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	CONTENTS	***CUPRINS***	***SOMMAIRE***	
Lei QIN **Jiachen FAN** **Xiuxing WANG**	Effects of Midsole Hardness and Insole Materials on Shock Absorption in Protective Boots	Influența durității tălpii intermediare și a materialelor pentru branțuri asupra capacității cizmelor de protecție de a absorbi șocurile	L'influence de la dureté de la semelle intermédiaire et des matériaux pour les semelles intérieures sur la capacité d'absorption des chocs des bottes de protection	**249**
Carmen GAIDĂU **Maria STANCA** **Demetra SIMION** **Mariana Daniela BERECHET** **Cosmin-Andrei ALEXE**	Collagen and Keratin Hydrolysates as Valuable Additives for Renewable New Products in Circular Economy	Utilizarea hidrolizatelor de colagen și cheratină ca aditivi valoroși pentru noi produse regenerabile în economia circulară	Les hydrolysats de collagène et de kératine comme additifs précieux pour de nouveaux produits renouvelables dans l'économie circulaire	**259**
Maryna ZHALDAK **Valentyna POLIUHA** **Olena MOKROUSOVA** **Anna OLESHKO** **Olena BUDIAKOV** **Taras KARAVAYEV**	Implementation of the Principles of Bioeconomy in Leather Production	Implementarea principiilor bioeconomiei în producția de piele	Mise en œuvre des principes de la bioéconomie dans la production de cuir	**267**
Sadman SADIK **Syed Mahedi HASEN**	Industrial Workers Efficiency in Indian Subcontinent: A Machine Learning Model Approach	Eficiența lucrătorilor din industria subcontinentului indian: o abordare a modelului de învățare automatizată	Efficacité des travailleurs dans l'industrie du sous-continent indien : une approche de modèle d'apprentissage automatique	**279**
Ivan IUNGIN **Olena MOKROUSOVA**	Composite Materials for Limb Prosthetics Liners	Materiale compozite pentru căptușeli de proteze pentru membrele inferioare	Matériaux composites pour les revêtements prothétiques des membres inférieurs	**285**
Cristina CARȘOTE **Iuliana ȘTIRBU**	The Investigation of a 17th Century Parchment Document	Investigații asupra unui document pe suport din pergament din secolul al XVII-lea	L'enquête sur un document en parchemin du XVIIe siècle	**295**
	European Research Area	Spaţiul european al cercetării	Espace Européen de la Recherche	**301**
	National and International Events	Evenimente naționale și internaționale	Événements nationaux et internationaux	**318**

EFFECTS OF MIDSOLE HARDNESS AND INSOLE MATERIALS ON SHOCK ABSORPTION IN PROTECTIVE BOOTS

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EFFECTS OF MIDSOLE HARDNESS AND INSOLE MATERIALS ON SHOCK ABSORPTION IN PROTECTIVE BOOTS

ABSTRACT. This study aimed to determine the influence of varying midsole hardness and insole materials on cushioning performance of protective boots. Twenty healthy male participants performed running tests with six conditions of protective boots, varying in midsole hardness (50 shore C-soft, 60 shore C-medium, 70 shore C-hard) and insole material (Thermoplastic Polyurethane, Polyurethane). The first peak vertical ground reaction force (1st PVGRF), impact duration (ID), and average vertical loading rate (AVLR) were measured by a force plate. The subjective cushioning evaluation was also conducted using a visual analogue scale. The results showed that midsole hardness had a significant effect on ID ($P = 0.048$, $\eta^2_p = 0.151$) and AVLR ($P = 0.048$, $\eta^2_p = 0.301$) but not on 1st PVGRF ($P = 0.222$, $\eta^2_p = 0.076$). The ID was longer and the AVLR was lower for hard shoes compared to soft shoes. Insole materials had no significant effect on any of the impact variables ($P > 0.05$). Subjective evaluations indicated that the medium-hardness shoes received the highest cushioning scores among the three hardness levels. The findings suggest that midsole hardness influences impact duration and loading rate, while insole materials do not significantly affect the shock absorption performance of protective boots.

KEY WORDS: protective boots, midsole hardness, insole material, shock absorption

INFLUENȚA DURITĂȚII TĂLPII INTERMEDIARE ȘI A MATERIALELOR PENTRU BRANȚURI ASUPRA CAPACITĂȚII CIZMELOR DE PROTECȚIE DE A ABSORBI ȘOCURILE

REZUMAT. Obiectivul acestui studiu a fost de a determina influența diferitelor durități ale tălpii intermediare și a materialelor pentru branțuri asupra capacității de amortizare a cizmelor de protecție. Douăzeci de bărbați sănătoși au efectuat teste de alergare cu cizme de protecție în șase condiții diferite, variind duritatea tălpii intermediare (50 shore C-moale, 60 shore C-mediu, 70 shore C-dur) și materialul branțului (poliuretan termoplastic, poliuretan). Cu ajutorul unei plăci de presiune s-au măsurat primul vârf al forței verticale de reacție a solului (primul PVGRF), durata impactului (ID) și rata medie de încărcare verticală (AVLR). Evaluarea subiectivă a amortizării a fost, de asemenea, efectuată folosind scala analog vizuală. Rezultatele au arătat că duritatea tălpii intermediare a avut un efect semnificativ asupra ID ($P = 0{,}048$, $\eta^2p = 0{,}151$) și AVLR ($P = 0{,}048$, $\eta^2p = 0{,}301$), dar nu și asupra primului PVGRF ($P = 0{,}222$, $\eta^2p = 0{,}076$). Durata impactului a fost mai lungă, iar rata medie de încărcare verticală a fost mai mică pentru pantofii duri, comparativ cu pantofii moi. Materialele branțurilor nu au avut un efect semnificativ asupra vreuneia dintre variabilele de impact ($P > 0{,}05$). Evaluările subiective au indicat că pantofii cu duritate medie au primit cele mai mari scoruri de amortizare dintre cele trei niveluri de duritate. Descoperirile sugerează că duritatea tălpii intermediare influențează durata impactului și rata de încărcare, în timp ce materialul branțului nu afectează în mod semnificativ capacitatea de absorbție a șocurilor a cizmelor de protecție.

CUVINTE CHEIE: cizme de protecție, duritatea tălpii intermediare, material pentru branț, absorbția șocurilor

L'INFLUENCE DE LA DURETÉ DE LA SEMELLE INTERMÉDIAIRE ET DES MATÉRIAUX POUR LES SEMELLES INTÉRIEURES SUR LA CAPACITÉ D'ABSORPTION DES CHOCS DES BOTTES DE PROTECTION

RÉSUMÉ. L'objectif de cette étude a été de déterminer l'influence de différentes duretés de semelle intermédiaire et de matériaux des semelles intérieures sur la capacité d'amortissement des bottes de protection. Vingt hommes en bonne santé ont effectué des tests de course avec des bottes de protection dans six conditions différentes, en faisant varier la dureté de la semelle intermédiaire (50 Shore C-mou, 60 Shore C-moyen, 70 Shore C-dur) et le matériau de la semelle intérieure (polyuréthane thermoplastique, polyuréthane). À l'aide d'une plaque de pression, la première force de réaction verticale maximale au sol (premier PVGRF), la durée d'impact (ID) et le taux de charge vertical moyen (AVLR) ont été mesurés. Une évaluation subjective de l'amortissement a également été réalisée à l'aide de l'échelle visuelle analogique. Les résultats ont montré que la dureté de la semelle intermédiaire a eu un effet significatif sur l'ID ($P = 0{,}048$, $\eta^2p = 0{,}151$) et l'AVLR ($P = 0{,}048$, $\eta^2p = 0{,}301$), mais pas sur le premier PVGRF ($P = 0{,}222$, $\eta^2p = 0{,}076$). La durée de l'impact a été plus longue et le taux de charge vertical moyen a été plus faible pour les chaussures dures que pour les chaussures souples. Les matériaux des semelles intérieures n'ont eu aucun effet significatif sur aucune des variables d'impact ($P > 0{,}05$). Des évaluations subjectives ont indiqué que les chaussures de dureté moyenne recevaient les scores d'amortissement les plus élevés parmi les trois niveaux de dureté. Les résultats suggèrent que la dureté de la semelle intermédiaire influence la durée de l'impact et le taux de charge, tandis que le matériau de la semelle intérieure n'affecte pas de manière significative la capacité d'absorption des chocs des bottes de protection.

MOTS CLÉS : bottes de protection, dureté de la semelle intermédiaire, matériau de la semelle intérieure, absorption des chocs

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INTRODUCTION

Lower limb injuries are a prevalent issue among individuals in high-impact professions who are frequently exposed to high-impact forces during activities such as running, landing, and other complex movements [1]. A systematic review reported that the incidence of lower extremity overuse injuries in workers exposed to high physical demands ranges from 27.5% to 61%, with the knee, lower leg, foot, and ankle being the most commonly affected areas [2]. These injuries can impair wearers' physical fitness, operational readiness, and quality of life, while also increasing medical costs and attrition rates [3]. Therefore, identifying risk factors and preventive measures for lower limb injuries in high-impact occupational settings is of paramount importance.

One potential risk factor for lower limb injuries is the impact force transmitted from the ground to the body during foot contact. Such impact forces can cause mechanical stress and damage to the musculoskeletal system, particularly the lower extremities [4]. The magnitude and rate of these impact forces are influenced by various factors, including the speed [5], mass [6], and posture of the runner [7], as well as the surface characteristics [8], and footwear properties [9]. Among these factors, footwear properties are the most modifiable and controllable, which received considerable attention from researchers and practitioners [10, 11].

Footwear properties can influence impact forces by altering the cushioning and biomechanical characteristics of foot-ground interaction [12]. Cushioning refers to the ability of footwear to absorb and dissipate impact energy, thereby reducing the peak and rate of impact forces [13, 14]. Biomechanical characteristics pertain to the kinematic and kinetic parameters of the lower extremity joints and segments, such as foot strike pattern, ankle dorsiflexion angle, knee flexion angle, and joint moments and powers, all of which can affect the distribution and transmission of impact forces along the lower extremity kinetic chain [15].

Protective boots are a specialized type of footwear designed to shield the feet and ankles of wearers from external hazards such as bullets, shrapnel, mines, and chemical agents. These boots are typically constructed from rigid and durable materials like leather, rubber, and steel to provide adequate protection and support. However, these materials may also compromise the cushioning and biomechanical properties of the boots, potentially increasing impact forces and the risk of lower limb injuries [3, 12]. Therefore, optimizing the design of protective boots is necessary to balance the trade-off between protection and cushioning.

The design of protective boots focuses on three primary components: the outsole, midsole, and insole. The outsole, as the outermost layer in contact with the ground, is designed to provide durability, grip, and resistance to environmental hazards. Although the outsole contributes to overall stability, its role in cushioning and shock absorption is limited compared to the midsole and insole, which are in direct interaction with the foot and ground reaction forces. The midsole, located between the outsole and the upper of the boot, serves as the primary shock-absorbing layer [16], typically made from materials such as ethylene-vinyl acetate (EVA), polyurethane (PU), or thermoplastic polyurethane (TPU). Midsole materials are selected based on their cushioning properties, with different hardness levels measured by the Shore C scale to modulate shock absorption and comfort. The insole, as the inner layer in contact with the foot, provides additional cushioning and comfort and is often made from materials like PU, TPU, or gel with varying thicknesses and densities to optimize foot support.

The midsole and insole can interact with each other, affecting the shock absorption performance of protective boots [17, 18]. However, there is a lack of research on the optimal combination of midsole hardness and insole materials for protective boots, and the existing literature presents inconsistent and inconclusive findings. Some studies suggest that cushioning insoles and softer midsoles can reduce impact forces and injury risk by lowering ground reaction forces and loading rates [19, 20]. Conversely, other studies argue that harder midsoles and stiffer insoles can provide better cushioning and stability by increasing the contact area and reducing foot deformation [21].

Therefore, the purpose of this study was to evaluate the effect of different combinations of midsole hardness and insole materials on the cushioning properties of protective boots. The study hypothesizes that: 1) Midsole hardness and insole materials significantly affect shock absorption performance, with shock absorption performance decreasing as midsole hardness increases, and 2) Insole materials significantly influence the shock absorption performance of protective boots.

MATERIALS AND METHODS

Participants

Twenty healthy male participants (age: 19.9 ± 0.8 years, height: 1.77 ± 0.05 m, weight: 67.6 ± 7.8 kg; shoe size: 41-43 French size) volunteered for this study. Participants were recruited from a local university through flyers and online advertisements. The inclusion criteria were: no history of lower limb injury or surgery in the past six months, no current pain or discomfort in the lower limbs, and regular participation in recreational running activities (at least three times per week). Exclusion criteria included any medical condition that could affect the biomechanical performance of the lower limbs, the use of orthotics or braces, and any allergy or intolerance to the materials of the protective boots. All participants provided written informed consent before the experiment commenced.

Footwear Description

The protective boots (Figure 1A) used in this study were custom-made by a local manufacturer, with a total weight of 960g per pair and a shoe upper height of 18 cm. The midsole thickness is 17.4 mm at the heel, while the outsole thickness is 3 mm, with a slip-resistant tread depth of 4 mm. The outsole is constructed from durable rubber material to provide traction and environmental protection, while the midsole is composed of polyurethane (PU) foam for shock absorption. The outsole and midsole are attached to the upper using an adhesive bonding process, which ensures a secure and durable connection that maintains the boots' structural integrity during impact activities. This bonding process was chosen to achieve a balance between flexibility and durability.

The midsoles (Figure 1B) were specifically designed with hardness levels of 50 (soft), 60 (medium), and 70 (hard) Shore C, based on previous research suggesting that these levels are relevant for evaluating the effect of midsole hardness on shock absorption and comfort. The insert insoles (Figure 1C) used in this study were made from Thermoplastic Polyurethane (TPU) and Polyurethane (PU), with thicknesses of 5.5 mm in the forefoot and 7.5 mm in the heel. The material of the main insole in this study was Kevlar with the thickness of 2.5mm. These materials were selected for their common use in protective footwear and their potential to differ in shock absorption and energy return. Figure 1 shows the protective boots and insoles used in the study. A schematic diagram depicting the cross-section of the protective boot, including the upper, lining, insert insole, main insole, midsole, and outsole, is presented in Figure 2.

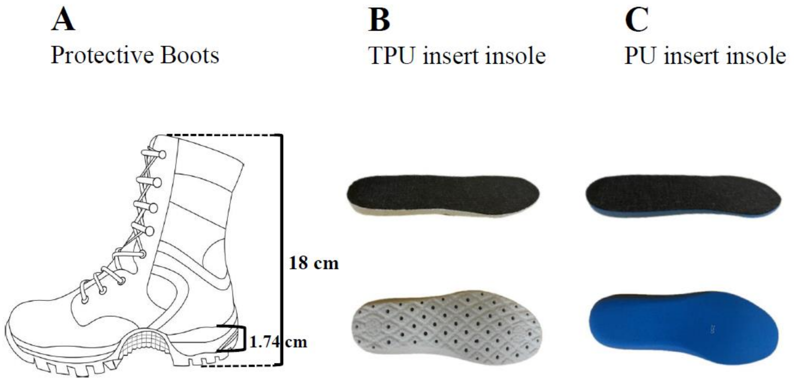

Figure 1. Protective boots and insoles used in this study, TPU: thermoplastic polyurethane; PU: polyurethane

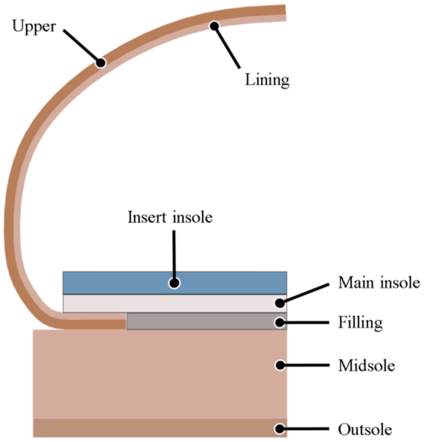

Figure 2. Schematic diagram of the cross-sectional view of the protective boot used in this study

Experimental Set-Up and Procedures

A force plate (Model 9281EA, Kistler Instrumente AG, Switzerland) was used to collect ground reaction forces during running (Figure 3). The force plate was embedded in the middle of a 12 m runway and the sampling frequency was set as 1000 Hz. The speed was monitored using timing gates (Smartspeed; Fusion Sport Inc., Burbank, CA, USA) placed one meter before and after the force plate.

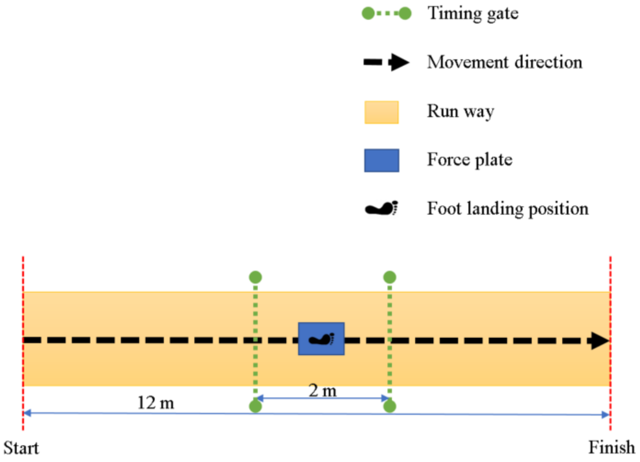

Figure 3. Experimental setup in this study

All experimental testing was conducted on the same day. Participants were first familiarized with the protective boots and the experimental tasks. To acclimate to the weight and feel of the footwear, the boots were worn while walking around the laboratory for 10 minutes. Practice trials of running with the boots were also completed until a comfortable and confident level was reached. After this familiarization period, the running tests were performed under six different conditions: three levels of boot midsole hardness (50-, 60-, 70 Shore C) combined with two different insole materials (PU and TPU). The order of conditions was randomized and counterbalanced across participants.

The running test involved three trials of running at a speed of 3.3 ± 5% m/s along the runway [22], ensuring that the right foot landed on the force plate. Participants were instructed to run naturally while maintaining a consistent speed throughout each trial. Participants were allowed a two-minute rest between trials.

After completing the running tests, participants provided subjective cushioning evaluation of the protective boots based on their experiences with the six different combinations of midsole hardness and insole materials. Using a 15 cm Visual Analogue Scale (VAS) [23], participants rated the cushioning performance for each condition. The left end of the scale represented "Very Poor," and the right end represented "Excellent." Participants placed a vertical mark on the scale reflecting their subjective assessment, and the subjective cushioning score for each condition was determined by measuring the distance from the left end of the scale to the marked line.

Data Reduction and Processing

The primary outcome variables were the first peak vertical ground reaction force (1^{st} PVGRF), impact duration (ID), and average vertical loading rate (AVLR). These variables were extracted from the ground reaction force (GRF) data collected during the running trials. The onset and offset of the stance phase were identified as the points where the vertical GRF exceeded and subsequently fell below a threshold of 10 N [14]. This ensured that only the stance phase of running was considered for analysis. Figure 4 illustrates a representative GRF curve and highlights the critical points used to compute AVLR.

Data outliers, such as those caused by irregular foot strikes or missteps, were identified through visual inspection of the force-time curves and were excluded from the analysis to maintain data integrity. The 1^{st} PVGRF was defined as the first noticeable peak in the vertical GRF during the stance phase, representing the initial force impact on the ground. The AVLR was calculated by determining the slope of the vertical GRF between 20% and 80% of the 1^{st} PVGRF [24], capturing the rate at which the vertical force was applied. The impact duration (ID) was defined as the time interval between the initial foot contact and the 1^{st} PVGRF. The following equations were used for these calculations:

$$\boldsymbol{AVLR = \frac{0.8\times 1^{st}\, PVGRF - 0.2\times 1^{st} PVGRF}{(t_{0.8} - t_{0.2})\times BW}} \qquad (1)$$

$$\boldsymbol{ID = t_{1st\ PVGRF} - t_{IC}} \qquad (2)$$

where $t_{0.2}$ and $t_{0.8}$ correspond to the time points at 20% and 80% of the 1^{st} PVGRF, respectively, $t_{1st\ PVGRF}$ is the time point corresponding to the 1^{st} PVGRF, and t_{IC} is the time point corresponding to the initial contact, BW is the body weight of the participant.

The ground reaction force was processed using Visual 3d (Version 6.0, C-motion, Inc., USA). The data were filtered using a fourth-order low-pass Butterworth filter with a cut-off frequency of 100 Hz. The GRF data was normalized by the subject's body weight (BW), and AVLR was expressed in body weight per second (BW/s).

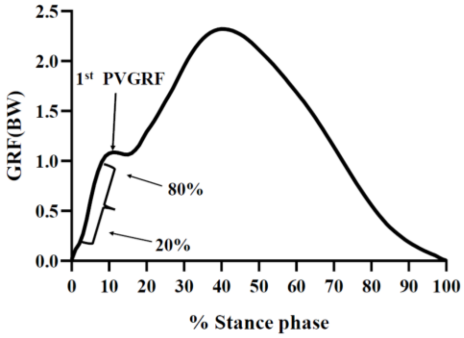

Figure 4. Representative ground reaction force curve showing key points for the first peak vertical ground reaction force and the calculation process of average vertical loading rate; 1^{st} PVGRF: first peak vertical ground reaction force; GRF: ground reaction force; BW: body weight

Statistical Analysis

Descriptive statistics (mean ± standard deviation) were calculated for each condition (three midsole hardness × two insoles). The assumptions of normality and homogeneity of variance were checked using the Shapiro-Wilk test and Levene's test, respectively. A two-way repeated measures analysis of variance (ANOVA) was performed to examine the main effects and interaction effects of the condition and the test on the outcome variables. The level of significance was set at 0.05. Post-hoc pairwise comparisons with Tukey correction were conducted to identify significant differences between conditions and tests. Partial eta-squared (η^2_p) was used to calculate the effect size, representing the proportion of variance attributed to each factor or interaction. Specifically, η^2_p values of 0.01, 0.06, and 0.14 were interpreted as small, medium, and large effects, respectively [25]. Statistical analyses were performed using SPSS software (Version 26, IBM Corp., USA).

RESULTS

Impact Variables

Table 1 shows the effects of different midsole hardness and insole materials on 1st PVGRF, ID, and AVLR during running. The results showed that there was no significant interaction effect between midsole hardness and insole materials for any of the impact variables ($p > 0.05$). The main effect of midsole hardness was significant for ID (F$_{(1.886,\ 35.84)}$ = 3.386, P = 0.048, η^2_p=0.151) and AVLR ID (F$_{(1.767,\ 33.57)}$ = 3.480, P = 0.048, η^2_p=0.301), but not for 1st PVGRF (F$_{(1.922,\ 36.51)}$ = 1.571, P = 0.222, η^2_p = 0.076). The ID was longer for Hard shoes than for Soft shoes (P = 0.049), and the AVLR was lower for Hard shoes than for Medium (P = 0.039) and Soft shoes (P = 0.029). The main effect of the insole materials was not significant for any of the impact variables ($p > 0.05$).

Table 1: Impact variables for different combinations of midsole hardness and insole materials during running

Variables	Insole Materials		Midsole Hardness		Midsole Hardness		Insole Materials		Interaction	
		Soft	Medium	Hard	*P*	η_p^2	*P*	η_p^2	*P*	η_p^2
1ST PVGRF (BW)	TPU	1.34(0.36)	1.37(0.34)	1.30(0.32)	0.222	0.076	0.953	0.001	0.874	0.004
	PU	1.32(0.38)	1.37(0.38)	1.31(0.35)						
ID (ms)	TPU	29.6(5.3)	30.5(6.1)	30.0(7.0)	0.048*	0.151	0.446	0.031	0.125	0.106
	PU	27.6(4.0)	29.8(4.8)	31.1(5.0)						
AVLR (BW/s)	TPU	56.79(18.23)	57.68(22.90)	55.14(18.02)	0.048*	0.301	0.700	0.008	0.209	0.192
	PU	59.80(21.93)	58.82(22.42)	52.92(18.45)						

Note: * p-value <0.05, The difference was statistically significant; TPU: thermoplastic polyurethane; PU: polyurethane; 1st PVGRF: first peak vertical ground reaction force; ID: impact duration; AVLR: average vertical loading rate; Soft, medium, and hard represent midsole hardness levels of 50, 60, and 70 Shore C, respectively.

Subjective Cushioning Performance

Figure 5 shows the subjective cushioning performance across different midsole hardness levels and insole materials. Results showed that there was no interaction between midsole hardness and insole materials for the subjective cushioning performance (F$_{(1.968,\ 35.420)}$ = 3.480, P = 0.637, η^2_p = 0.024), and further main effect analysis found that midsole hardness had a significant effect on the subjective cushioning (F$_{(1.846,\ 33.220)}$ = 7.070, P = 0.003, η^2_p = 0.292). Post hoc analysis indicated that the subjective cushioning scores were significantly lower in the Soft (P = 0.014) and Hard (P = 0.001) shoe conditions than in the Medium shoe condition. However, there were no insole materials effects on subjective cushioning (F$_{(1,\ 19)}$ = 1.101, P = 0.308, η^2_p = 0.058).

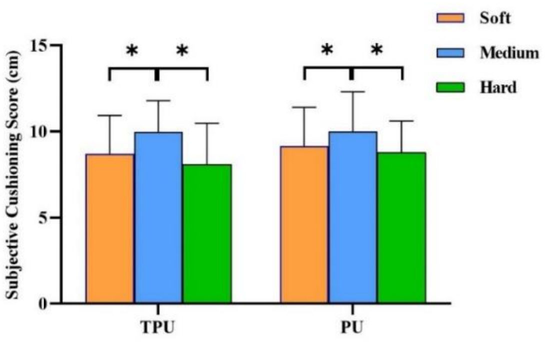

Figure 5. Subjective cushioning performance across different midsole hardness levels and insole materials. Note: TPU: thermoplastic polyurethane; PU: polyurethane. Soft, medium, and hard represent midsole hardness levels of 50, 60, and 70 Shore C, respectively.

DISCUSSION

This study aimed to explore the effects of midsole hardness and insole material on the shock absorption performance of protective boots during running. The findings reveal that midsole hardness significantly influences impact duration (ID) and average vertical loading rate (AVLR), while insole materials do not substantially affect these impact variables. Notably, the subjective evaluation of cushioning performance identified that boots with medium midsole hardness were rated as providing the best cushioning among the three hardness levels, indicating a clear preference for medium hardness over both softer and harder alternatives.

Effect of Midsole Hardness on Shock Absorption

The results of this study underscore the importance of midsole hardness in determining shock absorption performance during running. Our findings indicate that harder midsoles led to a longer ID and a lower AVLR compared to softer midsoles. This is consistent with previous research that suggested harder midsoles can increase the contact area and reduce foot deformation, leading to a decrease in loading rates and an extension of the impact duration [26]. The reduction in AVLR associated with harder midsoles suggests that these midsoles may be more effective in distributing impact forces over time, potentially mitigating the risk of injuries that result from high-impact activities.

Despite these benefits in terms of impact distribution, the subjective assessment revealed a clear preference for medium midsole hardness in terms of perceived cushioning. This preference aligns with earlier studies that found participants generally favor footwear that strikes a balance between softness and firmness [27]. In contrast, harder midsoles, while beneficial for prolonging the impact duration and reducing loading rates, might compromise the perceived comfort due to their stiffer nature, which can lead to a less cushioned feel during running [28, 29].

On the other hand, softer midsoles, which intuitively might seem to offer better cushioning, did not perform as well in this study. The shorter ID and higher AVLR observed with softer midsoles suggest that they may allow more rapid and forceful impacts, which could result in increased discomfort and potentially higher injury risk over time [30, 31]. These results suggest that while softer midsoles may initially feel more cushioned, they might not effectively reduce the overall mechanical stress on the body during repetitive high-impact activities such as running.

Effect of Insole Material on Shock Absorption

Contrary to our second hypothesis, the study found no significant effects of insole material (TPU vs. PU) on the measured impact variables, including 1st PVGRF, ID, and AVLR. These results imply that, within the context of the protective boots used in this study, the choice of insole material does not significantly alter the mechanical shock absorption properties during running. This finding diverges from some previous research that highlighted the potential of shock-absorbing insoles to reduce peak impact forces and lower the risk of injury by modulating ground reaction forces [30, 32].

A possible explanation for this discrepancy could lie in the design characteristics of the protective boots used in this study. The relatively thick and rigid outsole of these boots might have diminished the potential benefits of softer insole materials by limiting their ability to deform and absorb shock effectively [33]. Additionally, the overall construction of the boots, which includes a focus on protection and durability, may have led to a more uniform distribution of force that reduced the influence of insole material on the measured outcomes.

Moreover, the protective boots may have influenced the runners' biomechanics, including foot strike patterns and joint kinematics, which in turn could have affected the distribution and transmission of impact forces along the lower extremity kinetic chain [14, 21]. These biomechanical alterations might have overshadowed any potential differences between TPU and PU insoles, rendering their impact on shock absorption negligible in this particular setup.

Subjective Cushioning Performance

The subjective evaluations conducted in this study revealed a strong preference for medium midsole hardness in terms of perceived cushioning. Participants consistently rated the medium hardness as offering superior shock absorption compared to both softer and harder alternatives. This finding is particularly important as it highlights that subjective comfort does not always correlate directly with objective mechanical measures of shock absorption [34, 35].

The preference for medium midsole hardness could be attributed to its ability to provide an optimal level of cushioning that balances the firmness needed for stability with the softness required for comfort. Participants may have perceived the medium hardness as cushioning enough to absorb impacts effectively, without the excessive softness that could lead to instability or the excessive firmness that could result in discomfort [26]. These subjective assessments are critical in footwear design, as they directly impact user satisfaction and, by extension, the likelihood of long-term use and adherence to wearing protective boots in various settings.

Interestingly, the lack of a significant effect of insole material on subjective cushioning scores further reinforces the idea that midsole hardness plays a more dominant role in determining perceived comfort. Despite the theoretical differences in material properties between TPU and PU insoles, participants did not perceive a notable difference in comfort. This outcome suggests that the mechanical properties of the midsole, such as its hardness, may have a more substantial influence on overall cushioning and comfort perceptions in protective footwear.

However, the study also highlighted discrepancies between objective measures (1st PVGRF, ID, AVLR) and subjective assessments. While harder midsoles reduced AVLR and prolonged ID, they were less preferred by participants, who favored the medium hardness for its perceived cushioning. These differences underscore the complexity of assessing footwear effectiveness, as objective metrics may not fully capture the dynamic interactions between the foot, the boot, and the ground during movement [34, 36]. Factors such as individual biomechanics, running technique, and environmental conditions—elements that differ between controlled laboratory settings and real-world scenarios—can influence these interactions and lead to variations in comfort perception [35].

Moreover, subjective evaluations are inherently influenced by personal factors like past footwear experiences, preferences, and psychological biases, which can affect how cushioning and comfort are perceived, even when objective data suggests otherwise [36]. The controlled conditions of this study, while ensuring consistency, may not reflect the diverse environments where protective boots are typically used. Future research should explore these subjective-objective discrepancies by incorporating more varied testing environments and considering additional biomechanical factors, such as joint kinematics and muscle activation, to gain a comprehensive understanding of footwear performance.

Limitations

This study offers valuable insights into how midsole hardness and insole material affect shock absorption, but several limitations must be noted. The small, homogeneous sample of male university students limits the generalizability of the results to other groups, such as female or older personnel, who may respond differently to footwear. The controlled laboratory setting, while consistent, does not fully mimic the varied conditions of real-world field scenarios. Future studies should examine these factors in more diverse environments, such as different terrains and climates, to better understand their impact on injury risk. Additionally, this study focused mainly on vertical ground reaction forces and loading rates, but other biomechanical factors like joint angles and muscle activation should also be considered for a more comprehensive understanding of footwear performance.

CONCLUSIONS

This study investigated the effects of midsole hardness and insole material on the shock absorption performance of protective boots during running. The results showed that midsole hardness influenced the impact duration and loading rate, while insole material did not affect the shock absorption. The subjective cushioning evaluation also revealed that medium midsole hardness was preferred by the participants over soft or hard midsole hardness. These findings suggest that midsole hardness is an important factor to consider in the design of protective boots, and that medium midsole hardness may provide the optimal balance between protection and cushioning. Future studies should include other biomechanical and physiological variables, such as joint kinematics, muscle activation, and tissue stress, to further evaluate the influence of footwear properties on lower limb injury risk in demanding operational environments.

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COLLAGEN AND KERATIN HYDROLYSATES AS VALUABLE ADDITIVES FOR RENEWABLE NEW PRODUCTS IN CIRCULAR ECONOMY

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COLLAGEN AND KERATIN HYDROLYSATES AS VALUABLE ADDITIVES FOR RENEWABLE NEW PRODUCTS IN CIRCULAR ECONOMY

ABSTRACT. Collagen and keratin-based waste represents a valuable biomass resource with still insufficiently exploited potential. The leather industry and sheep breeding activity generate important protein waste based on collagen and keratin which at world level amounts to 5.6 million and 1 million tonnes, respectively, every year. The processing of protein-based waste through water or chemical-enzymatic hydrolysis, allows the refinement of the molecular weights and distribution with different potential functionalities for versatile new products with applications in industry (deliming agents, filling and finishing additives), agriculture, medicine, or other fields. The versatile properties as a function of hydrolysis process were shown by analyses of protein degradation (ATR-FTIR spectroscopy), molecular weight distribution (SDS-PAGE electrophoresis) and particle size distribution (DLS analyses). The specific molecular weight distribution of collagen and keratin hydrolysates after hydrolysis at 100°C and 130°C was highlighted, thus proving the potential of refining the compositions for different applications with ecological impact. The collagen hydrolysis at 100°C leads to fragmentation of large molecules into small molecules meanwhile the temperature of 130°C favors the increase of medium size population of peptides, in agreement with SDS-PAGE electrophoresis results. Instead, the small molecules of keratin were doubled by hydrolysis at 130°C, in good correlation with ATR-FTIR determination of AI/AA ratios.

KEY WORDS: protein hydrolysates, molecular distribution, collagen, keratin

UTILIZAREA HIDROLIZATELOR DE COLAGEN ȘI CHERATINĂ CA ADITIVI VALOROȘI PENTRU NOI PRODUSE REGENERABILE ÎN ECONOMIA CIRCULARĂ

REZUMAT. Deșeurile pe bază de colagen și cheratină reprezintă o resursă valoroasă de biomasă cu potențial încă insuficient exploatat. Industria de pielărie și activitatea de creștere a oilor generează importante deșeuri proteice pe bază de colagen și cheratină, care la nivel mondial se ridică la 5,6 milioane, respectiv 1 milion de tone în fiecare an. Prelucrarea deșeurilor pe bază de proteine prin hidroliză în apă sau chimico-enzimatică permite rafinarea greutăților moleculare și distribuția acestora, cu diferite potențiale funcționalități pentru noi produse versatile cu aplicații în industrie (agenți de decalcificare, aditivi de umplere și finisare), agricultură, medicină, sau alte domenii. Proprietățile versatile în funcție de procesul de hidroliză au fost demonstrate prin analize de identificare a degradării proteinei (spectroscopie ATR-FTIR), distribuție a greutății moleculare (electroforeza SDS-PAGE) și distribuție a dimensiunii particulelor (analize DLS). S-a evidențiat distribuția specifică a greutății moleculare a hidrolizatelor de colagen și cheratină după hidroliză la 100°C și 130°C, dovedind astfel potențialul de rafinare a compozițiilor pentru diferite aplicații cu impact ecologic. Hidroliza colagenului la 100°C duce la fragmentarea moleculelor mari în molecule mici, în timp ce temperatura de 130°C favorizează creșterea populației de dimensiuni medii de peptide, în acord cu rezultatele electroforezei SDS-PAGE. În schimb, ponderea moleculelor mici de cheratină s-a dublat prin hidroliză la 130°C, în bună corelație cu valoarea rapoartelor AI/AA determinate prin spectroscopie ATR-FTIR.

CUVINTE CHEIE: hidrolizate de proteine, distribuție moleculară, colagen, cheratină

LES HYDROLYSATS DE COLLAGÈNE ET DE KÉRATINE COMME ADDITIFS PRÉCIEUX POUR DE NOUVEAUX PRODUITS RENOUVELABLES DANS L'ÉCONOMIE CIRCULAIRE

RÉSUMÉ. Les déchets à base de collagène et de kératine représentent une ressource précieuse en biomasse dont le potentiel est encore insuffisamment exploité. L'industrie du cuir et l'activité d'élevage ovin génèrent d'importants déchets protéiques à base de collagène et de kératine qui s'élèvent respectivement à 5,6 millions et 1 million de tonnes par an au niveau mondial. Le traitement des déchets à base de protéines à l'aide de l'eau ou de l'hydrolyse chimique-enzymatique permet d'affiner les poids moléculaires et leur répartition avec différentes fonctionnalités potentielles pour de nouveaux produits polyvalents avec des applications dans l'industrie (agents de déchaulage, additifs de remplissage et de finition), l'agriculture, la médecine ou d'autres domaines. Les propriétés polyvalentes en fonction du processus d'hydrolyse ont été démontrées par des analyses de la dégradation des protéines (spectroscopie ATR-FTIR), de la distribution des poids moléculaires (électrophorèse SDS-PAGE) et de la distribution granulométrique (analyses DLS). La distribution du poids moléculaire spécifique des hydrolysats de collagène et de kératine après hydrolyse à 100°C et 130°C a été mise en évidence, prouvant ainsi le potentiel d'affinage des compositions pour différentes applications à impact écologique. L'hydrolyse du collagène à 100°C conduit à la fragmentation des grosses molécules en petites molécules tandis que la température de 130°C favorise l'augmentation de la population de taille moyenne de peptides, en accord avec les résultats de l'électrophorèse SDS-PAGE. Au lieu de cela, les petites molécules de kératine ont été doublées par hydrolyse à 130°C, en bonne corrélation avec la détermination ATR-FTIR des rapports AI/AA.

MOTS CLÉS : hydrolysats de protéines, distribution moléculaire, collagène, kératine

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INTRODUCTION

The leather industry is the oldest industry that reuses a waste, the animal skin. Although the ecological impact of processing 8 million tons of hides and skins annually in the world represents a reduction of 5 million tons of greenhouse gases (equivalent to the greenhouse gases produced by 1 million cars) [1], and the creation of products with added value, nevertheless, leather processing yield is 20-25 % and generates significant amounts of protein waste, which are mostly stored. The sheep breeding activity produces also low-quality wool which alongside with leather industry releases keratin-based waste amounting around 1 million tonnes annually [2].

Leather products are durable, processed with chemical materials containing heavy metals (basic salts of trivalent chromium), made from raw materials of petroleum origin (acrylic polymers, condensation syntans, phenol-formaldehyde resins, fatliquoring agents) or using energy-consuming chemicals (ammonium salts) and therefore, hardly biodegradable, which raises an important environmental problem regarding their storage, after the end of their life cycle.

The modern leather industry must respond to the principles of green chemistry [3], which must: i) prevent waste, ii) save materials, iii) use less dangerous materials, iv) start from benign chemical materials, v) be energy efficient, vi) use renewable raw materials, vii) reduce reaction intermediates, viii) use catalysis, ix) produce degradable materials, x) prevent and monitor pollution and, xi) prevent chemical accidents. The leather industry makes constant efforts to meet the requirements of green chemistry [4].

Organic waste in the European Union amounts to an estimated value of 138 million tons annually, of which almost 40% is stored [5], representing a serious environmental problem, which has boosted both research in the field and legislation in the direction of orienting the economy towards neutrality, circularity and products with a reduced carbon footprint. In this regard, intense research is being done on the replacement of non-biodegradable chemical materials or with fossil carbon content, with renewable materials, which help improve the biodegradability of leather, while maintaining the final quality and value of use, but with reduced environmental impact. The sustainability of leather processing is one of the most difficult problems of the leather industry, which must change a safe and versatile technological process (tanning with chromium III salts), which has dominated this industry for more than 150 years, with metal-free alternatives, without aldehydes, without bisphenols and to ensure biodegradability.

Superior valorization of collagen and keratin waste through separation, solubilization and refinement of the molecular weight allows the development of new materials with functionalization potential for applications in the leather industry (deliming agents, retanning, filling, finishing), agriculture, medicine or other fields [6].

The effects of the valorization of these by-products ensure the reduction in the number of chemical materials of petroleum origin and of the greenhouse gases emitted by the storage of this waste.

The work presents the possibility of making protein hydrolysates with different properties and functionalization potential through hydrolysis processes under different conditions, which allows obtaining versatile products. Different analytical methods like ATR-FTIR spectroscopy, SDS-PAGE electrophoresis, DLS were performed and confirmed the specific molecular weight distribution as a function of hydrolyses conditions.

MATERIALS AND METHODS

Collagen and keratin hydrolysates processed from leather and coarse wool waste, by chemical [7] and chemical-enzymatic [8] methods in the solid state (Figure 1), were dissolved in water, in a concentration of 10%, in order to be treated for molecular weight reduction and create new functional groups. These processes took place at 130°C, variable time (15, 30 and 240 minutes) and at 100°C, variable time (3, 13 and 20 hours) for collagen alkaline hydrolysate, and for keratin alkaline-enzymatic hydrolysate, respectively. The HICLAVE HV 110 L autoclave (HIRAYAMA Manufacturing Corporation) was used for hydrolyses at 100°C and 130°C. The particle size, polydispersity and Zeta potential were measured with Nanosizer NZ (Malvern), the molecular weight distribution by SDS-PAGE electrophoresis (Mini PROTEAN 3 Cell Bio-Rad) equipped with Gel Doc EZ Imaging System and ImageLab software, and the functional groups by FTIR spectrometry with Thermo Scientific™ Nicolet™ iS50 spectrometer (Thermo Fisher).

Figure 1. Collagen (left) and keratin (right) hydrolysates

The collagen and keratin hydrolysates at initial stage and after hydrolysis at 130°C or 100°C were labeled as listed in Table 1.

Table 1: Collagen and keratin hydrolysate labels

Label	Hydrolysate
HCZ0, P1	Alkaline collagen hydrolysate, solution 10%
HCZ15; HCZ30; HCZ240	Collagen hydrolysate processed at 130°C for 15 min, 30 min and 240 min
P1, P2, P3, P4	Collagen hydrolysate processed at 100°C for 3 h, 13 h and 20 h
HKV0	Alkaline-enzymatic keratin hydrolysate, solution 10%
HKV1; HKV2	Alkaline-enzymatic keratin hydrolysate processed at 130°C for 240 min

RESULTS AND DISCUSSION

The collagen and keratin hydrolysates in initial state with concentration of 10% dry substance and after hydrolyses at 130°C and 100°C, for different times, are shown in Figure 2 and the final products in Figure 3. From Figure 3 a very different aspect of collagen hydrolysates can be seen, suggesting the substantial influence of hydrolysis temperature. The aspect of keratin hydrolysate samples processed at 130°C was very similar, suggesting a good reproducibility (Figure 3c).

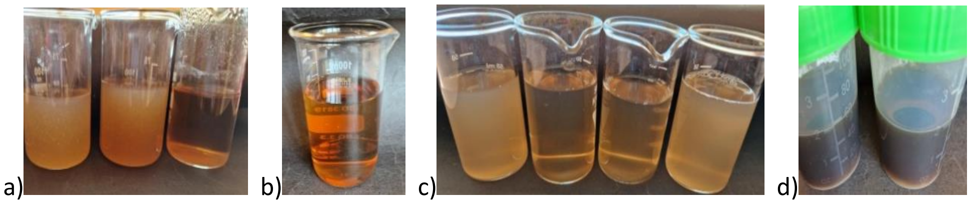

Figure 2. Collagen and keratin hydrolysates: a, b) initial collagen hydrolysate (HCZ0) and collagen hydrolysates obtained at 130°C (HCZ15; HCZ30; HCZ240); c) initial collagen hydrolysate (P1) and collagen hydrolysates obtained at 100°C (P2; P3; P4), and d) keratin hydrolysates (HKV1; HKV2)

The final products of collagen and keratin hydrolyses are shown in Figure 3.

Figure 3. Final products, collagen and keratin hydrolysates: HCZ240; P4 and HKV2

The determinations of particle sizes and Zeta potentials for the precursors, and the final collagen and keratin hydrolysates are presented in Tables 2-4 and Figures 4-6.

In Table 2 and Figure 4 an important decrease in the size of the particles can be seen as a result of hydrolysis at 130°C and a reduction in the Zeta potential, which indicates a tendency for the particles to agglomerate with the elimination of the aqueous layer that surrounds them with the decrease in polydispersity (PId), and finally, the polydispersity increases and the Zeta potential evolves in the negative range, as a result of the hydrolysis and the reactivation of the functional groups of the collagen. The increase in the population of small particles is significantly higher at the final hydrolysis time (8.7 nm with 42.2% ratio after 240 min of treatment as compared with 9 nm with 21.2% ratio after 30 min of treatment).

Table 2: Particle size, polydispersity and Zeta potential for collagen hydrolysates treated at 130°C

Sample	Majority populations						Average, nm	PId	Zeta potential, mV
	nm	%	nm	%	nm	%			
HCZ0	12.7	11.0	438.3	89.0	-	-	1804.0	0.7	-10.9
HCZ 15	11.6	17.2	438.2	76.2	5308	6.7	303.2	0.5	-4.6
HCZ 30	9.0	21.2	35.3	8.3	464	63.7	272.9	0.4	3.1
HCZ 240	8.7	42.3	755.7	28.2	5180	19.4	267.2	0.9	-3.8

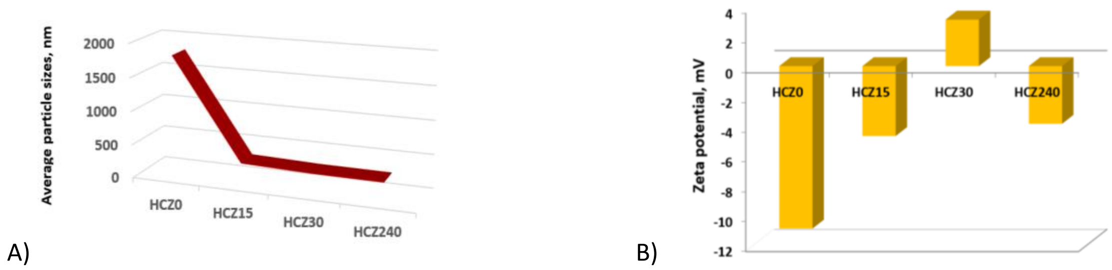

Figure 4. A) Evolution of average particle size and B) Zeta potential over hydrolysis time at the temperature of 130°C, for collagen hydrolysates

Table 3 and Figure 5 show the particle sizes and Zeta potentials for alkaline collagen hydrolysates processed at 100°C and different time. The decrease in particle size is more evident at the maximum hydrolysis time, with insignificant variations in Zeta potential, which suggests different types of particles, without such important particle associations, compared to hydrolysis at 130°C. The proportion of small particles remains constant. Figure 5 shows the evolution of particle size and Zeta potentials.

Table 3: Particle size, polydispersity and Zeta potential for collagen hydrolysates obtained at 100°C

Sample	Majority populations						Average, nm	PId	Zeta potential, mV
	nm	%	nm	%	nm	%			
P1	12.7	11.0	438.3	89.0	-	-	1804.0	0.7	-10.9
P2	11.1	7.9	671.3	64.8	5301	27.3	1652.0	0.8	-8.7
P3	8.8	5.3	-	-	280.5	94.7	673.9	0.6	-8.0
P4	5.8	9.6	118.9	29.3	376.1	61.0	309.5	0.5	-7.0

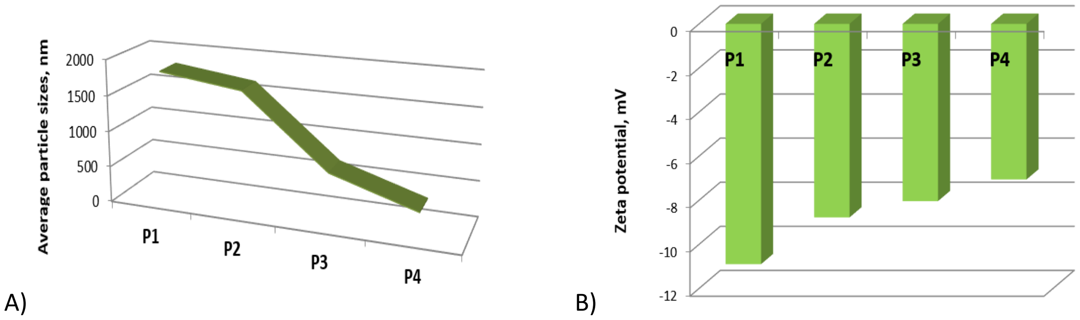

Figure 5. A) Evolution of particle size and B) Zeta potential over hydrolysis at the temperature of 100°C for collagen hydrolysates

Table 4: Particle size, Zeta potential and polydispersity for keratin hydrolysates

Sample	Majority populations						Average,	PdI	Zeta potential,
	nm	%	nm	%	nm	%	nm		mV
HKV0	-	-	601.3	62.6	3115.0	37.4	621.4	0.5	-33.5
HKV1	66.4	7.2	544.8	59.1	3943.0	33.7	561.3	0.5	-29.0
HKV2	36.4	6.7	511.7	62.0	3924.0	31.2	509.1	0.5	-28.3

Table 4 and Figure 6 present the characteristics of keratin hydrolysate particles for two parallel samples, KKV1 and HKV2 after hydrolyses at 130°C as compared to initial keratin hydrolysate HKV0.

It can be observed that, through hydrolysis, populations of small particles appear in proportions of 6.7-7.2%, the ratio of large particle populations decreases by 3.7-6.2%, the average size of the particles decreases, the polydispersity remains constant, and the Zeta potential indicates a slight decrease in stability. The appearance of larger particles suggests particle agglomeration and correlates with the decrease in Zeta potential.

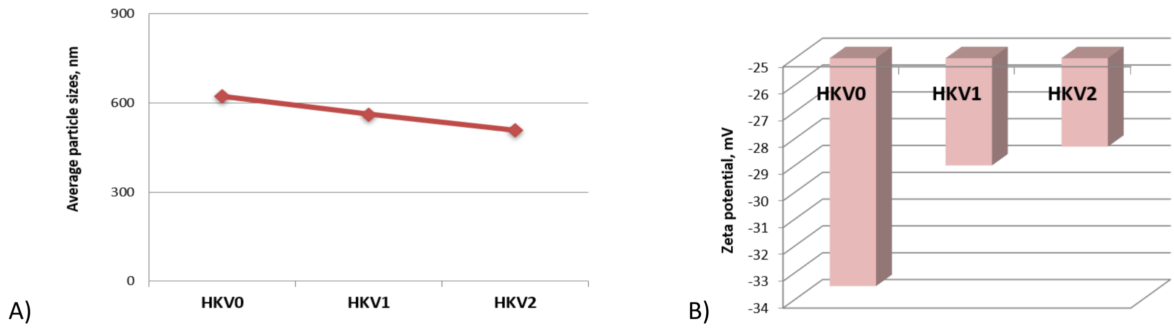

Figure 6. A) Evolution of particle size and B) Zeta potential over hydrolysis time at 130°C, for keratin hydrolysates

Hydrolysis at the temperature of 130°C leads to fragmentation of large peptide molecules into medium molecules (17-55 kDa) while preserving the share of small peptides and oligopeptides (Figure 7). The results of processing the SDS-PAGE electropherograms of P1-P4 hydrolysates are summarized in Figure 8, where the increase in the share of molecules with low weight (10-12 kDa) and the decrease of those with high weight (>150 kDa) can be clearly seen. The influence of hydrolysis conditions on molecules with medium molecular weight is small. In the case of keratin hydrolysates, the treatment at 130°C generated molecules of 10 kDa by cleavage of those with molecular weights of 60 kDa. The share of small molecules doubled by hydrolysis under pressure and at the temperature of 130°C (Figure 9).

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The results of FTIR-ATR spectrometry analyses of dried protein hydrolysates are presented in Figures 10-12. In Figure 10, the phenolic groups (1500-1000 cm^{-1}) for which the absorbance increases as a result of hydrolysis at 130°C are marked. The more intense yellow color of collagen hydrolysate (Figure 3) can be correlated with the change in phenolic groups of amino acids and generation of sensitive chromophores [9]. Other similar studies showed that the hydrolysis time does not change the polypeptide backbone (all specific amide bands are present), but they found a shifting of Amide A and Amide I to lower wavenumbers and a higher vibration of OH groups from 1037 cm^{-1} [10].

In Figure 11, a change can be observed at the level of OH groups, as a result of the hydrolysis at 100°C; the overlap of absorbances of samples P3 and P4 in this area suggests that the hydrolysis of 13 hours generates the same products as the one at 20 hours. In Figure 12 the keratin hydrolysates showed slight intensity modifications at the level of Amide A and Amide III bands.

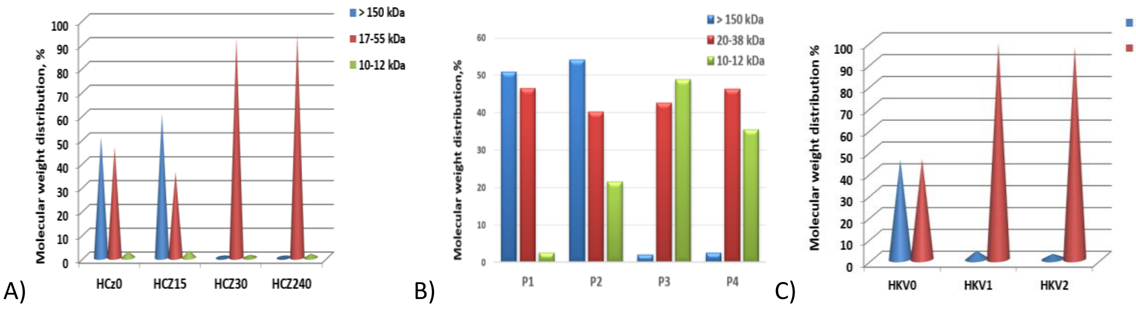

Figure 7. Molecular weight distributions of: A) collagen hydrolysates processed at 130°C; B) collagen hydrolysates treated at 100°C; C) keratin hydrolysate after processing at 130°C

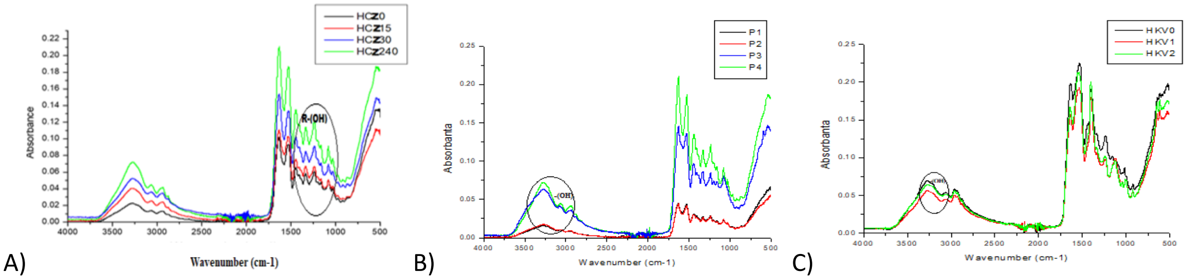

Figure 8. FTIR-ATR spectra for: A) collagen hydrolysates processed at 130°C; B) collagen hydrolysates processed at 100°C, and C) keratin hydrolysates processed at 130°C

The Amide I band region is related to the stretching vibration of the peptide carbonyl group (-C=O) involved in polypeptide backbone and represents a marker of secondary structure. The Amide A is due to N-H stretching vibration which is not dependent on protein backbone conformation and is very sensitive to intramolecular hydrogen bond strength. The absorption bands A and I signals are used in protein analysis because their signals are strong in a spectral region without other additional absorptions [11].

The ratio of the intensities of the Amide I/Amide A bands quantifies the cleavage of the collagen molecule [12], and are found in the FTIR-ATR spectra between the wave numbers 1600-1800 cm^{-1} (Amide I) and 3300-3500 cm^{-1} (Amide A) and is presented in Figure 13a-c.

The results show suggestive reductions in the AI/AA ratios, as a result of the cleavage of the collagen molecule under various conditions of temperature.

The biggest variations were recorded for keratin hydrolysate ($\Delta_{AI/AA}$=1.41), collagen hydrolysate processed at 130°C ($\Delta_{AI/AA}$=1.35) and lowest ratios were found for collagen hydrolysate processed at 100°C ($\Delta_{AI/AA}$=0.35).

The results are significant for the hydrolysates processed at 130°C, where there is a large share of particles with a size of 8.7-9.0 nm with a 31.3% increase after 140 minutes of hydrolysis compared to the initial product (11% of particles with 12.7 nm), and 21.1% increased ratio between the last two hydrolysis stages.

These particles could be populations of particles with medium molecular weights that split from particles with high molecular weights (Figure 7). Also, with these hydrolysates, the polydispersity increases significantly (from 0.4 to 0.9) and the Zeta potential changes (from 3.1 mV to -3.8 mV), confirming this hypothesis.

Instead, in the case of hydrolysates processed at 100°C, the hydrolysis step at 13 hours generates hydrolysates almost similar to those processed for 20 hours (Figure 8), in accordance with the data in Figure 13b regarding the AI/AA amide ratio. In the case of these hydrolysates, the share of particles with sizes of 280.5-376.1 nm increases to the value of 61.0-91.7%, when the medium particle size in the initial hydrolysate is 1804 nm (Table 2). And if we take into consideration the 29.3% population of particles with 118.9 nm generated after 13 hours of hydrolyses at 100°C, we can conclude that the populations of 118.9-376.1 nm are in the same ratio of 90.1-94.7% and the hydrolyses results are similar at 13 and 20 hours.

In the case of keratin hydrolysates, the stability of the particles is high, as can be seen from the higher absolute value of the Zeta potential (-28.3 mV to 29.0 mV), unlike that of collagen hydrolysates, which are weakly negatively (-3.8 mV to -10.9 mV) charged and tend to agglomerate.

In the case of keratin hydrolysates, the appearance of a population of particles with small sizes (35.4-66.4 nm) in the proportion of 6.7-7.2% is noted. The polydispersity, medium size and Zeta potential of the particles change insignificantly, which may be due to the association properties of the protein molecules (Table 4).

The AI/AA ratios confirm the changes in molecular distribution through heat treatments for collagen and keratin hydrolysates.

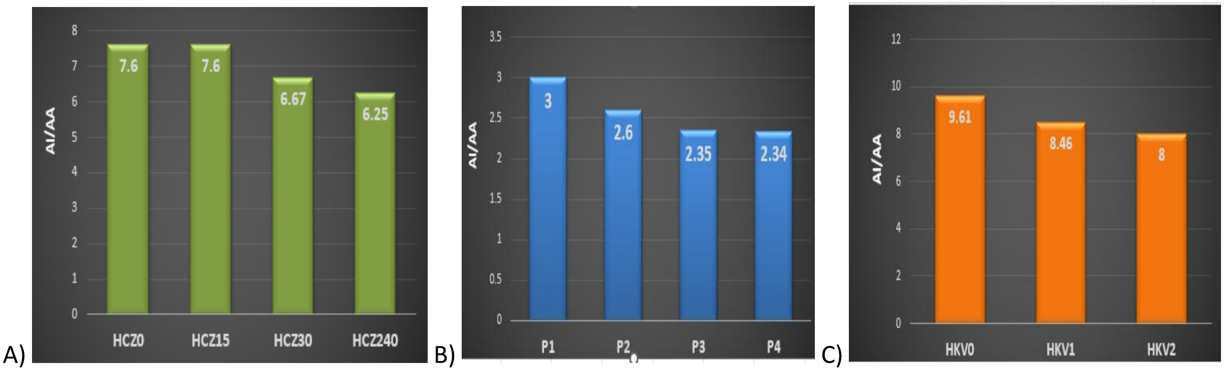

Figure 13. Decrease of the absorbance ratios of amide AI/AA bands for:
A, B) collagen hydrolysates and C) keratin hydrolysate

CONCLUSIONS

By-products from the leather and fur industry, as well as those generated from raising sheep with inferior wool quality, represent a valuable source of proteins that can be used to create new auxiliary chemicals for the leather industry, agriculture, medicine and other applications. Additional treatments under pressure and temperature can shape the molecular distribution of the composition of protein hydrolysates, which was highlighted by measurements through dynamic light scattering (DLS), gel electrophoresis (SDS-PAGE electrophoresis) and FTIR spectroscopy (ATR-FTIR). Low molecular weight peptides were generated by hydrolyses at 100°C and medium weight molecules after hydrolyses at 130°C for collagen hydrolysate. High molecular weight collagen hydrolysate ratios were decreased by hydrolysis at 100°C and 130°C. Keratin hydrolysate molecular weight decreased after hydrolyses at 130°C and molecules less than 10 kDa doubled.

Further studies on the correlation of the molecular weight and particle sizes needs to be performed as well as the separation by SDS-PAGE electrophoresis of proteins with molecular weight under 10 kDa. The potential applications of the new hydrolysates with different compositions, depending on the hydrolysis conditions (with an increased weight of components with low or medium molecular weights) will be investigated in future research.

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IMPLEMENTATION OF THE PRINCIPLES OF BIOECONOMY IN LEATHER PRODUCTION

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IMPLEMENTATION OF THE PRINCIPLES OF BIOECONOMY IN LEATHER PRODUCTION

ABSTRACT. Bioeconomy is a promising approach to addressing resource conservation and negative environmental impacts. Given the high potential of bioeconomy principles, many countries worldwide are focused on developing plans with a perspective up to 2050. The main sectors where bioeconomy principles are applied globally include agriculture, light industry, and bioenergy. In Ukraine, the bioeconomy strategy is developing at a slower pace. However, the developed 10R bioeconomy strategies can be adapted in Ukraine, considering the processing industry's development trends. Given the active development of agriculture in Ukraine, including many raw hides (cattle cow, bovine, etc.), the tasks of processing animal hides are relevant. It is known that a large amount of water, energy resources, and chemicals are used in such processing. A significant amount of waste is also generated, which can be used to implement bioeconomy principles. The study optimized the use of raw materials and chemicals by reducing or reusing water and solid leather production waste. It was found that the principles of R2 (Reduce), R3 (Reuse), R8 (Recycle), and R9 (Recover) can be implemented in leather production. The principles of R8 and R3, through the processing of biogenic raw materials and reducing the use of chemicals at the stages of leather production, respectively, have the highest efficiency before implementation.

KEY WORDS: bioeconomy, leather, raw hide, water and solid wastes, technological processing

IMPLEMENTAREA PRINCIPIILOR BIOECONOMIEI ÎN PRODUCȚIA DE PIELE

REZUMAT. Bioeconomia este o abordare promițătoare pentru conservarea resurselor și diminuarea impactului negativ asupra mediului. Având în vedere potențialul ridicat al principiilor bioeconomiei, multe țări din întreaga lume se concentrează pe dezvoltarea unor planuri cu o perspectivă până în 2050. Principalele sectoare în care principiile bioeconomiei sunt aplicate la nivel global includ agricultura, industria ușoară și bioenergia. În Ucraina, strategia în domeniul bioeconomiei se dezvoltă într-un ritm mai lent. Cu toate acestea, strategiile dezvoltate în domeniul bioeconomiei 10R pot fi adaptate în Ucraina, ținând cont de tendințele de dezvoltare ale industriei de prelucrare. Având în vedere dezvoltarea activă a agriculturii în Ucraina, ce include și prelucrarea multor tipuri de piei brute (bovine, de vițel etc.), operațiunile de prelucrare a pieilor animale sunt relevante. Se știe că în astfel de operațiuni se consumă o cantitate mare de apă, resurse energetice și substanțe chimice. De asemenea, se generează o cantitate semnificativă de deșeuri, care pot fi utilizate pentru implementarea principiilor bioeconomiei. Studiul a optimizat utilizarea materiilor prime și a substanțelor chimice prin reducerea sau reutilizarea apei și a deșeurilor solide din producția de piele. S-a constatat că principiile R2 (Reducere), R3 (Reutilizare), R8 (Reciclare) și R9 (Recuperare) pot fi implementate în producția de piele. Principiile R8 și R3, prin prelucrarea materiilor prime biogene și, respectiv, prin reducerea utilizării de substanțe chimice în etapele producției de piele, au cea mai mare eficiență înainte de implementare.

CUVINTE CHEIE: bioeconomie, piele, piele brută, apă reziduală și deșeuri solide, procesare tehnologică

MISE EN ŒUVRE DES PRINCIPES DE LA BIOÉCONOMIE DANS LA PRODUCTION DE CUIR

RÉSUMÉ. La bioéconomie est une approche prometteuse pour conserver les ressources et réduire l'impact négatif sur l'environnement. Compte tenu du potentiel élevé des principes de la bioéconomie, de nombreux pays du monde entier se concentrent sur l'élaboration de plans avec une perspective allant jusqu'en 2050. Les principaux secteurs dans lesquels les principes de la bioéconomie sont appliqués à l'échelle mondiale comprennent l'agriculture, l'industrie légère et la bioénergie. En Ukraine, la stratégie bioéconomique se développe à un rythme plus lent. Cependant, les stratégies développées dans le domaine de la bioéconomie 10R peuvent être adaptées en Ukraine, en tenant compte des tendances de développement de l'industrie de transformation. Compte tenu du développement actif de l'agriculture en Ukraine, qui comprend la transformation de nombreux types de peaux brutes (bovins, veaux, etc.), les opérations de transformation des peaux d'animaux sont pertinentes. De telles opérations sont connues pour consommer une grande quantité d'eau, de ressources énergétiques et de produits chimiques. En outre, une quantité importante de déchets est générée, qui peut être utilisée pour mettre en œuvre les principes de la bioéconomie. L'étude a optimisé l'utilisation de matières premières et de produits chimiques en réduisant ou en réutilisant l'eau et les déchets solides issus de la production du cuir. Il a été constaté que les principes R2 (Réduire), R3 (Réutilisation), R8 (Recycler) et R9 (Récupération) peuvent être mis en œuvre dans la production du cuir. Les principes R8 et R3, en traitant respectivement des matières premières biogéniques et en réduisant l'utilisation de produits chimiques dans les étapes de production du cuir, ont la plus grande efficacité avant leur mise en œuvre.

MOTS CLÉS : bioéconomie, cuir, peau brute, eau résiduelle et déchets solides, transformation technologique

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INTRODUCTION

The Lund Declaration outlines challenges related to global environmental issues, food security, healthcare, industrial restructuring, and energy security [1]. These problems are defined as persistent, complex, and pressing. However, their resolution may lead to further crises for future generations. Therefore, safety, health, well-being, and environmental preservation issues are becoming increasingly relevant [2, 3].

With the advancement of scientific and technological progress, economic growth has become the primary priority of economic activities worldwide, while environmental sustainability has gained significant importance in recent times. The role of bioeconomy is aimed at combining these priorities.

Over the past two decades, bioeconomy has demonstrated its viability as a sustainable business model and economic development form for countries worldwide. Thanks to the application of modern technological methods (in the extractive and processing industries), it has become possible to reduce the absolute amount of extracted energy used and environmental pollution by reducing greenhouse gas emissions [3]. The place and role of bioeconomy in solving global human problems are defined in strategic programs for the transition to a bioeconomic development path of national economies in countries such as the United States, the United Kingdom, and the European Union, as well as by the amount of financial resources allocated for their implementation at the international, regional, and local levels [4].

Given the high potential of bioeconomy, many countries worldwide are focused on creating development plans with a perspective up to 2050. In EU countries, bioeconomy has various development characteristics. For example, the bioeconomy of Finland, Sweden, Estonia, and Latvia is primarily focused on the forestry sector; in Italy and Portugal, 14% and 16% of the bioeconomy model is implemented in the field of biotextile production, respectively; 36% of the bioeconomy value added in Ireland and 35% in Denmark falls on the production of biochemicals, pharmaceuticals, polymeric materials, and rubber.

Since 2018, the EU has been implementing a bioeconomy strategy in three key areas: accelerating the bioindustry development, promoting the bioeconomic development of urban and rural areas, and protecting ecosystems [5].

In 2021, the EU published the report "Foresight Scenario for the EU Bioeconomy in 2050: The Future Transition of the Bioeconomy towards Sustainable Development and a Climate Neutral Economy". According to the EU report, the bioeconomy should be aimed at sustainable development and climate neutrality, as well as improving its inclusivity in EU member states' economic and social realities [5].

In Ukraine, the bioeconomy strategy is developing at a slow pace and has a fragmented nature. The main sectors in Ukraine where bioeconomy principles are applied are agriculture, light industry, and bioenergy. In this regard, a targeted policy for the development of the bioeconomy in Ukraine, supporting the bioeconomy sector, can become a driving force in the sustainable development of the national economy [5].

EXPERIMENTAL

Material and Methods

This study aims to develop a set of guiding principles of bioeconomy for effective implementation in leather production, focusing on resource conservation, reducing biogenic waste, and promoting reuse.

The object of this study is the technological processes and parameters of leather production.

The subject of this research is the typical patterns of solid and liquid waste generation at different stages of the leather production process.

A combination of general scientific and specialized methods was employed in this research: analysis and synthesis, a systemic approach, comparison, and generalization of official data from the State Statistics Service of Ukraine and the State Customs Service of

Ukraine. Methods of logical analysis and generalization of scientific literature, statistical data on the cultivation of raw hides, skins, and pigs, production, export, and import of tanned leather from raw hides were used.

The definitions of “bioeconomy” and “bioeconomy strategies” were interpreted through theoretical research methods, including analysis, systematization, and logical generalization. A hypothesis was put forward regarding the implementation of bioeconomic strategies by conserving resources, reducing the quantity, and reusing biogenic waste generated during leather production. The obtained assumptions and conclusions were confirmed by existing methods of processing leather industry waste aimed at creating an environmentally friendly direction by reducing the amount of water and solid waste.

Traditional technologies for processing animal hides into natural leather were used to formulate the principles of the bioeconomy and their application in leather production. The sequence of technological processes involves preparatory (beamhouse), tanning, and finishing treatments.

A list of the most commonly used chemicals and their consumption was analyzed for the research. The types and stages of obtaining water and solid waste were analyzed.

Information on known methods of reducing the consumption of chemicals for processing hides and methods of reusing waste for both leather production and the creation of products for other purposes was used.

RESULTS AND DISCUSSION

Implementation Pathways for the Bioeconomy

The scientific community interprets the bioeconomy as a vast system that connects natural resources, technologies, markets, people, and policies. Bioeconomy unites processes that were previously impossible to combine: business and sustainability; ecosystems and industry; innovative and traditional processes, technologies; raw materials of biogenic origin and finished products [6, 7].

Effective resource management and processing are also important directions of the bioeconomy. The conceptual model of the bioeconomy describes a system in which primary renewable resources, as well as secondary ones, which are waste, in the process of applying knowledge, innovations, and technologies, are transformed into environmentally oriented and resource-saving processes, products, and services. The originality of this phenomenon lies in the sustainability and efficiency of renewable resources [8].

The bioeconomy rethinks what is considered waste, using characteristic processes that can not only reduce waste generation but also reduce the number of raw materials required for production [5].

The first bioeconomy model was built on the principles of the “3R-strategy”. These principles included the “Reduce, Reuse, Recycle” strategies, which appeared in the 1970s [5]. In recent years, the number of bioeconomy strategies has increased, given the expediency of waste processing. As of 2024, 10R strategies have been proposed (Table 1). To systematize the directions of bioeconomy development, the 10R strategies are aimed at creating, preserving, and restoring the value of invested resources and understanding the different stages of their use in the bioeconomy. R-strategies are resources and principles for shaping a sustainable circular future.

The 10R-strategies are categorized into three groups that demonstrate the length of the waste cycle (short, medium, and long). The shorter the cycle, the more sustainable the strategy. The higher the strategy in the hierarchy, the tighter the waste loop. This means that the strategy requires fewer materials and is therefore more circular. Smaller numbers also indicate the beginning of the value chain, while larger numbers indicate the end [9].

Short cycles focus on more efficient production and product use: R0 – Refuse, R1 – Rethink, R2 – Reduce. Medium cycles focus on strategies to extend product lifespan: R3 –

Reuse, R4 – Repair, R5 – Refurbish, R6 – Remanufacture, R7 – Repurpose. Long cycles focus on alternative uses of the material: R8 – Recycle, R9 – Recover. The positive impact on circularity and overall sustainability is higher at the beginning of the material value chain, where the strategies are numerically the smallest and the waste cycle is the shortest [9].

Table 1: Description of R-strategies for a sustainable bioeconomy

Strategy	Name	Characteristic	Scope of application
R0	Refuse	A strategy that prohibits the use of certain materials considered harmful.	Agriculture, food, medical, pharmaceutical, pulp and paper, forestry, fuel and energy, chemical, mechanical engineering
R1	Rethink	A strategy focused on intensive product use through the introduction of new products to the market.	
R2	Reduce	This strategy aims to minimize consumption and increase production efficiency.	
R3	Reuse	Extending the lifespan of products through reuse for their original purpose.	
R4	Repair	Repair and maintenance of a faulty product to restore its functionality.	
R5	Refurbish	Restoring an old product to its original condition.	
R6	Remanufacture	Remanufacturing involves integrating product components that are still intact into new ones.	
R7	Repurpose	This strategy incorporates waste into another product for benefit or an alternative purpose.	
R8	Recycle	Using materials through recycling when a product can no longer be used, but it contains materials that can be recovered.	
R9	Recover	Extracting value from waste through composting organic waste (producing biogas).	

These 10R-strategies can be adopted in Ukraine to address the development of agriculture and the processing industry. Ukraine is an agricultural country with a constantly developing livestock industry. Given the number of livestock, the issue of animal skin processing is relevant. As a result of such processing, a significant amount of waste is generated that can be used in the implementation of bioeconomy strategies in Ukraine, using the example of the leather industry.

Dynamics of Leather Raw Material Volumes

The state of the livestock sector is a significant component of the Ukrainian economy, as evidenced by the analysis of raw hides and pig production volumes during 2019-2023 (Figure 1).

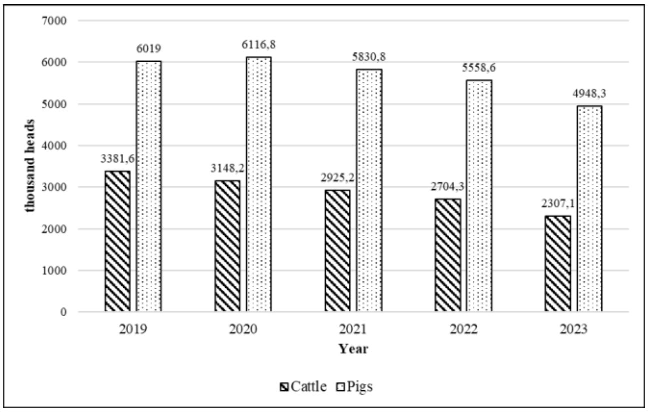


Figure 1. Dynamics of raw hides and pigs herd growth in Ukraine during 2019-2023 [10]

An analysis of the data in Figure 1 shows a gradual decrease in the number of raw hides raised during the studied period. As of 2019, this figure was 3381.6 thousand heads, and in 2023, it was 2307.1 thousand heads, a decrease of 31.7%.

A similar trend is observed in the case of pig farming. In 2019, the number of pigs raised was 6019.0 thousand heads, and in 2023, it was 4948.3 thousand heads, a decrease of 17.7%.

Overall, the number of pigs raised significantly exceeds the number of raw hides. Moreover, in 2019, the difference was 1.7 times, and in 2023, it was 2.2 times. As of 2023, Ukraine ranked 25th in the world in terms of pig exports and 32nd in terms of raw hides exports.

Based on this, it can be concluded that there is an objective availability of a sufficient number of hides obtained from livestock, and, accordingly, the emergence of tasks for processing leather raw materials. There are a significant number of leather enterprises in Ukraine: Kyiv (LLC “ULTRA LEATHER”), Voznesensk (LLC “V-CENTER”, LLC “UKRTAN”, LLC “UtaCo Ltd”), Berdychiv (LLC “SHKIRZAVODVELEC”), Vasylkiv (LLC “SLAVA”), Zhytomyr (LLC “EMI-UKRAINE LTD”), Lviv (LLC “STROFARIYA”), Bolekhiv (Tzov “SVIT SHKIRY”).

These enterprises provide sufficient volumes of natural leather production (Figure 2), however, an analysis over five years indicates a significant reduction in the production of leather from rawstock.

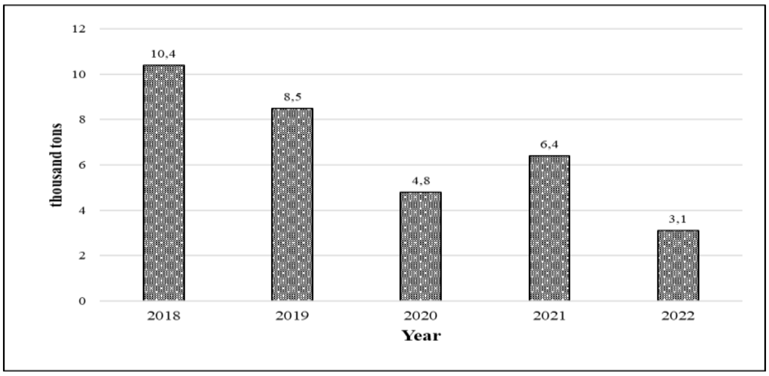


Figure 2. Dynamics of leather production volumes from raw hides in Ukraine during 2018-2022

Figure 2 demonstrates a more than threefold decrease in the production of leather from raw hides between 2018 and 2022. However, in 2021, compared to 2020, there was a 33.3% increase in the production of leather from raw hides. The most significant decline was observed in 2022 compared to the previous year [11].

It should be noted that Ukraine has a high export potential for semi-finished items made from hides and skins of bovine (Figure 3).

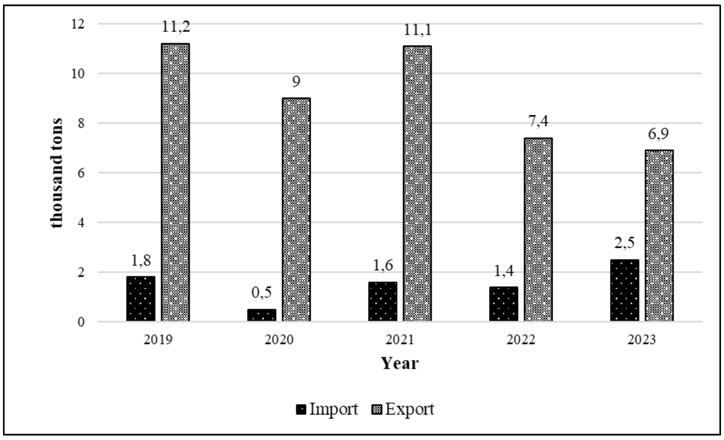


Figure 3. Dynamics of imports and exports of semi-finished items of bovine (HS code 4104) in 2019-2023, in physical terms

According to the State Customs Service of Ukraine, the dynamics of Ukraine's foreign trade in semi-finished items from bovine hides (HS code 4104) exhibited an unstable trend from 2019 to 2023. There was a tendency towards a decrease in exports of semi-finished items by 38.4% [12]. During 2019-2020, exports decreased by 19.6%. In 2021, this figure increased to 11.1 thousand tons. However, in 2023, there was a decline of 6.7% compared to 2022.

Export volumes were significantly higher than imports. However, while in 2020 exports exceeded imports by a factor of 18, in 2023 this ratio decreased to 2.7. An analysis [12] showed a decrease in imports of semi-finished items into Ukraine by 22.2% from 2019 to 2022. In 2023, there was an increase in this indicator from 1.4 thousand tons to 2.5 thousand tons compared to 2022, or 1.7 times [12]. Italy was the main importing and exporting country for semi-finished items in 2023. Its share in imports was 40.2%, and in exports, it was 91.4%. In addition, among the main importing countries were Kyrgyzstan with a share of 29%, and Kazakhstan with 14.3%, while among the exporting countries were Turkey and Poland with 6.8% and 1.1%, respectively [12].

Therefore, Ukraine has significant livestock numbers and efficient leather production, and thus, bioeconomy strategies in Ukraine can be implemented through resource-saving and waste processing of leather raw materials.

Implementation of Sustainable Bioeconomy Principles in Leather Processing

The leather production process involves a complex series of treatments of raw materials and semi-finished products, which can be divided into liquid processes (carried out in an aqueous environment using chemicals) and mechanical operations (changing the shape of the processed dermis structure) [13].

Generally, the leather production process is divided into three stages: preparatory (beamhouse), tanning, and finishing. The preparatory stage includes soaking, liming, unhairing, fleshing, splitting, deliming, bating. Preparatory processes are aimed at performing several sequential tasks: hydrating the dermis structure, loosening collagen fibers, removing interfibrillar proteins, hair, epidermis, and flesh, peptization of structural elements, and lowering pH for their structuring.

The fixation of the dermis structure is ensured by the tanning process, usually chrome tanning. Tanning provides stability to the leather semi-finished product to external factors: light, heat, ultraviolet radiation, and the action of microorganisms, and also forms high hydro-thermal stability and physical and mechanical properties. Subsequent retanning of the dermis is carried out with vegetable tannins and syntans to form the hygienic and organoleptic properties of leather, giving it softness, fiber density, and elasticity. During wet finishing, polymeric or mineral fillers, dyes, and fatliquoring materials complete the formation of the volume structure of the dermis, capable of elastic-plastic deformation, with a high level of elasticity and air permeability. The finishing stage of the leather surface includes drying and moisturizing processes and coating finishing, which include: setting, sammying, trimming, staking, drying, moisturizing, boarding and softening, buffing, dedusting, pressure treatment, as well as applying a protective coating to the grain surface of the leather.

After finishing, the leather acquires the necessary appearance and corresponding hygienic properties [14]. Acids, alkalis, chromium salts, tanning agents, solvents, sulfides, dyes, auxiliaries, and many other compounds used in the processing of leather raw materials to obtain natural leathers are not completely fixed in the dermis and create a significant amount of water waste (Ww – Water wastes). These wastes are the cause of increased levels of biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and total suspended solids (TSS).

It has been established that chemical compounds that are difficult to purify in wastewater are obtained during the tanning process. Considering that about 30-40 liters of water is used for each kilogram of raw hides, of which 35% is used during washing, and 55% is used during liquid processes or mechanical operations, a significant level of environmental pollution by leather production can be predicted [14].

The stages of the leather production process and the scheme of waste formation during the processing of leather raw materials are presented in Figure 4.

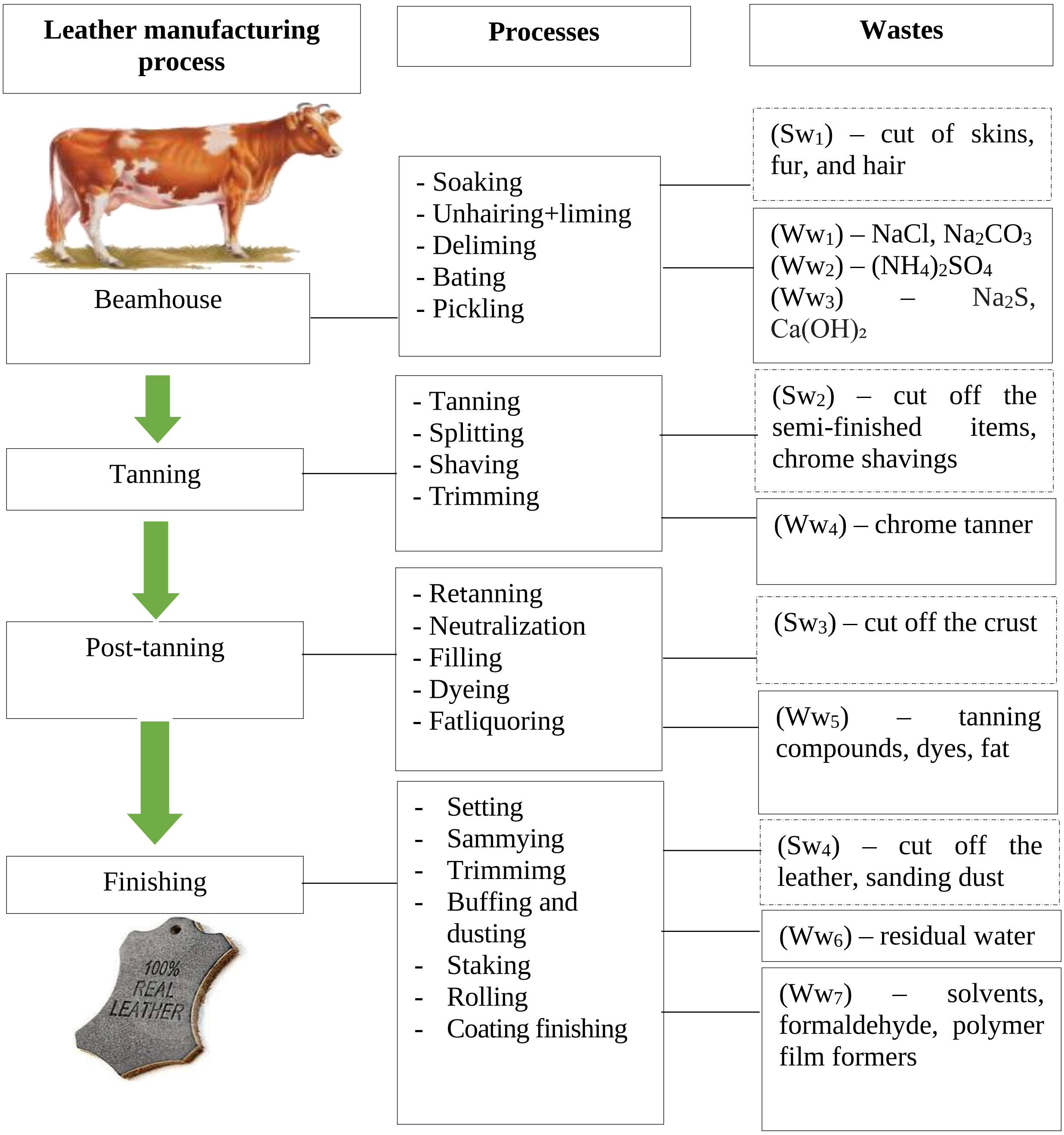


Figure 4. The leather manufacturing process and the waste materials produced at each stage

It is known that approximately 0.80 kg of waste is generated from each kg of raw hides. These wastes are used for the production of other materials, such as glue, gelatin, and protein feed for pets. Extracted collagen, peptides, and amino acids obtained from leather production waste are actively used in cosmetology, biopharmaceutics, wound healing materials, etc. [14].

During leather production, solid wastes (Sw – Solid wastes) is also generated, which poses a significant economic and environmental problem for society and the environment. According to research [15], the composition of solid waste from leather production includes removed salts, hair waste, shaving trimmings, leather shavings, etc. Additionally, during the treatment of leather production wastewater, sediments, and other solid waste are also formed.

Environmental problems associated with improper disposal of leather industry waste arise both from the quantity and quality of waste. On average, the leather industry produces 45-50 m^3 of water waste and 800 kg of solid waste per 1 ton of finished leather product. The processing of one ton of raw materials produces an average of 200 kg of finished tanned leather, 200 kg of tanned leather waste, 250 kg of untanned waste, and 50 m^3 of wastewater. The most common method of managing solid waste from the leather industry is landfilling. However, due to the unpleasant odor caused by putrefaction and the harmful content of fat-containing waste, landfilling negatively affects the soil and water resources of the environment [15]. In this regard, environmental protection agreements are gaining momentum worldwide, forcing the leather industry to reuse waste generated at various stages of leather production [16].

Today, there are many methods for processing leather industry waste aimed at creating an environmentally friendly direction by reducing the amount of water and solid waste.

As a result, the introduction of the principles of a sustainable bioeconomy in the processing of raw hides and skins will reduce waste generation and save the resource-saving raw stock.

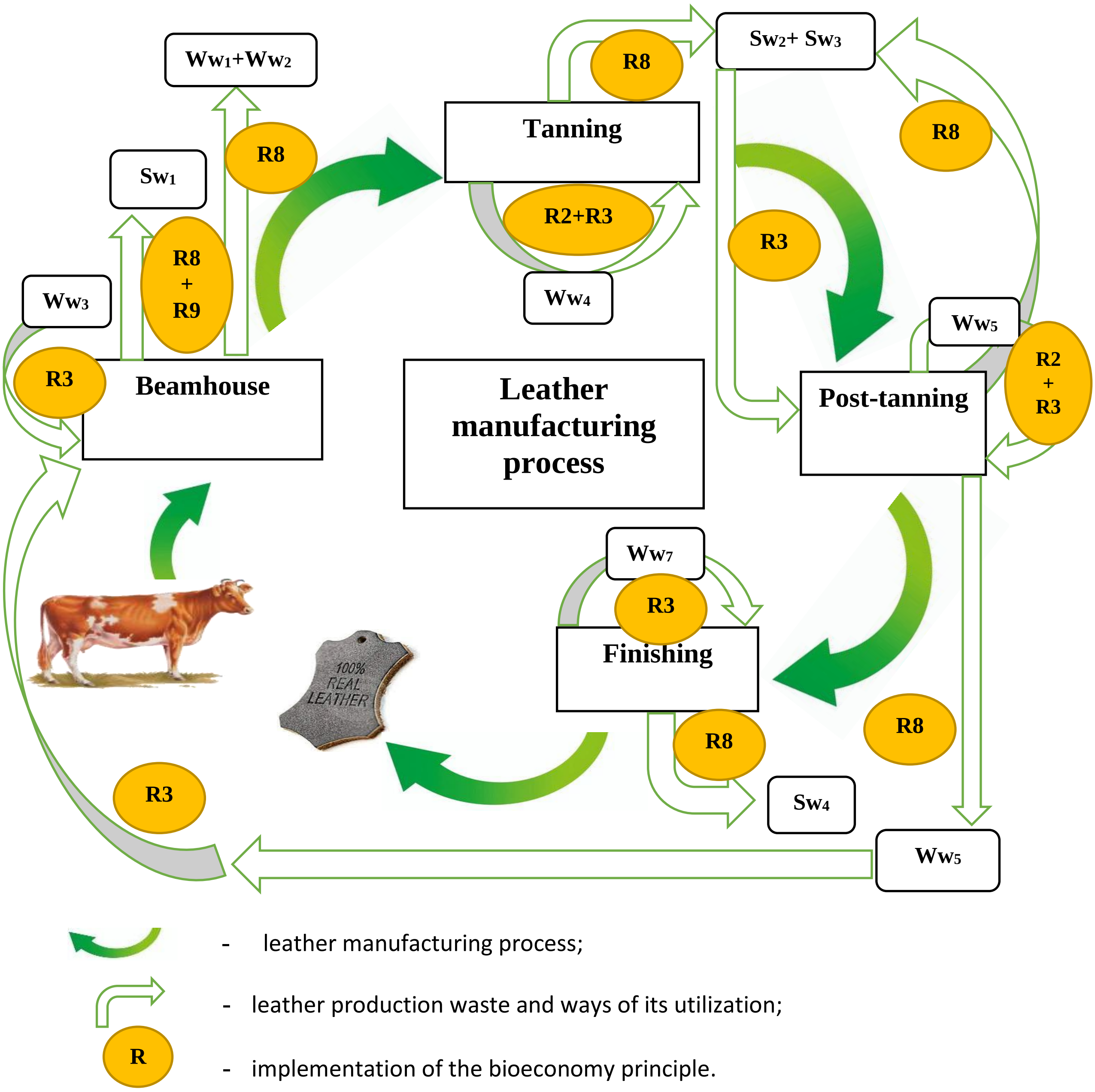
Among the existing 10R-strategies of the bioeconomy (Table 1) for the processing of leather raw materials, the following can be introduced: R2 – Reduce, R3 – Reuse, R8 – Recycle, R9 – Recover [5]. The sequence of leather production stages, a schematic representation of the formation of water and solid waste, and the appropriate introduction of the indicated principles of bioeconomy strategies are presented in Figure 5.

After the beamhouse stage, Sw_1 (cut of skins, fur, and hair), (Ww_1) – $NaCl$, Na_2CO_3; (Ww_2) – $(NH_4)_2SO_4$; (Ww_3) – Na_2S, $Ca(OH)_2$ are formed.

The implementation of the sustainable bioeconomy principle R3 can be achieved by reusing $Ca(OH)_2$ from Ww_3 (adjusting its concentration to– 10-15 g/l) [17]. Principles R8 and R9 can be ensured by recycling and recovering Sw_1 in other industries, respectively. Additionally, Ww_1, and Ww_2, formed at this stage of leather production, can be purified and used in other areas by implementing principle R8. For example, there are known methods for processing untanned solid waste to produce fleshing glue, collagen hydrolysates of varying degrees of dispersion, animal feed additives, components of water treatment filters, biohumus, plasticizers, mixtures for wool yarn sizing, etc. [18-23].

The implementation of the sustainable bioeconomy principle R9 is focused on the processing of fat-containing waste from the leather industry through anaerobic digestion to produce biogas. Typically, when using fat-containing waste, co-fermentation with cellulosic feedstock is used to stabilize the pH value [24].

The literature [24] discusses a method for obtaining biogas from water waste produced in the manufacture of chrome semi-finished products. The process involves the fermentation of pre-heat-treated chrome leather waste in the form of shavings and gelatin, with the latter being separated from chromium hydroxide during primary processing.



- leather manufacturing process;

- leather production waste and ways of its utilization;

- implementation of the bioeconomy principle.

Figure 5. Implementation of the principles of bioeconomy in leather manufacturing process

After the tanning stage, Sw_2 (cut off the semi-finished items, and chrome shavings) and Ww_4 (cut off the leather, and sanding dust) are formed.

The implementation of sustainable bioeconomy principle R2 in leather production can be achieved by reducing the amount of Ww_4 during the tanning process using montmorillonite [25]; R3 - by reusing purified water waste after the tanning process Ww_4 [26]; R8 – by recycling tanned waste Sw_2 and using it at the next stage of leather production in the filling process [21].

It has been established that the range of uses for tanned waste in recycling is significantly narrower. This is due to the presence of salts, mineral tannins, and fats in the waste; the formation of additional bonds with chemical materials in the protein structure, and, consequently, a change in the properties of collagen itself. The list of technologies different countries proposed for processing tanned by-products includes various methods for obtaining biogas and biodiesel, mineral or organic fertilizers, filler compositions for artificial leather, polymeric and composite materials, concrete mixtures, etc.

The implementation of principle R8 involves the recycling of tanned collagen-containing waste, which can be used as fillers in leather production. They fully retain the unique hygienic properties of natural leather. For filling leather semi-finished products, fleshing glue, a hydrolyzate obtained by an enzymatic method from untanned waste, is used. Retanning and filling are carried out with an alkaline hydrolyzate of chrome shavings, and an acid hydrolyzate using sulfuric and acrylic acids. Positive results were obtained when fatliquoring leather semi-finished products with a fat emulsion of synthetic fat, in the manufacture of which a hydrolyzate obtained by an enzymatic method of fleshing glue was used as an emulsifier and stabilizer [21, 27]. The use of collagen dissolution and dispersion products in coating finishing contributes to improving the hygienic properties of the finishing leather and increasing its adhesion to the leather.

In addition, collagen-containing waste is a valuable raw material for producing artificial leather. Tanned waste is subjected to mechanical fiberization before use, from which fabrics and non-woven materials are formed [20].

After the post-tanning stage, Sw_3 (cut off the crust) and Ww_5 (tanning compounds, dyes, fat) are formed.

The implementation of sustainable bioeconomy principles R2 and R3 can be achieved by reducing the amount and reusing Ww_5 respectively, during the post-tanning stage of leather production [21], while R8 will ensure the recycling of Sw_3 in the production of leatherboard, which is an auxiliary shoe material used in the manufacture of shoe components, such as backstays, insoles, etc. One of the most rational ways to utilize tanned waste is the production of leatherboard, which contains 70-75% leather fiber [20, 21].

It is advisable to process Sw_3 in such a way that it can be used to produce fillers for leather that can simultaneously chemically bond with it and retan it [21]. A large part of such fillers consists of partially hydrolyzed leather protein, that is, a substance that is close in its chemical composition to natural leather. In this regard, as a result of filling, it is necessary to expect the preservation of the most valuable quality of natural leather – its hygienic properties. When obtaining fillers for leather, the waste is detanned with an alkali solution, separated from chromium salts, washed, transferred to a solution when heated with water, and then polymerized together with vinyl monomers. The resulting products have a good effect when filling the leather. However, there are significant losses of alkali and chromium salts [20, 21].

After the finishing stage, Sw_4 waste (cut off the leather, sanding dust) and Ww_7 waste (solvents, formaldehyde, polymer film formers) are generated. The implementation of R3 sustainable bioeconomy principles can be achieved through the reuse of liquid Ww_7 waste [17]; R8 will allow the use of leather pieces, substandard products, defects, and trimmings of finished leathers as raw materials for the further production of various products or their finishing. Examples include the production of leatherboard, stamping buttons from scraps of sole, harness, saddle, or technical leathers, and the production of decorative and applied leather goods.

It should be noted that after each stage of leather production, water waste (Ww_1, Ww_2, Ww_3, Ww_4 and Ww_5), is generated, causing significant damage to the environment. Using waste treatment methods, these wastes can be used in other areas of agriculture and industry. Therefore, the implementation of principle R8 can be realized by recycling and using treated water waste for irrigation of agricultural lands, and R3 – by reusing treated wastewater in leather production [21].

According to the above and based on Figure 5, bioeconomy strategies can be implemented through (Figure 6):

- reducing the consumption of harmful chemicals during tanning and post-tanning processes (R2);
- reusing spent process liquids and products of leather waste recycling in the leather production process (R3);
- recycling solid waste and creating new products or materials (R8);
- recovering the chemical component of leather production waste into energy-useful compounds (R9).

Figure 6. Effectiveness of implementing the principles of bioeconomy in the leather manufacturing process

An analytical assessment of the potential for using bioeconomy strategies indicates that the total number of solutions for waste processing and resource conservation in leather production can be implemented according to the R8 (40%), R3 (40%), R2 (15%), and R9 (5%) principles.

CONCLUSIONS

Based on the findings, strategies R8 and R3 are deemed most suitable for the leather industry. These strategies enable efficient utilization of leather raw materials, leading to economic and resource savings in material and water usage, reduced costs for treating spent process liquids and wastewater, and the production of new technologically valuable materials for leather manufacturing or products for agriculture, other industries, medicine, and pharmaceuticals. Strategies R2, focusing on reducing chemical consumption, and R9, aimed at recovering waste from biogenic raw materials for bioenergy products, while beneficial, are expected to have a lesser impact on the leather industry.

Overall, the implementation of bioeconomy principles (R2, R3, R8, R9) within the leather production process can significantly reduce solid and water wastes, promoting the recycling and reuse of valuable secondary materials both within the leather industry and other sectors of the Ukrainian economy.

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Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European. Neither the European Union nor the granting authority can be held responsible.

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INDUSTRIAL WORKERS’ EFFICIENCY IN INDIAN SUBCONTINENT: A MACHINE LEARNING MODEL APPROACH

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INDUSTRIAL WORKERS’ EFFICIENCY IN INDIAN SUBCONTINENT: A MACHINE LEARNING MODEL APPROACH

ABSTRACT. The growing popularity of machine learning offers exciting possibilities for real-world applications. Since worker efficiency directly impacts a company’s bottom line, especially for small and medium businesses (SMEs), implementing these tools can be a game-changer. By improving worker efficiency, machine learning can help SMEs minimize losses and drive growth. This research explores the potential of AI model not to replace workers but to uplift them. In this study, we try to find out the industrial workers’ efficiency, especially in the Leather & Textiles industries, based on some parameters like expertise, education, salary, working hour, standard minute value (SMV), working position, key performance indicators (KPI) etc. The study investigates different regression models for predicting worker efficiency. Here we compare six models including Random Forest and XG Boost, using metrics like Mean Squared Error to find the best performing model. XG Boost and Histogram Gradient Boosting show the best results in predicting worker efficiency. XG Boost achieved high accuracy (R-squared around 0.78) with low errors (MSE around 0.01). Light GBM came in a close third, while Random Forest and Ada Boost did poorly. Machine learning techniques like XG Boost can significantly improve worker efficiency in the Indian subcontinent in leather-textile industries.

KEY WORDS: workers performance, industrial worker augmentation, data driven efficiency.

EFICIENȚA LUCRĂTORILOR DIN INDUSTRIA SUBCONTINENTULUI INDIAN: O ABORDARE A MODELULUI DE ÎNVĂȚARE AUTOMATIZATĂ

REZUMAT. Popularitatea din ce în ce mai mare a învățării automatizate oferă posibilități interesante pentru aplicații din lumea reală. Întrucât eficiența lucrătorilor are un impact direct asupra profitului unei companii, în special pentru întreprinderile mici și mijlocii (IMM-uri), implementarea acestor instrumente poate duce la o revoluționare. Îmbunătățind eficiența lucrătorilor, învățarea automatizată poate ajuta IMM-urile să reducă la minimum pierderile și să stimuleze creșterea. Această cercetare explorează potențialul modelului AI nu de a înlocui lucrătorii, ci de a-i ajuta să-și îmbunătățească performanțele. În acest studiu, s-a încercat determinarea eficienței lucrătorilor din industrie, în special din industria de textile și pielărie, pe baza unor parametri precum expertiza, educația, salariul, programul de lucru, valoarea minutelor standard (SMV), funcția, indicatorii cheie de performanță (KPI) etc. Studiul investighează diferite modele de regresie pentru prezicerea eficienței lucrătorilor. Se compară șase modele, inclusiv Random Forest și XG Boost, folosind indici de cuantificare precum Mean Squared Error pentru a găsi cel mai performant model. XG Boost și Histogram Gradient Boosting prezintă cele mai bune rezultate în ceea ce privește prezicerea eficienței lucrătorilor. Cu XG Boost s-a obținut o precizie ridicată (R-pătrat în jurul valorii de 0,78) cu puține erori (MSE în jur de 0,01). Light GBM s-a clasat pe locul trei, la distanță apropiată, în timp ce Random Forest și Ada Boost au fost nesatisfăcătoare. Tehnicile de învățare automatizată precum XG Boost pot îmbunătăți semnificativ eficiența lucrătorilor din subcontinentul indian din industria de textile și pielărie.

CUVINTE CHEIE: performanța lucrătorilor, îmbunătățirea performanțelor lucrătorilor din industrie, eficiență bazată pe date.

EFFICACITÉ DES TRAVAILLEURS DANS L’INDUSTRIE DU SOUS-CONTINENT INDIEN : UNE APPROCHE DE MODÈLE D'APPRENTISSAGE AUTOMATIQUE

RÉSUMÉ. La popularité croissante de l’apprentissage automatique offre des possibilités captivantes pour des applications concrètes. Étant donné que l’efficacité des travailleurs a un impact direct sur les résultats d’une entreprise, en particulier pour les petites et moyennes entreprises (PME), la mise en œuvre de ces outils peut conduire à une révolution. En améliorant l’efficacité des travailleurs, l’apprentissage automatique peut aider les PME à minimiser le gaspillage et à stimuler la croissance. Cette recherche explore le potentiel du modèle d’IA non pas pour remplacer les travailleurs mais pour les aider à améliorer leurs performances. Dans cette étude, on a tenté de déterminer l’efficacité des travailleurs de l’industrie, en particulier dans l’industrie du textile et du cuir, sur la base de paramètres tels que l’expertise, l’éducation, le salaire, les heures de travail, la valeur standard des minutes (SMV), la fonction, les indicateurs clés de performance (ICP) etc. L’étude examine différents modèles de régression pour prédire l’efficacité des travailleurs. Six modèles, dont Random Forest et XG Boost, sont comparés à l’aide d’indices de quantification tels que l’erreur quadratique moyenne pour trouver le modèle le plus performant. XG Boost et Histogram Gradient Boosting affichent les meilleurs résultats en matière de prévision de l’efficacité des travailleurs. Une grande précision (R au carré d’environ 0,78) avec peu d’erreurs (MSE d’environ 0,01) a été obtenue avec XG Boost. Light GBM arrivait en troisième position, tandis que Random Forest et Ada Boost n’étaient pas satisfaisants. Les techniques d’apprentissage automatique telles que XG Boost peuvent améliorer considérablement l’efficacité des travailleurs du sous-continent indien dans l’industrie du textile et du cuir.

MOTS CLÉS : performance des travailleurs, amélioration de la performance des travailleurs industriels, efficacité basée sur les données.

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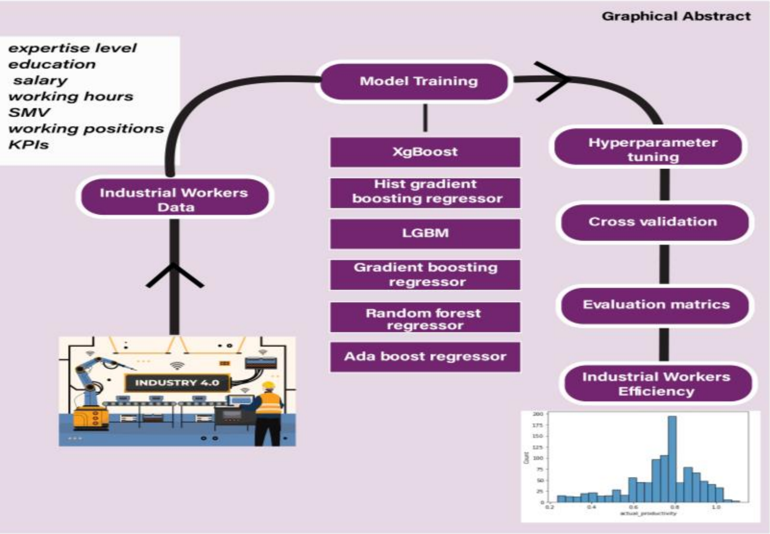

INTRODUCTION

Textile and leather industry are the two most prominent sectors in the Indian subcontinent countries' economy, especially in Bangladesh, the world's second garments exporter after China. Leather sectors also doing well to hold the 8th position in worldwide exports [1]. In this region workers play a great role in the countries' GDP. Most of the workers are poor and earn too low an income to lead a quality life compared to the rest of the world. Many of them migrate abroad to earn more, which also contributes to the countries' remittance [2].

Table 1: South Asian region comparison

Country	Leather and textile industry	Workers (Million)
Bangladesh	2930	4.22
India	5400	13.6
Pakistan	1300	24.7

Gaining an understanding of how businesses behave in real time and dynamically opens up new possibilities for structuring and controlling the whole value chain in an industrial sector. Technology is integrated in the industry for better performance and monitoring the real time data. IOT, Machine learning optimize the time and costs to utilize the best output from the manual workers [3].

Machine learning can improve workers' productivity and decision-making by giving them tools that can supplement rather than replace their jobs. The goal of this project is to investigate how machine learning models can be used to forecast and enhance worker productivity in the Indian subcontinent's leather and textile sectors. This study attempts to find the best machine learning models for this purpose by concentrating on factors including experience, education, pay, working hours, Standard Minute Value (SMV), working position, and Key Performance Indicators (KPIs) [4].

Recent advancements in machine learning provide a powerful toolkit for analyzing large datasets and identifying patterns that can inform decision-making. By leveraging these technologies, predictive models can be developed that offer insights into factors influencing worker efficiency and suggest actionable interventions.

The application of machine learning in industrial settings has been explored in various studies. Prior research has demonstrated the potential of regression models in predicting outcomes such as equipment failure, production quality, and worker performance. However, the specific context of leather and textile industries in the Indian subcontinent presents unique challenges and opportunities, necessitating tailored approaches [5-7].

METHODOLOGY

Data was collected from several leather and textile factories in the Indian subcontinent over a period of one year. The dataset comprises records of workers' performance metrics and attributes. The key parameters recorded for each worker include expertise level, education, salary, working hours, standard minute value (SMV), working positions, Key performance indicators (KPIs). Before training the models, the data was preprocessed to handle missing values, categorical variables, and scaling. Feature selection was performed to identify the most relevant variables for predicting worker efficiency. Correlation analysis, mutual information, recursive feature elimination (RFE) methods were employed. Six regression models were implemented and trained on the processed dataset including Random Forest, XGBoost, Light GBM, Histogram Gradient Boosting, Ada Boost, Linear Regression. Hyperparameter tuning was conducted using Grid Search and Random Search methods to find the optimal settings for each model. Cross-validation was used to ensure the robustness and generalizability of the models. A 10-fold cross-validation technique was applied, where the dataset was divided into 10 subsets. Each model was trained on 9 subsets and validated on the remaining subset, and this process was repeated 10 times. The average performance metrics were calculated to evaluate the models. The models were evaluated using the following metrics: Mean Squared Error (MSE), R-squared (R^2) and Mean Absolute Error (MAE).

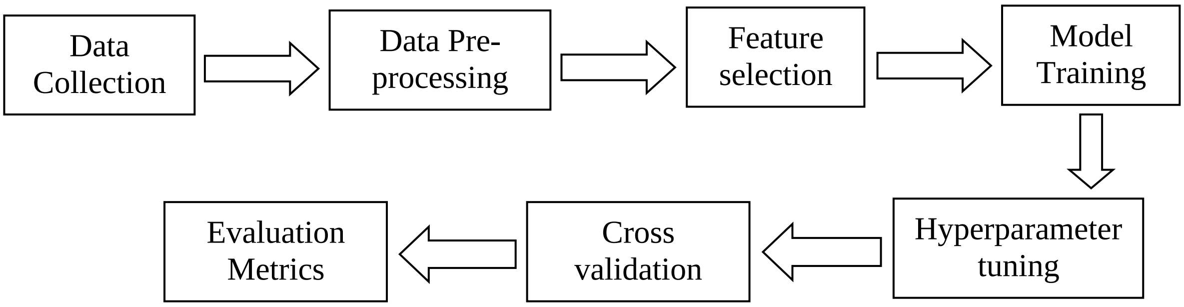

Figure 1. Flowchart of the methodology

Random Forest

This is an ensemble learning method that builds multiple decision trees and combines their outputs to improve prediction accuracy. Each tree is trained on a random subset of the data, and the final output is an average of individual predictions [8]. In this study, Random Forest serves as a baseline ensemble model, though it performed poorly compared to other models.

XGBoost

Extreme Gradient Boosting (XGBoost) is a powerful and efficient gradient boosting algorithm. It sequentially builds new trees to correct errors made by previous ones, making it highly effective for structured data [9]. In this study, XGBoost achieved the highest accuracy, as seen in Table 2, due to its robustness in handling complex relationships in data.

LightGBM

Light Gradient Boosting Machine (LightGBM) is another gradient-boosting framework designed for efficiency, especially with large datasets. It uses a leaf-wise tree growth algorithm, making it faster than XGBoost in some cases [10]. LightGBM performed well in this study, showing competitive accuracy with minimal errors.

Histogram Gradient Boosting

This is a variant of gradient boosting that uses histograms to bin continuous features, which speeds up computation and reduces memory usage [11]. It works well with high-dimensional data and showed strong performance in the study, second only to XGBoost in Table 2.

AdaBoost

Adaptive Boosting (AdaBoost) focuses on instances that previous models misclassified, adjusting their weights to improve performance on difficult cases. However, it is generally less effective with complex datasets, and in this study, AdaBoost struggled with worker efficiency prediction, as indicated by its poor performance in Table 2 [12].

Linear Regression

This is a simple model that establishes a linear relationship between input features and the target variable. While it is easy to interpret, Linear Regression is often limited in handling complex, non-linear data [13]. Here, it serves as a basic benchmark but did not yield competitive results compared to more sophisticated models.

For "Mean Squared Error and R Squared Error" Tests cross-validation was used, specifically a 10-fold cross-validation technique. This process involved dividing the dataset into ten subsets, where each model was trained on nine subsets and validated on the remaining subset, iterating this process ten times. The performance metrics (MSE and R²) were averaged across the ten folds to produce stable and reliable estimates for each model's effectiveness in predicting worker efficiency.

3000 employee data was short out at first and divided the data into two phase such as train dataset and test datasets. Applied the different machine learning model and find out the proper efficiency based on different parameters. Finally compared them for better output and optimized.

RESULTS

Mean Squared Error and R Squared Error Tests

Six different model run with the data and compared the mean squared error and R squared error tests. It defines the best performing models and compares the values among them.

Table 2: Different Model Value Comparison

Model Name	R^2 error	Mean square error
XgBoost	0.78	0.01
Hist gradient boosting regressor	0.76	0.01
LGBM	0.71	0.01
Gradient boosting regressor	0.40	0.01
Random forest regressor	-0.32	0.02
Ada boost regressor	-0.75	0.02

XGBoost is the best-performing model for predicting worker efficiency, followed closely by the Histogram Gradient Boosting Regressor and LightGBM. Random Forest and AdaBoost perform poorly, with negative R^2 scores and higher MSE, suggesting they are not suitable for this specific task.

Employee Productivity Ratio

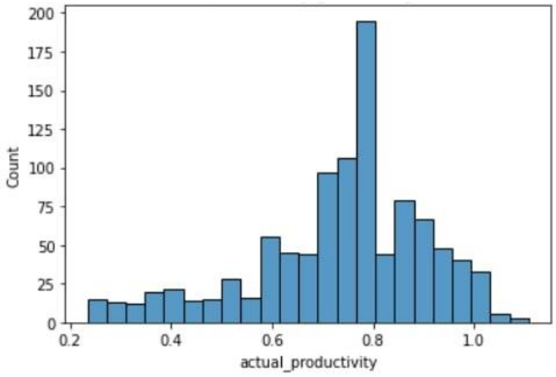

Figure 2. Employees efficiency rate range 0 to 1

The histogram helps to understand the general efficiency levels of workers in the study. It shows where most workers fall in terms of productivity and can help identify if there is a significant group of underperformers or high performers. If the goal is to improve overall productivity, interventions can be targeted towards increasing the productivity of those workers who fall into the lower productivity bins. 200 employees' productivity is near about 0.8 between the range of 0 to 1. Half of the employees' efficiency is up to 0.5.

Interpreting the Role of Key Features

Standard Minute Value (SMV)

SMV was identified as one of the most important factors. Higher SMVs correlated with lower efficiency, suggesting that complex or time-intensive tasks contribute to reduced productivity.

Expertise Level and Education

Workers with higher levels of expertise and education exhibited higher efficiency scores. This insight suggests that investing in worker training could enhance productivity.

Working Hours and Position

The analysis indicated diminishing returns for long working hours, highlighting that optimizing shift lengths could prevent burnout and maintain productivity. Workers in supervisory or skilled positions generally had higher efficiency scores, suggesting a hierarchical influence on productivity.

Model Comparison

From the comparison of models, XGBoost and Histogram Gradient Boosting Regressor stand out as the most effective models for predicting worker efficiency. Both models have high R^2 scores and low MSE values, indicating strong predictive accuracy and reliability. LightGBM also performs well but is slightly less accurate than the top two models. In contrast, Random Forest Regressor and AdaBoost Regressor perform poorly, with negative R^2 scores and higher MSE values. These results suggest that these models are not suitable for predicting worker efficiency in this context, possibly due to overfitting or an inability to capture the relationships in the dataset effectively.

DISCUSSION

XGBoost is the best-performing model for predicting worker efficiency, followed closely by the Histogram Gradient Boosting Regressor and LightGBM. Random Forest and AdaBoost perform poorly, with negative R^2 scores and higher MSE, suggesting they are not suitable for this specific task. XGBoost outperforms all other models with the highest R^2 score (0.78), indicating that it explains 78% of the variance in worker efficiency. The low MSE of 0.01 further suggests that the model makes very accurate predictions with minimal error. Histogram Gradient Boosting Regressor performs almost as well as XGBoost, with a slightly lower R^2 score of 0.76. It also has an MSE of 0.01, making it a strong contender in terms of prediction accuracy. LightGBM shows decent performance with an R^2 score of 0.71 and an MSE of 0.01. It is not as strong as XGBoost or Histogram Gradient Boosting but still provides reasonable accuracy. Gradient Boosting Regressor performance drops significantly compared to the top three, with an R^2 score of 0.40. Although the MSE remains low at 0.01, the model explains only 40% of the variance in the data. Random Forest has a negative R^2 score, which suggests that it performs worse than a horizontal line predicting the mean of the data. The higher MSE of 0.02 indicates larger prediction errors, making it unsuitable for this task. AdaBoost performs the worst, with an R^2 score of -0.75. Like Random Forest, it has a higher MSE of 0.02, indicating poor model performance and large prediction errors.

CONCLUSION

Machine learning models, particularly XGBoost, show great promise in enhancing worker efficiency in the leather and textile industries of the Indian subcontinent. By providing accurate predictions and insights, these models can help SMEs optimize their operations, reduce losses, and promote growth.

Acknowledgments

Sadman Sadik conceptualized and supervised the whole experiment. Syed Mahedi Hasen programmed, analyzed the data and optimized the model.

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COMPOSITE MATERIALS FOR LIMB PROSTHETICS LINERS

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COMPOSITE MATERIALS FOR LIMB PROSTHETICS LINERS

ABSTRACT. Managing the soft tissues of residual limbs in individuals with lower limb amputations presents a significant challenge. Unlike the plantar tissues of an intact foot, the soft tissues of the residual limb are unaccustomed to mechanical loading. Consequently, the loads transferred to the residual limb by the prosthetic socket can frequently lead to the development of ulcers and other skin issues including infection. This review aimed to comprehensively analyze current research about perspective materials used for prosthetic liners. The most promising materials used for liners includes composite materials, leather and combining phase change materials. Optimizing the material composition of prosthetic liners requires a comprehensive approach that considers both mechanical and surface properties.

KEY WORDS: prosthetic liners, composite materials, limb

MATERIALE COMPOZITE PENTRU CĂPTUȘELI DE PROTEZE PENTRU MEMBRELE INFERIOARE

REZUMAT. Gestionarea țesuturilor moi ale membrelor reziduale la persoanele cu amputații ale membrelor inferioare prezintă o provocare semnificativă. Spre deosebire de țesuturile plantare ale unui picior intact, țesuturile moi ale membrului rezidual nu sunt obișnuite cu sarcina mecanică. În consecință, sarcinile transferate de manșonul protezei către membrul rezidual pot duce frecvent la dezvoltarea de ulcere și alte probleme ale pielii, inclusiv infecții. Această trecere în revistă și-a propus să analizeze într-o manieră cuprinzătoare cercetările actuale despre materialele de perspectivă utilizate pentru căptușelile protetice. Cele mai promițătoare materiale utilizate pentru căptușeli includ materiale compozite, piele și materiale combinate cu schimbare de fază. Optimizarea compoziției materialelor căptușelilor protetice necesită o abordare cuprinzătoare care să ia în considerare atât proprietățile mecanice, cât și cele de suprafață.

CUVINTE CHEIE: căptușeli proteze, materiale compozite, membru inferior

MATÉRIAUX COMPOSITES POUR LES REVÊTEMENTS PROTHÉTIQUES DES MEMBRES INFÉRIEURS

RÉSUMÉ. La gestion des tissus mous des membres résiduels chez les personnes amputées des membres inférieurs présente un défi important. Contrairement aux tissus plantaires d'un pied intact, les tissus mous du membre résiduel ne sont pas habitués aux charges mécaniques. Par conséquent, les charges transférées au membre résiduel par le manchon de prothèse peuvent fréquemment conduire au développement d'ulcères et d'autres problèmes cutanés, y compris l'infection. Cette revue visait à analyser de manière approfondie les recherches actuelles sur les matériaux potentiels utilisés pour les revêtements prothétiques. Les matériaux les plus prometteurs utilisés pour les revêtements comprennent les matériaux composites, le cuir et la combinaison de matériaux à changement de phase. L'optimisation de la composition des matériaux des revêtements prothétiques nécessite une approche globale qui prend en compte à la fois les propriétés mécaniques et de surface.

MOTS CLÉS : revêtements prothétiques, matériaux composites, membre inférieur

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INTRODUCTION

Prosthetic limbs have become an integral part of modern healthcare, providing individuals who have experienced limb loss with the opportunity to regain mobility and improve their quality of life. Traditionally, these prosthetic limbs have been constructed using a variety of materials, including metal, plastic, and rubber. However, the development of composite materials has opened up new possibilities for the design and fabrication of prosthetic limbs, particularly in the area of limb prosthetic liners. Prosthetic liners play a crucial role in the comfort and functionality of prosthetic devices, serving as the interface between the residual limb and the prosthetic socket. Their significance is further accentuated by the global shortage of trained prosthetists, which highlights the need for well-designed and easily adjustable prosthetic components.

Recent advancements in materials and manufacturing techniques, such as 3D printing, have enabled the fabrication of customized prosthetic liners that can better accommodate individual anatomical variations and user preferences [1]. However, the functionality of these 3D-printed liners is still a concern, and more robust research is required to fully understand their impact on end-user outcomes [2]. Materials like silicone and thermoplastics have been widely used in prosthetic liners, offering improved comfort and reduced skin irritation [3].

Incorporating innovative technologies, such as osseointegration and implanted interfaces, into prosthetic liners has the potential to enhance prosthetic function and user acceptance, ultimately improving the quality of life for individuals with limb amputations [3].

Composite materials, which are made up of two or more constituent materials with different physical or chemical properties, offer a number of advantages over traditional materials. These materials can be engineered to have high strength-to-weight ratios, which is particularly important for the design of prosthetic limbs that must be both durable and lightweight. Additionally, the ability to manipulate the properties of individual materials within a composite can allow for the creation of complex designs that take advantage of the unique properties of each component.

Skin nanomaterials are mainly composite materials, generally containing metal- and carbon-based materials. Ionic gels, ionic liquids, hydrogels, and elastomers have become the focus of attention due to the sensitivity, multimodal, and memory properties of their materials [4].

The prosthetic socket, which interfaces directly with the residual limb, plays a vital role in user comfort and skin health. An ideal socket material should provide a snug fit, minimize skin irritation, and manage perspiration effectively. Sakthivel Sankaran *et al.* [5] highlight the importance of reducing allergic reactions, friction, and ensuring proper pressure distribution. Recent advancements in socket materials have yielded promising results in creating a more comfortable and skin-friendly environment for users.

MATERIALS AND METHODS

Over 60 literature sources from Google Scholar and PubMed databases were checked. The search terms included combinations of «lower limb prosthetic liners», «prosthetic liners», «liners materials», «prosthetic materials». The search was limited to papers published in English between 2019 and 2024 except searching for clinical cases (1999-2024). In order to select relevant publications, the following search strategies were utilized:

1) Phrase searching – keywords were enclosed in quotation marks to search for exact matches;
2) Use of Boolean operators AND, OR, and NOT to combine keywords and refine the search;
3) Use of the wildcard character (*) to substitute for one or more unknown characters within a keyword.

RESULTS

Research and clinical trials have consistently demonstrated the significant impact of prosthetic liner design and material properties on user comfort and functional outcomes. Studies have investigated the relationship between liner elasticity, conductivity, and coefficient of friction, finding that these factors can influence residual limb comfort and satisfaction. For example, Lee *et al*. [6] found that liners with higher elasticity and lower conductivity were associated with improved user comfort. Additionally, clinical trials have compared various liner types, such as silicone vs. polyethylene foam, and observed benefits like reduced pistoning and improved suspension with specific designs. MacLean *et al*. [7] demonstrated that liners with a higher coefficient of friction can improve suspension and reduce in-socket movement. Furthermore, research into temperature regulation within the prosthetic socket has shown promising results for liners containing phase-change materials. Ferris *et al*. [8] found that liners with phase-change materials can help regulate temperature and reduce discomfort for amputees.

Overall, these findings contribute to the ongoing development of prosthetic liners that are more comfortable, effective, and tailored to individual user needs. Future research is needed to further explore the long-term benefits of specific liner designs and their impact on functional outcomes for prosthesis users.

The principle of liner evaluation is to evaluate whether amputees have a positive experience after donning the liner [9].

Choice of materials employed in the construction of prosthetic liners is of paramount importance within the realm of prosthetic design and engineering, as these components serve as the critical interface between the user's residual limb and the prosthetic liners.

Material Types and Properties

Liners can be made of elastomeric materials (gels or silicones) or of open/closed cell foam materials. The selection of appropriate materials for prosthetic liners is crucial to ensure optimal comfort, function, and durability for amputees. Important material key properties must include elasticity, breathability, moisture management, biocompatibility and overall comfort as well as durability. The last one is also considered for economic reasons.

Table 1: Comparison of the most popular material types for lower limb prosthetic liners

Key Properties of Prosthetic Liner Materials							
Material	Elasticity	Breathability	Moisture Management	Durability	Comfort	Biocompatibility	References
Silicone	High	Moderate	Good	High	Excellent	Generally good	[10]
Polyethylene Foam	Moderate	High	Good	Moderate	Good	Generally good	[11, 12]
Gel liners	High	Moderate	Excellent	Moderate	Excellent	Generally good	[13]
Aerogels	High	Excellent	Excellent	Moderate	Excellent	Generally good	[14]
Hydrogels	High	Excellent	Excellent	Moderate	Excellent	Generally good	[15]
Hybrid Liners	Varies	Varies	Varies	Varies	Varies	Varies	[16]
PCM liners	Moderate	Good	Varies	Generally good	Excellent	Generally good	[17]

Recent research has further emphasized the importance of these material properties. For example, Ali *et al*. [10] investigated the mechanical properties of different prosthetic liner materials and found that silicone liners generally exhibited higher elasticity and shear strength, which can contribute to improved comfort and suspension. These liners are made from a soft, rubbery material that can conform to the shape of the residual limb, providing a custom fit and reducing the risk of skin irritation. Silicone liners are often used in combination with other materials, such as gel or fabric, to enhance their properties and performance. More recent studies have also explored the use of innovative materials, such as hydrogels and aerogels, for prosthetic liners. These liners contain a gel-like material that can provide cushioning and pressure relief, particularly for individuals with sensitive skin or pressure sores. Gel liners can be used alone or in combination with other materials, such as silicone or fabric. These materials offer potential benefits in terms of comfort, moisture management, and pressure distribution.

For example, Cagle *et al*. [18] investigated the properties of hydrogel liners and found that they have good breathability and load-bearing capabilities. Zhang *et al*. [19] explored the use of aerogel-based liners for improved temperature regulation and moisture management.

Based on the general description both types of gel liners – aero-based and hydrogels – could be a good choice. In fact, aero-gel and hydrogel liners are both innovative materials used in prosthetic applications, but they offer distinct properties and benefits (Table 2).

Table 2: The distinct properties of gel liners types

Feature	Aero-Gel Liners	Hydrogel Liners
Structure	Highly porous, lightweight material	Gel-like, hydrophilic material
Moisture Management	Excellent, due to high porosity	Excellent, due to hydrophilic nature
Temperature Regulation	Can incorporate phase-change materials	Can help maintain a cool environment
Pressure Distribution	Even distribution	Cushioning and pressure relief
Durability	Moderate	Moderate
Comfort	Generally comfortable	Generally comfortable

Aerogel-based Materials

Aerogel-based materials first were developed as thermal insulation in lightweight protective clothing and footwear for extreme temperatures, shelters for military personnel in the field, military and aerospace vehicles, protection for electronic equipment, tank engine, etc. [20]. Aero-gels excel hydrogels in breathability and temperature regulation, while hydrogels provide excellent moisture management and cushioning. The optimal choice for a specific amputee may depend on individual needs and preferences. The study by Lee *et al*. [21] highlights the potential of silica aerogels for prosthetic liners. These ultralight materials boast excellent breathability and moisture management, addressing common issues associated with traditional liners. Additionally, their hydrophobic nature could potentially reduce perspiration build-up within the socket, promoting skin health.

Phase Change Materials (PCMs)

Phase change materials (PCMs) are a class of thermo-responsive materials that can be utilized to trigger a phase transition which gives them thermal energy storage capacity [17]. When incorporated into prosthetic liners, PCMs can help regulate temperature and improve comfort for amputees. Maintaining a consistent temperature can help prevent skin irritation, blistering, and other skin problems associated with prosthetic use. This is especially important for individuals with sensitive skin or underlying medical conditions. A comfortable and well-regulated temperature can improve the overall function and performance of the prosthetic limb. By reducing discomfort and distractions, PCMs can help amputees engage in more physical activities and maintain a higher quality of life. However, PCMs could not function by itself, they should be encapsulated within a suitable material to prevent leakage and ensure proper functioning.

Composite Materials: Strength Meets Lightweight Design

Composite materials, which are formed by combining two or more different materials with distinct properties, have gained increasing attention in the field of prosthetic liner development. These materials offer the potential to enhance the performance and comfort of prosthetic liners by combining the advantages of various components. For example, composite liners incorporating carbon fiber or Kevlar can provide increased strength and durability, while other components can contribute to factors such as elasticity, breathability, and moisture management.

Recent advancements in materials have significantly improved the functionality, comfort, and affordability of these devices. Traditional metallic prosthetics, while strong, can be bulky and heavy. Composite materials, particularly carbon fiber-reinforced polymers, offer a compelling alternative. These materials boast an excellent strength-to-weight ratio and biocompatibility**,** making them ideal for prosthetic applications. Researchers like Timoshkov *et al*. [22] have explored the use of various composite materials like carbon fiber, Kevlar, and glass fiber, each with unique mechanical properties that cater to specific prosthetic limb requirements. Results showed that formulations grouped into three categories based on mechanical strengths: the weakest were laminates with fibers of perlon or nyglass stockinette, spectralon, nylon, and cotton, ranging between 18 and 42 megapascals (MPa); the midrange was fiberglass, ranging between 67 and 109 MPa; the highest strengths were found in carbon fiber laminates, ranging between 236 and 249 MPa.

Perlon, a type of nylon, has historically been a common material used in the construction of prosthetic sockets. Known for their durability and formability, perlon sockets have been a staple in the prosthetics industry for many years. Due to the limitations of perlon and advancements in materials science, the prosthetics industry has seen a shift towards more advanced materials. Carbon fiber-reinforced polymer (CFRP) composites are increasingly used in prosthetic applications due to their excellent strength-to-weight ratio and biocompatibility [22, 23]. These materials offer advantages over traditional metallic components, particularly in addressing stress shielding issues in joint replacements [23]. For prosthetic sockets, CFRP composites demonstrate superior mechanical properties compared to other materials. A study found that carbon fiber layers exhibited higher flexural strength, shear stress resistance, and impact strength than jute or glass fibers [24]. Another investigation revealed that carbon fiber sockets outperformed perlon sockets in tensile strength and fatigue resistance, with carbon fiber sockets showing a safety factor of 1.35 compared to 0.22 for perlon [25].

One innovative approach to the use of composite materials in prosthetic limb design involves the use of additive manufacturing-based molding techniques. These techniques allow for the fabrication of prosthetic components, such as fingers, using the same materials and techniques employed in high-grade aerospace components. This method involves the creation of a three-layer composite structure, with a carbon-fiber structural shell, a lightweight foam filler, and a soft urethane grip surface. In the study conducted by Bhatt *et al*. [26], this approach was shown to be a viable alternative to current methods of prosthetic hand production. Other composite materials are also being explored for use in prosthetic limb liners. Among these are not only carbon fiber composites, but also advanced materials such as graphene and carbon nanotubes. Graphene and carbon nanotubes have been shown to offer superior mechanical properties and relatively low densities, making them attractive options for the development of lightweight, high-performance prosthetic limbs. Overall, the use of composite materials in the design and fabrication of prosthetic limb liners represents a promising area of research and development.

Polymeric Composites

The design of prosthetic devices has become increasingly sophisticated in recent years, driven by the imperative to improve the overall quality of life for individuals with limb differences. Polymeric composites have emerged as a promising class of materials for the fabrication of prosthetic liners, offering a unique combination of strength, flexibility, and biocompatibility. Traditionally, prosthetic liners have been constructed from a variety of synthetic polymers, such as polyethylene and polyurethane. However, the mechanical properties of these materials have often been limited, leading to issues with durability and comfort. The incorporation of reinforcing fibers, such as carbon or glass, into polymeric matrices has shown great potential in enhancing the mechanical properties of prosthetic liners, while maintaining the desired flexibility and biocompatibility.

One of the key advantages of using fiber-reinforced composite materials for prosthetic liners is the ability to tailor the mechanical properties to the specific needs of the user. By varying the type, orientation, and volume fraction of the reinforcing fibers, as well as the matrix material, the stiffness, strength, and anisotropic behavior of the composite can be customized to provide a precise fit and optimal performance [27]. Furthermore, the use of additive manufacturing techniques, such as 3D printing, has enabled the fabrication of complex, patient-specific prosthetic liners with intricate internal geometries and surface textures [28]. Polymer composites have revolutionized the prosthetics industry, offering a range of benefits over traditional materials like perlon. These materials are engineered to provide optimal performance, comfort, and durability for prosthetic liner users.

Silicon-based materials have long been utilized in the realm of prosthetic liners, providing a versatile and dynamic solution for individuals seeking comfort, durability, and enhanced functionality in their prosthetic devices. The inherent properties of silicon, including its biocompatibility, flexibility, and resistance to wear and tear, have made it a prime choice for medical applications, particularly in the context of prosthetic limb design and fabrication. Silicone has become a staple in the production of prosthetic liners due to its ability to conform to the unique contours of the residual limb, distributing pressure evenly and minimizing the risk of skin irritation or breakdown [9].

Natural Fiber-Reinforced Composites (NFRCs)

The examples of NFRCs for prosthetic liners [29] demonstrate the continued efforts to explore sustainable and environmentally-friendly materials for this application. Such composites include natural fibers, such as *Boehmeria nivea* (ramie), embedded within an epoxy matrix, offering a potentially more durable and customizable prosthetic liner solution that leverages the inherent properties of naturally-derived materials. The case study of *Boehmeria nivea* natural fabric reinforced epoxy matrix composite [30] further demonstrates the feasibility of incorporating natural materials into advanced prosthetic designs while maintaining desirable mechanical properties. In this study, the authors report on the successful fabrication and testing of a hybrid laminate reinforced with natural fibers, indicating the potential for natural fiber-based materials to be utilized in prosthetic applications. The other case study on the fabrication and testing of hybrid laminates reinforced with natural fibers [31] also underscores the growing interest and viability of natural materials in advanced composite applications.

Natural Leather for Prosthetic Liners

While conventional synthetic polymers and advanced materials have been the predominant focus of research and development in the field of prosthetic technology, the ancient origins of prosthetic medicine suggest that natural materials, such as leather, have played a significant role throughout the evolution of prosthetic solutions [32]. Historically, the utilization of natural leather has been explored as a potential solution for addressing the unique challenges associated with prosthetic suspension and comfort in veterinary patients [33]. The inherent properties of leather, including its conformability, breathability, and ability to mold to the contours of the residual limb, make it a potentially viable option for improving the overall comfort and suspension of prosthetic liners, particularly in populations where the use of vacuum or suction-based systems may be limited, such as in veterinary patients [33].

However, the adoption of leather as a prosthetic liner material is not without its own set of challenges. Leather, like other natural materials, is subject to degradation and wear over time, potentially compromising the long-term durability and performance of the prosthetic device. Furthermore, the availability and cost-effectiveness of leather as a prosthetic material may vary significantly depending on geographic location, market conditions, and the specific requirements of the prosthetic application, potentially presenting logistical barriers to its widespread implementation in liners manufacturing. Nowadays, perspectives of leather use in prosthetic liners have shifted, with the development of advanced synthetic materials and manufacturing techniques that can potentially offer improved performance, customization, and cost-effectiveness compared to traditional leather-based solutions.

Ultimately, the selection of the most appropriate prosthetic liner material, whether it be natural leather or a synthetic alternative, must be carefully evaluated based on the specific needs and requirements of the patient, the intended use case, and the available resources and expertise within the prosthetic design and fabrication ecosystem [34].

Natural Plant-Derived Fibers for Prosthetic Liners

Natural plant-derived fibers for prosthetic liners have been investigated as a potential solution to address the limitations of traditional leather, as they offer a more sustainable and potentially more customizable approach to prosthetic liner design. Natural fibers, derived from plants or animal tissues, offer several potential advantages for prosthetic liner applications. Natural fiber-reinforced composites show promise for lower-limb prosthetic designs. Among these fibers a number of materials are used, including flax (linen), hemp, bamboo, sisal, cotton and jute [34]. The continued exploration of natural and synthetic materials, as well as the ongoing advancements in material science and prosthetic manufacturing techniques, will undoubtedly shape the future of prosthetic liner design and the utilization of natural leather within this critical domain [30]. Studies have explored materials like rattan fiber and alfa fiber [35] for prosthetic sockets, demonstrating good mechanical properties and potential for affordability. These composites offer benefits such as sustainability, comfort, and safety in prosthetic applications. Research has also focused on evaluating the mechanical properties of natural fiber-reinforced prosthetic sockets [36] and incorporating computational biomechanical models to assess prosthetic effectiveness [37]. While synthetic fiber-reinforced composites offer superior strength and durability, they can be expensive, stiff, and uncomfortable. Natural fiber-reinforced composites**,** such as those made from Ramie, kenaf, pineapple, and banana fibers, present a promising alternative. These materials offer a low-cost, comfortable, and sustainable option for prosthetic sockets, as evidenced by research by Endalkachew Gashawtena *et al*. [38]. However, natural fibers may not possess the same strength and durability as synthetic counterparts, requiring careful material selection and composite development [37].

Smart/Personalized Prosthetic Liners

Despite the existence of literature reporting the experience of individuals with amputation with different liners, confounding factors, methodological rigour and issues with validity and reliability of outcomes preclude meaningful clinical decision-making. The findings of *ex vivo* tests need to be confirmed by human subject experiments to establish liner prescription clinical guidelines [39]. Prosthetic liners are currently designed to fit individuals generically rather than specifically. A more adaptive, «smart» liner that could conform to the residual limb more precisely might enhance skin health at the stump-socket interface and improve the accuracy of topological tracking [40]. This diagnostic tool could track changes throughout the day, considering factors like activity level, body position, and the forces exerted on the limb by the prosthetic socket. To maintain the comfort and functionality of the liner, the embedded sensors should possess similar mechanical properties as the liner itself, being flexible, pliable, and thin. This would ensure that the sensors do not interfere with the liner’s performance or cause discomfort [41].

Personalized prosthetic liners require innovative design and manufacturing methods to seamlessly integrate sensor technologies. This integration will facilitate biomechanical and physiological characterization of the prosthesis-limb interface, enabling objective comparisons and assessments of socket system quality. For example, Brothers *et al*. [42] created a transtibial impact-reducing liner combined with integrated haptic feedback to enhance comfort and restore proprioceptive senses. The impact-reducing liner includes impact reduction over pressure-intolerant regions, impact redistribution over pressure-tolerant regions, and a variable volume system that dynamically adjusts to changes in the residual limb's volume throughout the day. The haptic feedback system employs force-sensitive resistors located on various regions of the prosthetic foot. These sensors transmit via Bluetooth to vibrational nodes embedded in the liner to provide the user with real-time feedback. Prototype testing has shown positive results in reducing pressure similar to the field's gold standard.

While 3D printing offers potential benefits, its current limitations for soft materials, including high costs, lengthy manufacturing times, and suboptimal material properties, hinder its widespread adoption in prosthetic liner production. Cryogenic Computer Numeric Control (CNC) machining presents a promising alternative for rapidly manufacturing soft polymer products [43]. This technique involves freezing elastomeric material below its glass transition temperature (Tg) and then machining it using traditional CNC tools. This approach offers a fast and cost-effective solution for creating prototypes with high accuracy and conformity. Thus, in the study [43] the liner machining process took 4 hours approximately with use of CNC tools and resulted in better thermal properties with respect to the current liner solution.

CONCLUSIONS

Optimizing the material composition of prosthetic liners requires a comprehensive approach that considers both mechanical and surface properties. Composite materials hold great promise for the development of advanced prosthetic limb liners with improved performance, antimicrobial properties, and biocompatibility. The integration of materials such as graphene, carbon nanotubes, and silver nanoparticles into composite structures offers opportunities to create highly customized and functional prosthetic liners that can enhance the comfort, mobility, and overall quality of life for individuals with limb loss or amputation. Careful selection and design of prosthetic liners are crucial in ensuring the comfort, functionality, and long-term success of prosthetic devices, making them an essential component of modern prosthetic care.

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THE INVESTIGATION OF A 17TH CENTURY PARCHMENT DOCUMENT

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THE INVESTIGATION OF A 17TH CENTURY PARCHMENT DOCUMENT

ABSTRACT. This study presents the investigation of a chrisov written on parchment, issued by Ștefan Lupu, the prince (voivode) of Moldavia (1659-1661), in 1660, from the collection of the National Museum of History of Romania (MNIR), in Bucharest. By using an analytical protocol based on corroboration of macroscopic and microscopic observations with the attenuated total reflection infrared spectrometry (ATR-FTIR) and X-ray fluorescence spectroscopy (XRF), information concerning parchment, inks and pigments were obtained. The Ștefan Lupu' chrisov is written on high quality goat parchment, matte, smooth, velvety, and it presents only a few manufacturing defects. ATR-FTIR analysis revealed a well-preserved structure of the collagen molecules, with a low level of hydrolytic decay. According to the XRF results, ferogallic and golden inks were used to write the Chrisov text whereas the ornaments were painted with vermilion pigment (for red color), verdigris pigment (for green color), Co-based pigment (for blue color) and fine gold powder. Both inks and pigments show a very good state of conservation.

KEY WORDS: parchment, degradation, inks, pigments, ATR-FTIR, XRF

INVESTIGAȚII ASUPRA UNUI DOCUMENT PE SUPORT DIN PERGAMENT DIN SECOLUL AL XVII-LEA

REZUMAT. Acest articol prezintă rezultatele obținute la investigarea unui hrisov scris pe pergament, emis de Ștefan Lupu, voievodul Moldovei (1659-1661), în 1660, din colecția Muzeului Național de Istorie a României (MNIR), din București. Prin utilizarea unui protocol analitic bazat pe coroborarea observațiilor macroscopice și microscopice cu datele obținute prin utilizarea spectroscopiei în infraroşu cu reflexie totală atenuată (ATR-FTIR) și a spectroscopiei de fluorescență cu raze X (XRF) au fost puse în evidență informații referitoare la pergament, cerneluri și pigmenți. Astfel, hrisovul lui Ștefan Lupu este scris pe pergament din piele de capră de calitate superioară, fiind mat, neted, catifelat și prezentând doar câteva defecte de fabricație. Analiza ATR-FTIR a relevat o structură bine conservată a moleculelor de colagen, cu un nivel scăzut de degradare hidrolitică. Conform rezultatelor XRF, cernelurile ferogalică și pe bază de pulbere de aur au fost utilizate pentru a scrie textul hrisovului, ornamentele fiind realizate cu pigmenți pe bază de vermilion (pentru culoarea roșie), verdigris (pentru culoarea verde), pigment pe bază de cobalt (pentru culoarea albastră) și pe bază de pulbere fină de aur. Atât cernelurile cât și pigmenții prezintă o stare de conservare foarte bună.

CUVINTE CHEIE: pergament, degradare, cerneluri, pigmenți, ATR-FTIR, XRF

L'ENQUÊTE SUR UN DOCUMENT EN PARCHEMIN DU XVIIe SIÈCLE

RÉSUMÉ. Cette étude présente l'enquête sur un chrisov écrit sur parchemin, émis par Ștefan Lupu, le prince (voievod) de Moldavie (1659-1661), en 1660, de la collection du Musée National D'histoire de la Roumanie (MNIR), à Bucarest. En utilisant un protocole analytique basé sur la corroboration d'observations macroscopiques et microscopiques avec la spectrométrie infrarouge à réflexion totale atténuée (ATR-FTIR) et la spectroscopie de fluorescence X (XRF), des informations concernant le parchemin, les encres et les pigments ont été obtenues. Le chrisov de Ștefan Lupu est écrit sur du parchemin en peau de chèvre de haute qualité, mat, lisse, velouté, et il ne présente que quelques défauts de fabrication. L'analyse ATR-FTIR a révélé une structure bien préservée des molécules de collagène, avec un faible niveau de décomposition hydrolytique. D'après les résultats de la XRF, des encres ferogalliques et dorées ont été utilisées pour écrire le texte de Chrisov tandis que les ornements ont été peints avec du vermillon (pour la couleur rouge), du pigment vert-de-gris (pour la couleur verte), du pigment à base de cobalt (pour la couleur bleue) et de la poudre d'or fine. Les encres et les pigments présentent tous deux un très bon état de conservation.

MOTS CLÉS : parchemin, dégradation, encres, pigments, ATR-FTIR, XRF

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INTRODUCTION

Historical parchment objects, such as manuscripts, documents, and maps, hold immense historical value as irreplaceable testimonies of human history. These artifacts serve as inexhaustible sources of information on both national and universal culture and civilization, allowing us to connect with the past, understanding the evolution of societies, and appreciating the cultural achievements of our ancestors. The time over which such objects maintain their ability to completely convey the intangible and tangible values decisively depends on the conditions in which they are stored or displayed and how they are restored.

Parchment, obtained by processing the animal skin, is mostly composed of collagen, the main structural protein of skin. The complex structure of collagen, which hierarchically consist of structural levels (molecules, fibrils and fibers), along with their close interconnectivity contributes to the exceptional mechanical strength and durability of parchment. However, in the case of historical parchments, the synergetic action of the environmental factors, such as temperature, humidity, light irradiation, chemical pollutants, solvents, and biological agents (fungus, bacteria, rodents, insects) results in collagen alteration over time [1-4]. Additionally, the manufacturing process can alter collagen's structure in ways that initiate its deterioration [5].

This study is dedicated to the investigation of a chrisov written on parchment, issued by Ștefan Lupu, the prince (voivode) of Moldavia (1659-1661), in 1660, from the collection of the National Museum of History of Romania (MNIR), in Bucharest. The approach used consisted on corroboration of macroscopic and microscopic observations with the information obtained by Fourier-transform infrared with attenuated total reflectance (ATR-FTIR) and X-ray fluorescence spectroscopy (XRF). Macroscopic and microscopic observations [6] provided information on animal species used for the parchment manufacture, the manufacturing defects, and indications for inks and pigments identification. The ATR-FTIR was used to identify the materials added to parchment in the manufacturing process or those formed during ageing, as well as to detect chemical changes in the molecular structure of collagen [1-4, 7], whereas the pigments and inks used for decorating and writing were identified by X-ray fluorescence (XRF) spectroscopy [2, 3, 8, 9].

METHODS

Digital Microscopy

The microscopic observations were carried out with a portable digital microscope Dino-Lite AD7013MZ with a resolution of 1.3 Megapixels and by using x50 and x150 magnifications.

Fourier-Transform Infrared Spectroscopy with Attenuated Total Reflection (FTIR-ATR)

The FTIR-ATR measurements were carried out using a portable Alpha spectrometer (Bruker Optics) equipped with a Platinum ATR module. Spectra were recorded in the 4000 – 400 cm^{-1} spectral range with a 4 cm^{-1} resolution, using 32 scans. OPUS 7.0 software was used for processing and evaluating the spectra.

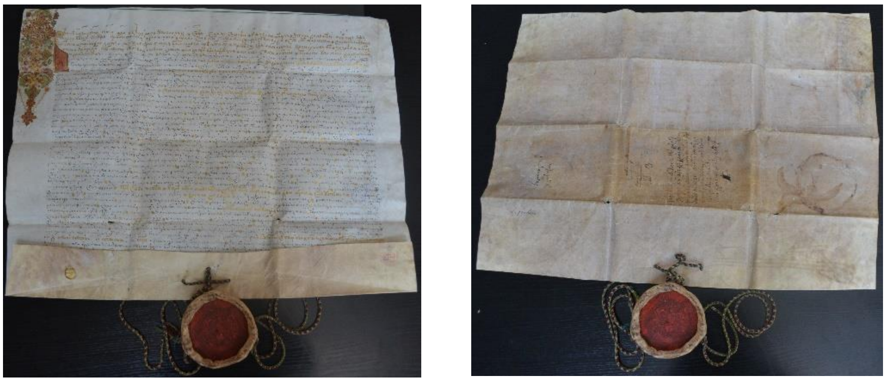
X-ray Fluorescence Spectroscopy (XRF)

The XRF measurements were carried out using an InnovX Alpha Series 6000 portable spectrometer with x-ray fluorescence with W anticathode, fitted with internal standardization and equipped with an Si PIN diode detector with U = 10-35 KV, I = 10-50 µA and < 190 eV FWHM resolution. XRF spectroscopy was used to determine the elemental composition of inks and pigments added to parchment.

RESULTS AND DISCUSSIONS

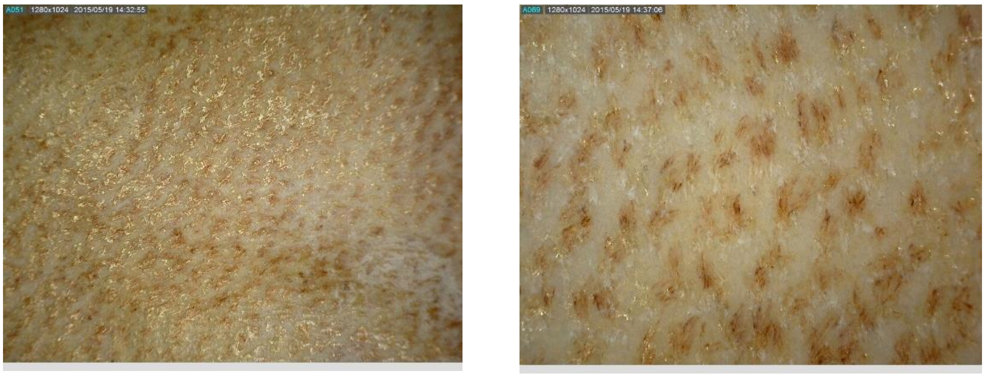
Assessment of Parchment Conservation State

The document has a regular shape (a length of 63.2 cm and a width of 63.1 cm), with a thickness of about (0.22 -0.31) mm, which may indicate the use of an old animal skin. The parchment is prepared for writing only on the *corium* side, with a matte appearance and white color. On the hair follicles side, the parchment has a granular, waxy appearance (Figure 1). The microscopic investigation of the hair follicles pattern revealed that the parchment was made of goatskin (Figure 2).



(a) (b)

Figure 1. The historical parchment document belonging to the National Museum of Romanian History: (a) front image and (b) back image



(a) (b)

Figure 2. Microscopic images: (a) 50x and (b) 150x, showing typical goat skin arrangement of hair follicles

The parchment exhibits just a few manufacturing defects, such as calcium carbonate deposits obstructing the hair follicles openings and a hole (Figure 3). Uneven calcium carbonate deposits on the surface of parchment can be attributed to the reaction between residual calcium hydroxide from the manufacturing process, which was not thoroughly washed away, allowing it to penetrate the fiber structure of the hide and hair follicle orifices, and carbon dioxide from the air. Additionally, the presence of calcium carbonate may result from the use of chalk powder during the finishing stage to bleach and degrease the parchment [2, 10]. The oval-shaped hole (Figure 3) was formed while the parchment was drying under tension on a wooden frame, whether circular or rectangular. At this stage, the still-wet hides are smoothed out by scraping with a crescent-shaped knife known as a *lunellarium* [1, 2, 10], which carries the risk of overly thinning certain areas and consequently leading to the formation of holes. Controlled, slow, and gradual drying, away from sunlight and in an environment with good air circulation, prevented contraction caused by excessive water loss, thereby ensuring the superior quality of the final product [2].

Figure 3. Manufacturing defects specific to parchment: calcium carbonate deposits in hair follicles orifices, and hole formed during drying under tension

The visual examination of the parchment document indicates a rather good conservation state. However, the document has been kept in folded form and therefore retains traces (holes and exfoliations) of this method of preservation (Figure 4). This preservation has helped to protect the written surface of the parchment, as surface degradation with the formation of oxidized fats and liquids spots has been reduced to the exposed area on the verso, which was in permanent contact with the environment (Figure 4).

Figure 4. Typical degradations of the parchment document: hole formed due to folding storage, exfoliation, oxidized fats and fat and liquids spots

Inks and Pigments Identification

The XRF spectroscopy was used to identify the inks (black and golden) and pigments (red, green, blue and golden) applied on the parchment document. Table 1 presents the chemical elements detected for each type of ink and pigment while their XRF spectra are shown in Figures 5 and 6.

Based on the XRF analysis (Table 1, Figure 5), the document was written using iron gall ink and gold-based ink [2, 3]. Iron gall ink typically consists of iron sulfate ($FeSO_4$), also known as green vitriol, galls (growths on oak trees caused by parasitic insect stings), Arabic gum, and a solvent like water, wine, or vinegar [10]. This ink was widely used in Europe from the Middle Ages through the 19th century.

The color palette of pigments applied on the parchment document includes red, green, blue and gold. By correlating XRF data (Table 1, Figure 6) with microscopic observations, the following pigments were identified: vermilion (HgS), a Cu-based pigment, a Co-based pigment, and fine gold powder. ATR-FTIR analysis of the blue area confirmed that the copper-based pigment is verdigris ($Cu(CH_3COO)_2 \bullet H_2O$). In the same area (Figure 7), calcium carbonate, calcium oxalate, and aluminosilicates were detected. The presence of calcium carbonate supports both microscopic observations and XRF results. Aluminosilicates could be from either surface dirt or fine pumice stone particles (amorphous aluminum silicate), which were used to create the parchment's velvety texture and microporous structure for ink and pigment adhesion [2] whereas calcium oxalate likely resulted from a fungal attack [11].

Table 1: XRF results for the pigments and inks

Area	Identified elements	Results
black ink	Ca, **Fe,** S, K, Pb, Cu, Zn, Sr	iron gall ink
golden ink	Ca, **Au,** S, Fe	gold-based ink
red	**Hg, S,** Ca, Au, P, K (Co, Fe, Cu, Cl)	vermilion
green	Ca, **Cu**, Au, K, P, S, Fe, Co	Cu-based pigment
blue	Ca, Hg, Au, S, Fe, K, **Co** (Cl, Cu)	Co-based pigment
golden	Ca, **Au,** P, S, Fe (Cl, Cu)	fine gold powder

Note 1. Ca and S elements are from the gypsum or chalk-based preparation layer. K comes from parchment.
Note 2. The chemical elements in brackets are present in very small quantities.

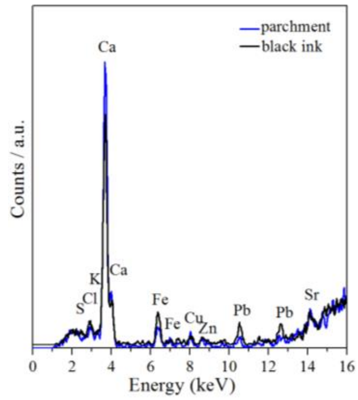


Figure 5. The XRF spectrum of the black ink as compared to that of parchment alone

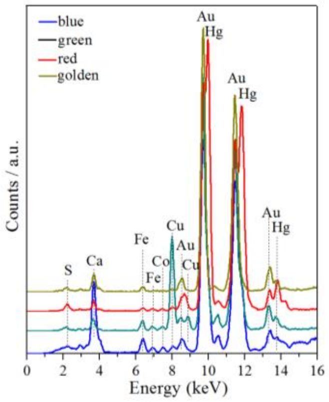


Figure 6. The XRF spectrum of the red, green, blue and golden colors

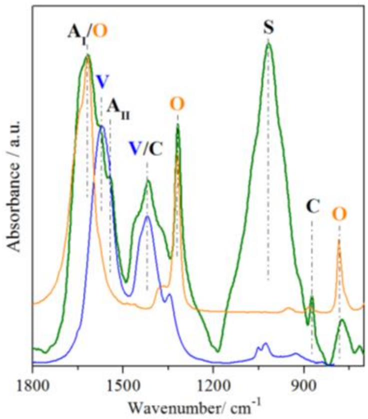


Figure 7. The ATR-FTIR spectrum of the green color (green line) as compared with those of verdigris (blue line) and calcium oxalate (orange line). Collagen absorption bands (A_I and A_{II}) as well as those attributed to verdigris (V), calcium oxalate (O), calcium carbonate (C) and aluminosilicates (S) are highlighted.

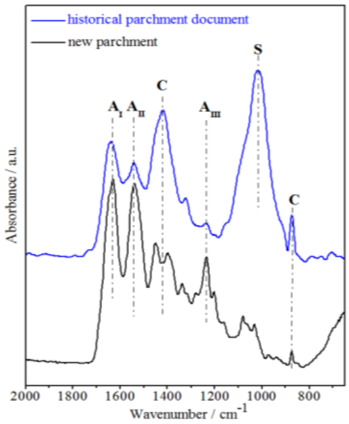


Figure 8. The ATR-FTIR spectrum of the historical parchment (blue line) as compared with that of a newly-manufactured parchment (black line). Collagen absorption bands (A_I, A_{II} and A_{III}) as well as those attributed to calcium carbonate (C) and aluminosilicates (S) are highlighted.

Molecular Alteration of Parchment

The main infrared absorption bands of collagen were used to identify the chemical modifications at molecular level. In Figure 8, the ATR-FTIR spectrum of historical parchment document is compared with the spectrum of a newly-manufactured parchment. The three specific bands of collagen, most commonly used in infrared protein studies, namely amide I, amide II, and amide III [12] are evidenced. The variation in the intensity and position of amide bands in historical parchment (Figure 8) is associated with a conformational re-arrangement of the native collagen molecules. This occurs as a result of the weakening and eventual breaking of covalent bonds within the helical chains of the collagen molecule [3].

CONCLUSIONS

In this study, optical microscopy, infrared spectroscopy in attenuated total reflection mode (ATR-FTIR), and X-ray fluorescence (XRF) spectroscopy were used to investigate a 17th-century chrisov written on parchment. The document was issued in 1660 by Ștefan Lupu, the prince (voivode) of Moldavia (1659-1661), and is part of the collection of the National Museum of History of Romania (MNIR) in Bucharest.

The chrisov, written on high-quality goat parchment, features a matte, smooth, and velvety surface. Despite traces of folding, the document is well-preserved, with the folds helping to protect the front of the parchment. Surface degradation, such as the formation of oxidized fats, is limited to the verso, which has been more exposed to environmental conditions.

ATR-FTIR analysis revealed only slight conformational changes in the native collagen molecules, attributed to the weakening and eventual breaking of covalent bonds within the helical chains of collagen.

XRF results identified the use of iron gall and gold-based inks for the text, while the ornaments were painted using vermilion (for red), verdigris (for green), a Co-based pigment (for blue), and fine gold powder. Both the inks and pigments are in excellent condition.

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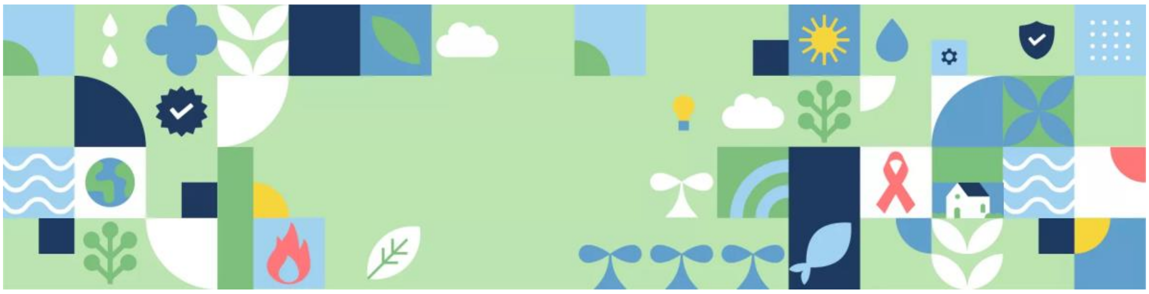
EUROPEAN RESEARCH AREA

COTANCE NEWSLETTERS

Starting with January 2019, the COTANCE Council has issued 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/leather/newsletter, and were also published in the 2019-2023 issues of *Leather and Footwear Journal*. Newsletters 10 and 11 of 2024 are given below.



NEWS 10/2024

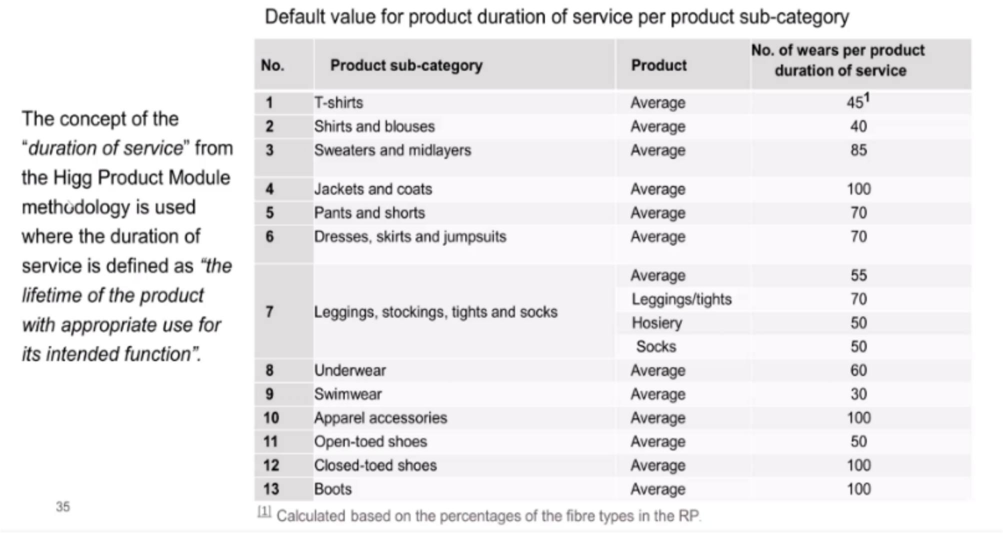
The Industry is Concerned: Durability versus Fast Fashion

COTANCE (Leather), CEC (Footwear), IFF (Fur) & IWTO (Wool) Unite to Defend naturally durable materials in Front of the Product Environmental Footprint Category Rules (PEFCR) Technical Secretariat on Apparel & Footwear (A&F).

COTANCE, CEC, IFF, and IWTO have voiced in a joint statement, significant concerns about the current method for calculating the *"Duration of Service"* of apparel and footwear products. The main concern is the precedent that such metrics is setting in the wider EU regulatory context. Indeed, EU Regulations such as the Taxonomy, the ESPR, the Green Claims Directive, CSRD and CS3D are building the markets of the future. An immature methodology for calculating the environmental footprint of apparel and footwear products risks having highly damaging effects on the diversity and competitiveness of the industries in the ecosystem.

What's wrong with the current A&F durability metrics? They penalise natural, longer-living materials like leather, fur or wool and the consumer products made with them.

Joint Statement



Default value for product duration of service per product sub-category

The concept of the "*duration of service*" from the Higg Product Module methodology is used where the duration of service is defined as *"the lifetime of the product with appropriate use for its intended function"*.

No.	Product sub-category	Product	No. of wears per product duration of service
1	T-shirts	Average	45[1]
2	Shirts and blouses	Average	40
3	Sweaters and midlayers	Average	85
4	Jackets and coats	Average	100
5	Pants and shorts	Average	70
6	Dresses, skirts and jumpsuits	Average	70
7	Leggings, stockings, tights and socks	Average	55
		Leggings/tights	70
		Hosiery	50
		Socks	50
8	Underwear	Average	60
9	Swimwear	Average	30
10	Apparel accessories	Average	100
11	Open-toed shoes	Average	50
12	Closed-toed shoes	Average	100
13	Boots	Average	100

35

[1] Calculated based on the percentages of the fibre types in the RP.

The primary concern lies in the unit of measurement adopted by the Cascale-led Technical Secretariat developing the methodology and the representativeness of the default values for the durability of apparel and footwear products taken from *Higg.*

The signatories of the joint statement consistently opposed that the measure is expressed in a number of "wears" rather than actual time in "years". This approach, taken over from the Higg Product Module, where it was set up by "expert judgement", does not reflect the true lifespan of products, nor the opinion of all the sector's stakeholders.

Moreover, neither the product segmentation nor the default values for the duration of service consider different materials' unique properties.

As a result, the method favours products that are bought and thrown away after a few "wears" and penalises those designed to last much longer than what the methodology can offer.

COTANCE

European Footwear Confederation

INTERNATIONAL IFF FUR FEDERATION

IWTO International Wool Textile Organisation

The organisations representing the views of the Footwear, Fur, Leather and Wool industries propose that the duration of service should be expressed in years rather than wears and that the durability performances that materials confer to products are appropriately integrated in the product segmentation or the reference flow.

This change would provide a more accurate and meaningful assessment of a product's lifespan, aiding both consumers and manufacturers in making informed decisions.

The European leather industry is committed to sustainability and to ensuring that the sustainability features of leather are recognised and acknowledged. By addressing these methodological flaws, we can better align with the EU's sustainability goals and support a greener future.

We invite stakeholders, policymakers, and consumers to engage with us in this important debate. Your support and feedback are crucial in shaping a sustainable and durable future for the apparel and footwear industry and its supply chains for natural and renewable materials.

For more detailed information, please visit our website: https://www.euroleather.com or contact COTANCE Secretariat at cotance@euroleather.com

If you want to go further:

Socio-economic and Environmental Analysis of the Effects of Regulation 2023/1115/EU on the European Leather Sector| **Study**

Environmental footprint, COTANCE | **Article**

Environmental Footprint Methods, European Commission| **Article**

NEWS 11/2024

Leather: Turning Waste into Climate Action

Did you know that hides and skins which aren’t transformed into leather, generally end up in landfills, left to decompose? At first glance, it might not seem like a big issue—but here’s the reality:

as animal-derived materials break down, they release significant amounts of greenhouse gases (GHGs).

Here's an even bigger shocker: industry estimates reveal that **40% of all cattle hides—134 million hides every year—go to waste globally**! That's not only a massive loss of natural, renewable resources but also a major contributor to CO_2- equivalent emissions each year.

If skins and hides aren't transformed into leather, they end up in landfills, left to naturally rot—so what's the problem?

Globally, **40% of cattle hides—134 mln annually—go to waste,** emitting over **40 mln tonnes of CO_2 each year**—equal to the yearly emissions of 8.7 mln cars 🚗

Transforming hides into leather is part of the solution in the fight against climate change.

The Surprising Impact of Waste

In the leather industry, we know that this is a sad waste of natural, renewable resources with an important environmental impact. However, the latest analysis of the Leather and Hide Council of America (LHCA) shows that the impact was much greater than previously thought. Using the ReFED impact calculator, the LHCA reassessed earlier estimates—and the findings are truly eye-opening.

It turned out, that just one tonne of hides rotting in a landfill creates over 13 tonnes of CO_2 equivalent emissions. That's **8 times more** than we thought!

So, what does this look like on a global scale?

🚗 The yearly emissions of **8.7 million cars**
🌳 The CO_2 absorbed by **660 million trees over 10 years**
🏠 Enough energy to power **5 million homes for a year**

Now imagine if we transformed all those discarded hides into leather.

Here's what we'd achieve:

- **Avoid 100 million tonnes of CO_2** equivalent emissions annually of rotting hides.
- **Store CO_2 safely** and durably in leather, generating just 13.3 million tonnes of CO_2e emissions (thanks to efficient tanning processes like Eco2L/Green Deal).
- **Replace up to 3 billion m^2 of fossil-fuel-based materials** in fashion and beyond, reducing even more climate impact.

The Takeaway?

Turning hides into leather is more than just a craft—it's a powerful solution to fight fashion-induced climate change, reduce waste, and create beauty that lasts.

Leather is a timeless circular material with a vital role to play in sustainability. Let's share its story and give it the recognition it truly deserves!

Learn more from the LeatherBiz article

edited by

COTANCE

In cooperation with

LEATHER AND HIDE
COUNCIL OF AMERICA

You want to know more:
A startling revelation | LeatherBiz article
The study on "Carbon Footprint of European Bovine Leather (COTANCE) | Study
Preliminary Life Cycle Assessment Report 2024-03 (LHCA) | Web
Leather and Hide Council of America | Website

LEATHER INDUSTRY PUBLISHES MANIFESTO AHEAD OF COP29

The international leather industry has published a new leather Manifesto on October 15th, 2024, signed by 23 organizations, ahead of the 2024 United Nations Climate Change Conference (COP29). The Manifesto stresses the importance of the need for informed, holistic measures of the impact of materials and focuses on the ways in which leather can be part of the climate change solution, highlighting the positive role of long-lasting leather products in reducing consumption and climate impact.

Read the full Manifesto below:

A Manifesto for Leather on the Occasion of COP29
Buy Better, Buy Less, Buy Leather

Consumption is one of the key drivers for man-made climate change. Consumers are driven to want more, buy more and ultimately discard more and more products, many of which are of poor quality, have short life spans and are designed to be discarded and replaced, rather than repair or repurposed. There is no better example of this than the fast fashion industry which uses a claimed 350 million barrels of oil a year and produces 282 billion kilogrammes of greenhouse gases from the production of polyester alone. Some 100 billion garments are produced annually with as many as 45 billion never being worn. Of those that are, most are discarded after 7-10 wears, resulting in 92 million tonnes waste going to land fill every year[1]. This situation is only expected to get worse, with

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[1] https://earth.org/statistics-about-fast-fashion-waste/

Textile Exchange reporting that consumption of polyester alone, rose from 63 million tonnes in 2022 to 71 million tonnes in 2023[2]. Fashion is responsible for approximately 10% of total global greenhouse gas emissions and despite The Fashion Charter, set up in 2018 to provide a pathway to net-zero emissions by 2050, emissions remain unsustainably high.

Fashion is not the only sector blighted by an excess of consumption and the related environmental impacts, including climate change. It is no surprise then, that governments around the world are developing regulations intended to reduce the impact of the products that we buy every day, driving improvement in sustainable design, circularity and extended producer responsibility. Regulations like the requirement for Digital Product Passports (DPP) in the draft EU Ecodesign for Sustainable Products regulation (ESPR) will give consumers greater insight on the impact of the production of their products, as well as their expected lifespan, repairability and end of life options, allowing for better, more sustainable purchases. Keeping products for longer due to their innate durability and potential for repair will give consumers the opportunity to buy better and importantly, buy less.

Leather is an ideal material to meet these ambitions. Leather utilises an unavoidable by-product to manufacture a versatile, durable material that can be used to make long-lasting, repairable products with a huge potential for circularity. Owners will cherish their leather products, repairing them and even passing them on to subsequent owners. Products made from long-lived leather can have an undeniably positive action in reducing the climate impact of fashion and other sectors. Indeed, research has found that the climate change impacts of natural fibres in garments were negative if the number of wears was increased by 50% because emissions associated with the manufacture of a new synthetic garment were averted[3].

However, leather faces considerable challenges, not only from the nonsensical claims of agenda groups, which undermine brand and consumer confidence but also well-intentioned but misguided regulatory efforts. Leather is one of the derived products listed in Annex 1 of the EU Deforestation Regulation, despite there being no evidence that it is a driver of deforestation. Indeed, analysis by the School of Advanced Studies Sant'Anna has shown that demand for hides has no direct influence on the number of cattle reared and slaughtered and as such, does not drive deforestation[4]. Furthermore, the study found that the impact of the EUDR on the leather sector could be devastating and achieve nothing for the reduction of deforestation. It could however, result in millions of hides being discarded to rot in landfill, with the associated emissions of greenhouse gases.

Similarly, giving consumers greater understanding of the expected lifetime of their products is to be welcomed but it will be essential that the measures used are evidence-based and realistic. The current proposals in the EU’s draft Product Environment Category Rules for Apparel & Footwear, which may form the basis of the DPP under the EPSR, are not and in no way represent the true lifespan of leather goods. If consumers are not told the true story of leather, they may simply opt for cheaper, short-lived synthetic products, driving consumption of fossil fuels and waste.

The undersigned note that the Framework for Action proposed by the Presidency for COP 29 includes a call for an ‘Inclusive process for inclusive outcomes’. We wholeheartedly support this call. The leather industry is constantly working towards ever greater sustainability and circularity, but our efforts will be undermined if regulators and brands do not give proper consideration to the real impacts and benefits of naturals materials like leather. We humbly request that the voice of the leather sector be heard in the development of the policies and regulations needed to combat manmade climate change.

Therefore, we, the undersigned organisations, call on the COP to endorse our call to:

- Recognise the cyclical, climate efficient nature of leather and its potential for a positive contribution to reducing the climate impacts of consumer products. In particular, a full and

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[2] https://textileexchange.org/app/uploads/2024/09/Materials-Market-Report-2024.pdf

[3] Stephen G. Wiedemann *et al.*, Resources, Conservation and Recycling (2023), Volume 198, 107119

[4] https://www.euroleather.com/images//documents/Socio-economic_and_environmental_analysis_of_the_effects_of_the_EUDR_on_the_European_leather_sector.pdf

proper impact assessment of the role of leather as a driver of deforestation and the development of reliable measures of the lifespan of materials and products and their impact on consumption

- Support LCA methodologies that accurately account for the environmental impact of all materials, including end of life properties and the consequences of use and substitution.
- In keeping with the aspiration for reduced consumption, greater circularity and reduced waste, to promote ‘slow fashion’, durable products, and items that can be used many times, repaired and refurbished, and last for years.
- Wherever feasible to encourage the use of natural fibres like leather and reduce unnecessary reliance on fossil-fuel-based materials.

Signatories to the Leather Manifesto

- Alliance Française du Cuir (AFC)
- Australian Hide Skin and Leather Exporters' Association Inc (ASHLEA)
- Centre for the Brazilian Tanning Industry (CICB)
- Centro Tecnológico das Indústrias do Couro (CTIC)
- China Leather Industry Association (CLIA)
- Confederation of National Associations of Tanners and Dressers of the European Community (COTANCE)
- Fédération Française des Cuirs et Peaux (FFCP)
- Fédération Française Tannerie Megisserie (FFTM)
- International Council of Hides, Skins and Leather Traders Association (ICSHLTA)
- International Council of Tanners (ICT)
- International Union of Leather Technologists and Chemists Societies (IULTCS)
- Leather Cluster Barcelona (LCB)
- Leather & Hide Council of America (LHCA)
- Leather Naturally (LN)
- Leather UK (LUK)
- One 4 Leather (O4L)
- Society of Leather Technologists and Chemists (SLTC)
- Sustainable Leather Foundation (SLF)
- Türkiye Deri Sanayicileri Derneği (TDSD)
- UNIC Concerie Italiane (UNIC)
- Verband der Deutschen Lederindustrie e.V. (VDL)
- Wirtschaftsverband Häute/Leder (WHL)
- Zimbabwe Leather Development Council (ZLDC)

IULTCS NEWSLETTER

IULTCS **Newsleather**

Stay curious, informed and connected

Edition 1, 2024

Welcome

This is the inaugural edition of our scientific newsletter, dedicated to providing the latest updates on research, regulatory developments, technology, and standard methods in the leather industry. Our goal is to keep you also informed about the most recent IULTCS news from our Member Societies.

In this first issue, we aim to give you an overview of all the eight IULTCS Commissions and update you on the activities of three Commissions, highlighting the work of each commission.

Throughout the year, our newsletters will cover specific topics such as news from our members, congress information, new publications, patents, and interviews with scientists, tanners, and regulatory specialists.

We hope this newsletter becomes a valuable resource for you, fostering a deeper understanding and appreciation of the dynamic world of leather science and technology. Please invite your colleagues and friends to subscribe.

Thank you for joining us on this journey. We look forward to your feedback and contributions in future editions.

Please share your comments and suggestions to secretary@iultcs.org. Thank you.

Warm regards, *The IULTCS Officers and Commission Chairs*

IULTCS PRESIDENT MESSAGE – Dr. Joan Carles Castell

I want to take a moment to welcome the “IULTCS Newsletter”!

At the time where the debates of the future of the leather industry play out in forums and social media, it is extremely relevant that those of us who are technologist and chemists contribute with commentary and insights that are exclusively based on scientific fundamentals.

This newsletter will also provide a unique opportunity for current and future chairmen to pass along information on the activities of each commission, including updates about the coming IULTCS Congress.

I would like to thank the promoters of this initiative. There is no doubt that this newsletter will reinforce the IULTCS objective of “maintaining regular contacts and effective cooperation between the Associates”.

IULTCS SECRETARY MESSAGE – Dr. Luis A. Zugno

The Newsleather is an exciting IULTCS collaboration focusing on science and research for the leather industry. This much-needed publication aims to foster communication among leather association members and inject motivation and optimism into the industry.

A heartfelt thank you to Dr. Giancarlo Lovato for his support on this project, and to Dr. Alberto Cattazzo for organizing subscriptions and distributing the newsletters. This newsletter belongs to all IULTCS associates and the entire leather community. My role is to edit and work together with you on producing the next editions.

Keep Tanning!

The IULTCS has eight Commissions with Chairs that are responsible for specific areas of knowledge in the Leather Industry. Here is a brief overview of their activities. For additional information please consult www.IULTCS.org.

International Union Leather Test Methods Commissions (IUC-IUF-IUP)

IUC Chairman – Dr. Tiziana Gambicorti

IUF/IUP Chairman – Gustavo Defeo

The IUC-IUF-IUT Commissions have the following roles:

Under a special arrangement with ISO, the IULTCS is responsible for developing the leather test methods for publication as joint ISO Standards (ISO/IULTCS methods).

Following the Vienna Agreement, the IULTCS Commissions hold technical meetings together with the corresponding European CEN/TC 289 Working Groups to prepare new leather test methods and to revise the existing ones. These Standards are approved in parallel at the international and European levels.

CEN/TC 289 is divided into four Working Groups:

- WG1 – Chemical test methods on Leather
- WG2 – Physical test methods
- WG3 – Fastness test methods
- WG6 – Test methods for tannery chemicals.

Those interested in participating in the development of leather test methods are encouraged to join the regular online technical meetings.

International Union of Environment Commission (IUE)

Daniele Bacchi – Chairman

The IUE Commission has the following roles:

The IUE Commission, comprising representatives from nearly 30 countries, convenes annually to address environmental issues and technological solutions related to pollution in tanneries. Drawing on global field developments and experiences, the IUE has crafted technical guidelines aimed at environmental protection within the leather industry.

International Union of Liaison and Communication Commission (IUL)

Julian Osgood – Chairman

The IUL Commission has the following roles:

Establishing and maintaining a network of global contacts within the leather industry that have a legitimate interest in and an authoritative platform to express opinions on issues affecting the industry.

Establishing and maintaining external media contacts for events or issues that may require an industry response.

International Union of Sustainability Commission (IUS)

Kim Sena - IUS Chairman

The Sustainability Commission oversees activities such as advising on sustainability policies, coordinating with various stakeholders, and making Recommendations on environmental programs.

This includes areas like energy and water conservation, water management, circular economy and environmental impact assessment.

International Union of Training Commission (IUT)

Ivan Kral – Chairman

The IUT Commission has the following roles:

Establishing a framework for global leather education/training facilities; identifying global education/training facilities for the leather industry; identifying and “validate” a continuing professional development (CPD) program for leather industry people.

International Union of Research Commission (IUR)

Dr. Volker Rabe – Chairman

The IUE Commission has the following roles:

The optimum basis for a sustainable leather industry is a high-performance leather article and a positive image of the leather making process. The development of best practice technology, continuous improvement of the leather making process, and development of state-of-the-art eco-friendly chemicals are keys for success. These need to be supported by sound scientific processes and entrepreneurial innovation. It is the aim of the IUR to encourage global research projects and establish technology platforms to meet these requirements.

IULTCS COMMISSIONS REPORTS

Chemical Methods – *Dr. Tiziana Gambicorti*

LATEST PUBLISHED ISO/IULTCS TEST METHODS

- **ISO 11936:2023 - IULTCS/IUC 42**

Leather - Determination of certain bisphenols

New: The standard specifies a method for the determination of total extractable content in solvent (methanol) of Bisphenols A, B, F and S in leather, using liquid chromatography coupled with DAD/FLD/MS/(MS/MS) detector.

- **ISO 21135:2024 - IULTCS/IUC 442**

Chemicals for the leather tanning industry - Determination of certain bisphenols

New: The standard specifies a method for the determination of total extractable content in solvent (methanol) of Bisphenols A, AF, B, F and S in chemicals for the leather tanning industry, using liquid chromatography coupled with DAD/FLD/MS/(MS/MS) detector.

- **ISO 18218-1:2023 - IULTCS/IUC 28-1**

Leather - Determination of ethoxylated alkylphenol. Part 1: Direct method

Revision: The standard has been amended to eliminate chemicals for tannery as possible samples limiting the standard only for leather’s samples: in fact, only ISO 18218-2 (Indirect method) provides acceptable results for that type of matrices.

- **ISO 20137:2023 - IULTCS/IUC 36**

Leather - Chemicals tests – Guidelines for testing critical chemicals in Leather

Revision: The list of critical chemicals has been updated, as well as related standards.

- **ISO 23702-1:2023 - IULTCS/IUC 39-1**

Leather — Per- and polyfluoroalkyl substances. Part 1: Determination of non-volatile compounds by extraction method using liquid chromatography

Revision: The list of determinable substances has been updated, in accordance with the corresponding standard for Footwear sector.

STANDARDS UNDER DEVELOPMENT:

- **ISO/FDIS 17234-1 - IULTCS/IUC 20-1**

Leather — Chemical tests for the determination of certain azo colourants in dyed leathers. Part 1: Determination of certain aromatic amines derived from azo colourants

Revision: The standard has been updated, adding Annex E for including colourants as samples and Annex F for describing a procedure for determination of free aromatic aniline in colourant and leather

- **ISO/DIS 23649 - IULTCS/IUC 400**

Chemicals for the leather tanning industry – Determination of cyclosiloxanes

New: The standard specifies a method for the determination of the total content of octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) in chemicals for the leather. This method requires the use of Gas chromatography (GC) equipped with a single quadrupole mass spectrometer (MS).

- **ISO/CD 25202 - IULTCS/IUC 40**

Leather - Chemical analysis – Determination of glutaraldehyde content

New: The standard specifies a method for the determination of free and released glutaraldehyde in leathers, based on liquid chromatography (LC).

RECENT ACTIVITIES OF THE WORKGROUPS

For **WG1**, the group is working on skin testing, we do not have the date for the next meeting nor the agenda.

For **WG6**, of which I am the coordinator, instead, the last meeting was held October 9th, with the following agenda items:

- Interlaboratory results of the determination of melamine on chemicals
- Advancement of the standard on the determination of glutaraldehyde on chemicals

Research – *Dr. Volker Rabe*

Two topics will be addressed in this Newsleather: the current status of the bisphenol regulation, which has been the subject of much discussion in recent years and the IULTCS Young Leather Scientist Grants (YLSG) 2025.

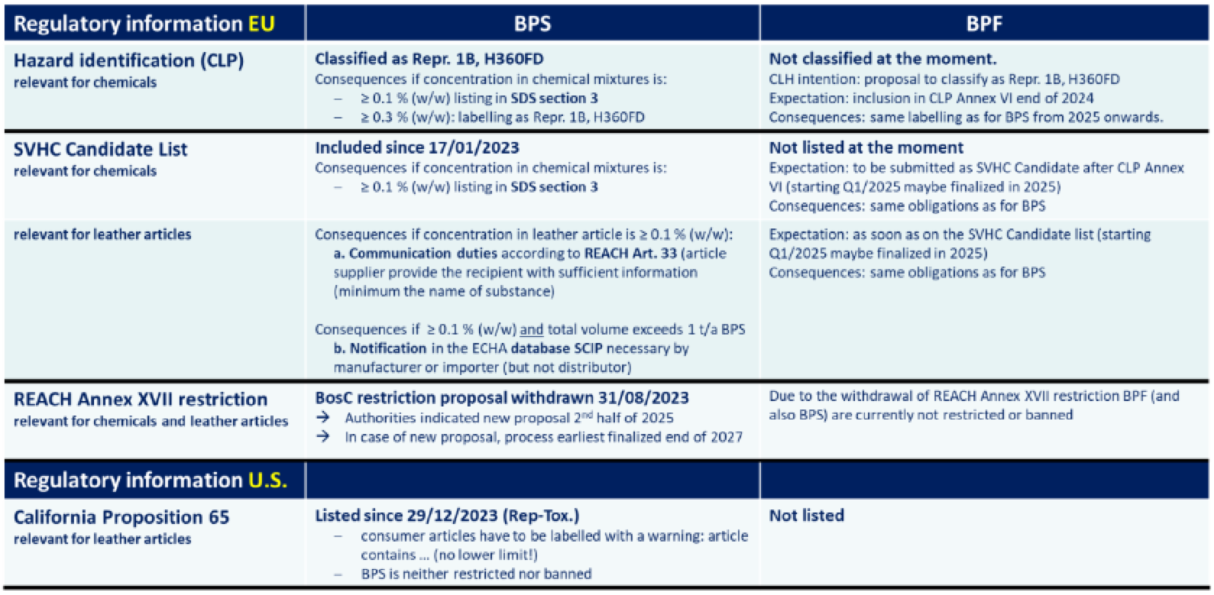
The leather industry is currently facing a variety of challenges. In addition to the current economically challenging environment and the recruitment of adequately trained young talent, the industry is also faced with an increasing number of legal regulations, particularly from Europe. This not only affects the chemicals used in leather production, but also increasingly the leather article itself.

BISPHENOLS

Since only two bisphenols are relevant to leather tanning—Bisphenol S (BPS) and Bisphenol F (BPF)—the overview in Table 1 focuses solely on these two. To provide a comprehensive update, I reached out to the European Chemistry for Textile and Leather (EUCTL) and obtained the latest information, for which I would like to thank the EUCTL Secretariat.

As of mid-2023, following the decision by Germany's Federal Office for Chemicals (the authority for REACH) to temporarily withdraw the dossier, neither BPS nor BPF is currently restricted or banned by legislation. However, the authorities have indicated that a new proposal will be available by mid-2025. This suggests that any restrictions on bisphenols for chemicals and leather articles would not come into effect until late 2027 at the earliest.

On a related note, ISO 11936:2023, a new standard for the determination of total bisphenol content in leather, was introduced this year to help measure these substances. Despite the regulatory delays, efforts to reduce bisphenol levels are ongoing.



Regulatory information EU	**BPS**	**BPF**
Hazard identification (CLP) relevant for chemicals	**Classified as Repr. 1B, H360FD** Consequences if concentration in chemical mixtures is: – ≥ 0.1 % (w/w) listing in **SDS section 3** – ≥ 0.3 % (w/w): labelling as Repr. 1B, H360FD	**Not classified at the moment.** CLH intention: proposal to classify as Repr. 1B, H360FD Expectation: inclusion in CLP Annex VI end of 2024 Consequences: same labelling as for BPS from 2025 onwards.
SVHC Candidate List relevant for chemicals	**Included since 17/01/2023** Consequences if concentration in chemical mixtures is: – ≥ 0.1 % (w/w) listing in **SDS section 3**	**Not listed at the moment** Expectation: to be submitted as SVHC Candidate after CLP Annex VI (starting Q1/2025 maybe finalized in 2025) Consequences: same obligations as for BPS
relevant for leather articles	Consequences if concentration in leather article is ≥ 0.1 % (w/w): a. **Communication duties** according to **REACH Art. 33** (article supplier provide the recipient with sufficient information (minimum the name of substance) Consequences if ≥ 0.1 % (w/w) and total volume exceeds 1 t/a BPS b. **Notification** in the ECHA **database SCIP** necessary by manufacturer or importer (but not distributor)	Expectation: as soon as on the SVHC Candidate list (starting Q1/2025 maybe finalized in 2025) Consequences: same obligations as for BPS
REACH Annex XVII restriction relevant for chemicals and leather articles	**BosC restriction proposal withdrawn 31/08/2023** → Authorities indicated new proposal 2nd half of 2025 → In case of new proposal, process earliest finalized end of 2027	Due to the withdrawal of REACH Annex XVII restriction BPF (and also BPS) are currently not restricted or banned
Regulatory information U.S.		
California Proposition 65 relevant for leather articles	**Listed since 29/12/2023 (Rep-Tox.)** – consumer articles have to be labelled with a warning: article contains … (no lower limit!) – BPS is neither restricted nor banned	**Not listed**

***Table 1:** Regulatory information on Bisphenols – Status September 2024*

YLSG 2025

I would like to take this opportunity to once again highlight the IULTCS Young Leather Scientist Grants (YLSG) 2025. As part of the IULTCS's commitment to nurturing young talent in the leather industry, these grants were established. The awards are open to scientists under the age of 35 who are affiliated with a university or leather school and are working on projects aimed at improving leather production, whether through chemical or mechanical innovations. Detailed information about the specific requirements for each award can be found on the IUR Research Commission page on the IULTCS website https://iultcs.org/commissions/iur-research-commission/

Please not only consider potential projects but also actively promote YLSG 2025 to ensure a dynamic and diverse selection of submissions. A big thank you once again to the sponsors of these awards!

Test Methods – *Gustavo Defeo*

Report of the activities in the IULTCS IUF and IUP Technical Committees - November 2023 to October 2024

The meetings of the IUP / CEN TC 289 WG2 and IUF / CEN TC 289 WG3 commissions were convened on the same days one after the other. In the period November 2023 / October 2024 we organized both technical committees in five opportunities each on the following dates: November 24, 2023; January 25, April 8, June 17 and September 24, 2024. We participated in the plenary on 10 October 2024, and we have planned a final meeting on December 2 to conclude the 2024. In abstract: ten ordinary meetings, one plenary, two meetings scheduled by the end of the year.

Activities

During this period, we have completed the review and published the new versions of the ***ISO 2418:2023 Leather - Chemical, Physical, Mechanical and Fastness tests - Position and Preparation of Specimens for Testing***, and the ***ISO 2419:2012 Leather – Physical and Mechanical Tests - Specimen and Test Piece Conditioning*** standards, both initiated by the past convener.

In the new versions of both standards, we've eliminated the repetitions of some scopes. Among the decisions made, we chose to leave the placement and preparation of samples in the new ISO 2418, limiting ISO 2419 to the only conditioning. We have improved the English language terminology on both standards according to ISO requirements.

Following this activity, we continue with the revision of a series of standards considering that:

- Both these standards are transversal for the IUC (Chemical tests), IUP (physical-mechanical tests) and IUF (fastness tests) standards and therefore each of the three commissions will have to take them into account for future updates.
- During our meetings we came across the correct wording to be used on future standards updates, following ISO recommendations. The representatives of the different countries participating to our committees, will be responsible to translate these expressions to their respective languages.

The completion of both these updated represent the final step begun three years ago in IUF / CEN TC 289 WG3 with the replacement of the old textile ISO 105 A 01 with the more specific **ISO 7906 Leather — Tests for color fastness — General principles of testing** standard, which transversalities obliged our commission to initiate an updates campaign that will gradually occur following the usual regular revisions.

The first standards that we have updated are listed in the activities described for each working group:

IUP Commission / CEN TC 289 WG2

ISO 2419:2024 Leather - Physical and mechanical tests – Specimen and test piece conditioning.

ISO 2417:2016 Leather - Physical and mechanical tests - Determination of the static absorption of water

ISO 3377-2:2016 Leather - Physical and mechanical tests – Determination of tear load - Part 2: Double edge tear

ISO 17236:2016 Leather - Physical and mechanical tests – Determination of extension set.

ISO 3379:2015 Leather - Determination of distension and strength of surface (Ball burst method)

ISO 17232 - Leather - Physical and mechanical tests - Determination of heat resistance of patent leather

ISO 5403-1 - Leather - Determination of water resistance of flexible leather - Part 1: Repeated linear compression (penetrometer)

IUF Commission / CEN TC 289 WG3

ISO 20433:2012 Leather - Tests for color fastness – Color fastness to cracking.

ISO 20701:2018 Leather - Tests for color fastness – Color fastness to saliva

ISO 11641 - Leather - Tests for color fastness - Color fastness to perspiration

ISO 11642 - Leather - Tests for color fastness - Color fastness to water

In addition of these updates, we have finished drafting two new standards:

ISO/DIS 25089 - Leather - Tests for color fastness – Color fastness to sea water which is an adaptation to the leather matrix of the ISO 105-E02:1994 "Textiles — Tests for color fastness — Part E02: Color fastness to sea water standard.

ISO/DIS 7979 Leather – Tests for color fastness – Color fastness to hydroalcoholic mixtures

IULTCS NEWSLETTER

Newsleather

Stay curious, informed and connected

Edition 2, 2024

Welcome

This is the second edition of our scientific newsletter, dedicated to providing the latest updates on research, regulatory developments, technology, and standard methods in the leather industry.

In this issue, we have activity reports from the Environmental, Sustainability, and Training Commissions.

Starting with the January Newsleather we will have valuable interviews with scientists, tanners, and regulatory specialists. This will be an opportunity to learn personal insights, experiences, career inspiration and to broaden our knowledge base.

Thank you for joining us on this journey. We look forward to your feedback and contributions in future editions.

Please share your comments and suggestions to secretary@iultcs.org.

Thank you and warm regards,
Dr. Luis A. Zugno, editor

Environmental – *Daniele Bacchi*

IULTCS Environmental Commission (IUE) Virtual Meeting Summary

On November 19, 2024, the IUE held a productive virtual meeting with the participation of 27 delegates from 13 countries. The primary objective of the IUE Commission is to address environmental challenges and explore technological solutions within the tanning industry, supported by a series of documents now available on the IULTCS website.

The IUE is now concentrating on updating these documents to address the evolving challenges faced by the sector. The commission has decided to begin with a review of two crucial documents: IUE2 (Recommendations for Tannery Solid By-Product Management) and IUE3 (Document on Total Dissolved Solids in Tannery Effluent). Both topics are significant to the tanneries worldwide.

The meeting commenced with a warm welcome from the IULTCS President Dr. Castell, who underscored the urgent environmental issues confronting the industry. Mentioning that while the IULTCS does not provide direct solutions, it aims to highlight best practices that can be adopted throughout the sector.

The IUE Chairman encouraged participants to share their insights for a comprehensive update of the documents in line with the UN 2030 sustainability and circularity goals by March 2025. The meeting also illuminated the challenges faced by small-scale tanneries in India, particularly regarding compliance with the stringent total dissolved solids (TDS) standards and solid waste management. The participants noted the lack of adequate sewage treatment facilities in many regions, which often necessitates costly zero liquid discharge systems to address TDS issues.

Advancements in China concerning the treatment of wet blue shavings were shared, and the need for participants to exchange their experiences to establish industry benchmarks was emphasized.

The significance of IUE documents was reiterated, as they serve not only as guidelines for the tanning industry but also as tools for communicating the industry's commitment to sustainability and circularity to external stakeholders and governments. Additionally, discussions explored the environmental impacts of chlorides and sulfates, focusing on techniques to mitigate their discharge in the tannery effluent.

The IUE Chairman requested that country delegates consider proposing modifications to the documents and submit their feedback by December 2024.

We emphasize the importance of participation from as many countries as possible in this initiative. Through collaborative efforts, we can develop documents that truly reflect the sector's needs. We encourage stakeholders to identify and recommend experts who can actively contribute to the commission's work.

The next IUE meeting is scheduled for mid-February 2025.

Sustainability – *Kim Sena*

IULTCS Sustainability Commission (IUS) Report

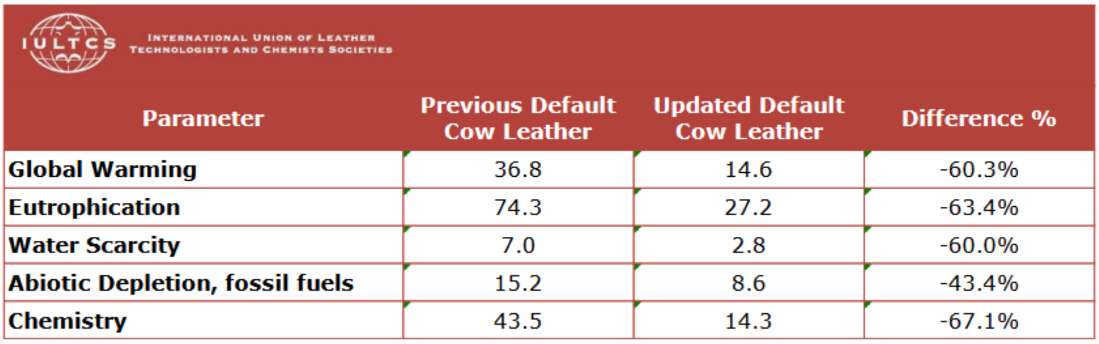
On October 29, 2024, the Higg MSI (Higg Materials Sustainability Index by Worldly) published an update that included the results of the new Leather Naturally and Leather Working Group joint life cycle assessment (LCA) submission. The study was carried out by the consultancy company Spin360. The study aimed at being the most comprehensive environmental impact assessment for cow leather, adding value in establishing a global benchmark on leather production. Due to its geographical, technological and technical representativeness, the submitted LCA replaced the previous results available for leather in the platform.

Scope Numbers:
- 92 leather articles
- 48 tanneries
- 20 countries

The results were expressed in 5 impact categories:
1. Global Warming
2. Eutrophication
3. Water Scarcity
4. Resource Depletion, fossil fuels
5. Chemistry

Following the Higg MSI approval of the presented study, the new data has now superseded the old information, revealing that leather now has a significantly reduced environmental impact compared to the previous data.

On Table 1 we have the comparison between the previous and updated results showing the significant reduction in all the impact categories.



INTERNATIONAL UNION OF LEATHER TECHNOLOGISTS AND CHEMISTS SOCIETIES

Parameter	Previous Default Cow Leather	Updated Default Cow Leather	Difference %
Global Warming	36.8	14.6	-60.3%
Eutrophication	74.3	27.2	-63.4%
Water Scarcity	7.0	2.8	-60.0%
Abiotic Depletion, fossil fuels	15.2	8.6	-43.4%
Chemistry	43.5	14.3	-67.1%

Table 1: *Comparison between the five old and new impact categories*

Note: The above results are expressed in Higg Points after a normalization undertaken on the LCA midpoints. The Higg Points are non-dimensional.

The Higg MSI is used by designers and procurement teams to make better decisions and source more sustainable fibers.

Despite clear instructions from Higg MSI to compare only similar materials (e.g., virgin polyester vs. recycled polyester or different leather types), it is often misused to compare different materials. Therefore, updating the environmental impact data for leather at the Higg MSI was a crucial step in ensuring the leather results more accurately reflect the industry average.

The study also underscored opportunities to further improve the data quality for leather and other materials, while more importantly showcasing the myriads of possibilities in the optimization of leather’s supply chain.

This study exemplifies the power of collaboration among key organizations in the sector. By promoting similar initiatives, the industry can provide greater value to society. Sharing best practices and relentlessly pursuing the reduction of environmental impacts should remain top priorities. Collaboration is the most effective path to achieving these goals.

Training – *Ivan Kral*

IULTCS Training Commission (IUT) Report

The objective of the IUT is to establish a framework for global leather education/training facilities. Also to bring together training providers for leather education. Properly trained and educated professionals are the key assets of every organization and company. This is especially crucial in today's landscape, with the numerous challenges related to quality, productivity, environmental concerns, and new regulations.

The industry requires a new generation of leather technicians and chemists, as well as ongoing professional development and lifelong learning for all technicians and managers across all organizations.

The recent closure of the Institute for Creative Leather Technologies (ICLT) has sparked a discussion about the future of leather education.

Industry leaders recognize the critical importance of education and training. In response, the informal group SOLES (Supporters of Leather Education and Science) is working on a proposition to determine the necessary steps to preserve and protect the integrity of formal leather education and training.

Over the past few months, the group has engaged in intensive discussions with the primary objective of identifying the industry's needs, the types of training required, and how industry professionals can collaborate to ensure the continuity of training for the leather sector.

There are varying educational needs, such as higher education degrees and courses with on-site laboratories for research and application tanneries. Additionally, professional development and lifelong learning require modular short-term courses and seminars, including online and blended formats.

Globally, several training providers and institutes offer education and courses both in person and through remote online learning. The UNIDO Leather Panel maintains a list of these education and training providers. It is important to keep this list updated, and we encourage that any changes be communicated with the IUT or the Leather Panel. The list of training institutions is available at: https://leatherpanel.org/organizations-categories/leather-professional-education-institutions.

Well-educated and trained personnel are vital for the future success of every company and organization. In today's fast-paced and ever-evolving industry, having skilled professionals who are equipped with the latest knowledge and expertise is crucial. This is why it is essential for the industry to actively engage in the activities of the IUT Commission.

Through collaborative efforts, the IUT Commission can develop comprehensive training programs that address the specific needs of the sector, ensuring that professionals are well-prepared to meet current and future challenges.

Moreover, continuous professional development and lifelong learning are key components in maintaining a competent and adaptable workforce in the leather industry.

November 28, 2024

NATIONAL AND INTERNATIONAL EVENTS

THE 10th EDITION OF THE INTERNATIONAL CONFERENCE ON ADVANCED MATERIALS AND SYSTEMS (ICAMS 2024)

The 10th edition of the International Conference on Advanced Materials and Systems – ICAMS 2024 was organized by INCDTP – Leather and Footwear Research Institute (ICPI) on October 30th – 31st, 2024, as an online event. The 2024 edition of ICAMS was a successful one, with a number of 70 papers presented by authors and co-authors from 16 countries (Ukraine, Bulgaria, Lithuania, Vietnam, Portugal, Spain, Ethiopia, Bangladesh, Kazakhstan, Hungary, Indonesia, Türkiye, Greece, South Korea, Denmark and Romania).

The keynote session comprised three presentations on topics of major interest, held by internationally renowned experts – Dr. Robert J. Mitchell from School of Life Sciences, Ulsan National Institute of Science and Technology, South Korea, with the presentation titled “Addressing the Silent Pandemic: Coupling Predatory Bacteria with Other Antibacterials as a Powerful Deterrent to Multidrug-Resistant Pathogens”, Dr. Izabela Cristina Stancu from the National University of Science and Technology POLITEHNICA of Bucharest, Romania, with the paper “Next3DBone – Engineering Bioinspired Biomaterials for 3D Printing to Stimulate Bone Regeneration”, and Lóránt Kiss from Budapest University of Technology and Economics, with the presentation “Enhancing the Applicability of Surface-Activated Ground Tire Rubber in Natural Rubber-Based Mixtures for Sustainable Recycling”.

In addition, the conference also featured a Workshop titled “Outcomes of the Erasmus+ Project DigitalFashion”, which focused on developing and implementing e-learning resources for virtual prototyping of clothing, as well as a training session on Academic Article-Writing Techniques and Publication Ethics held by MDPI Open Access Publishing Romania representative Diana Rădulescu.

The conference papers were divided into six topics:

- Advanced Materials and Nanomaterials;
- Biomaterials and Biotechnologies;
- Innovative Systems, Technologies and Quality Management;
- Ecological Processes for Circular and Neutral Economy;
- Creative Industries and Cultural Heritage;
- Education and Digitalization.

The Conference Proceedings with selected *in extenso* papers is published by SCIENDO (DeGruyter, Poland), under ISBN 9788367405805, available on the conference website, www.icams.ro, as well as on the SCIENDO platform, https://sciendo.com/book/9788367405805.

INSTRUCTIONS FOR AUTHORS

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

Paper Format

Title. Title (Centered, 12 pt. TNR font) should be short and informative. It should describe the contents fully but concisely without the use of abbreviations.

Authors. The complete, unabbreviated names should be given (Centered, 10 pt. TNR font), along with the affiliation (institution), city, country and email address (Centered, 9 pt. TNR font). The author to whom the correspondence should be addressed should be indicated, as well as email and full postal address.

Abstract. A short abstract in a single paragraph of no more than 200-250 words must accompany each manuscript (8 pt. TNR font). The abstract should briefly describe the content and results of the paper and should not contain any references.

Keywords. Authors should give 3-5 keywords.

Text

Introduction. Should include the aims of the study and results from previous notable studies.

Materials and Methods. Experimental methods should be described clearly and briefly.

Results and Discussions. This section may be separated into two parts. Unnecessary repetition should be avoided.

Conclusions. The general results of the research are discussed in this section.

Acknowledgements. Should be as short as possible.

References. Must be numbered in the paper, and listed in the order in which they appear.

Diagrams, Figures and Photographs should be constructed so as to be easy to understand and should be named "Figures"; their titles should be given below the Figure itself. The figures should be placed immediately near (after or before) the reference that is being made to them in the text. Figures should be referred to by numbers, and not by the expressions “below” or “above”. The number of figures should be kept to minimum (maximum 10 figures per paper).

Tables. Should be numbered consecutively throughout the paper. Their titles must be centered at the top of the tables (10 pt. TNR font). The tables text should be 9 pt. TNR font. Their dimensions should correspond to the format of the Journal page. Tables will hold only the horizontal lines defining the row heading and the final table line. The tables should be placed immediately near (after or before) the reference that is being made to them in the text. Tables should be referred to by numbers, and not by the expressions “below” or “above”. The measure units (expressed in International Measuring Systems) must be explicitly presented.

Formulas, Equations and Chemical Reactions should be numbered by Arabic numbers in round brackets, in order of appearance, and should be aligned left. The literal part of formulas should be in Italics. Formulas should be referred to by Arabic numbers in round brackets.

Nomenclature. Should be adequate and consistent throughout the paper, should conform as much as possible to the rules for Chemistry nomenclature. It is preferable to use the name of the substances instead of the chemical formulas in the text.

References should be numbered consecutively throughout the paper in order of citation in square brackets; the references should list recent literature also. Footnotes are not allowed. If the cited literature is in other language than English, the English translation of the title should be provided, followed by the original language in round brackets. Example: Handbook of Chemical Engineer (in Romanian), vol. 2, Technical Press, Bucharest, **1951**, 87.

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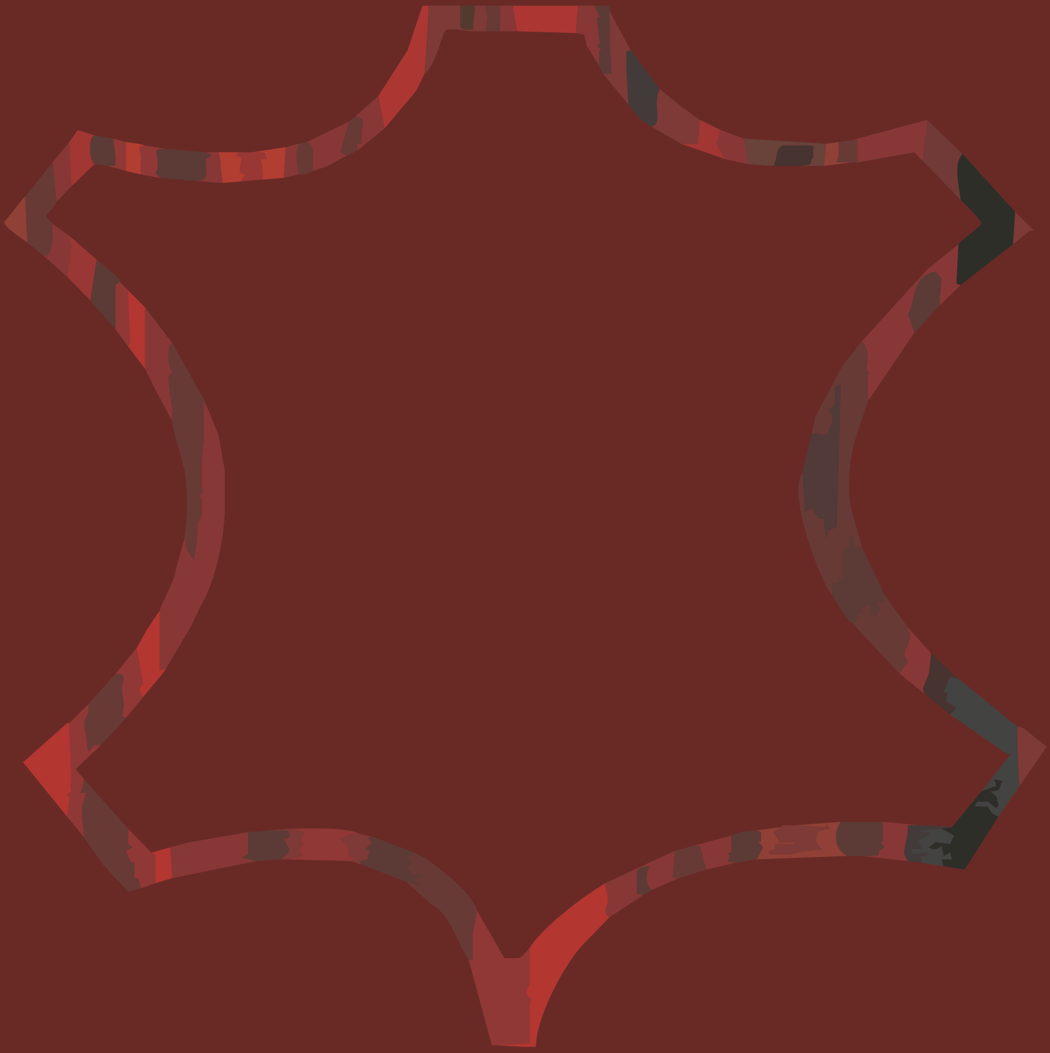

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