR font) should be short and informative. It should describe the contents fully but concisely without the use of abbreviations.
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Introduction. Should include the aims of the study and results from previous notable studies.
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